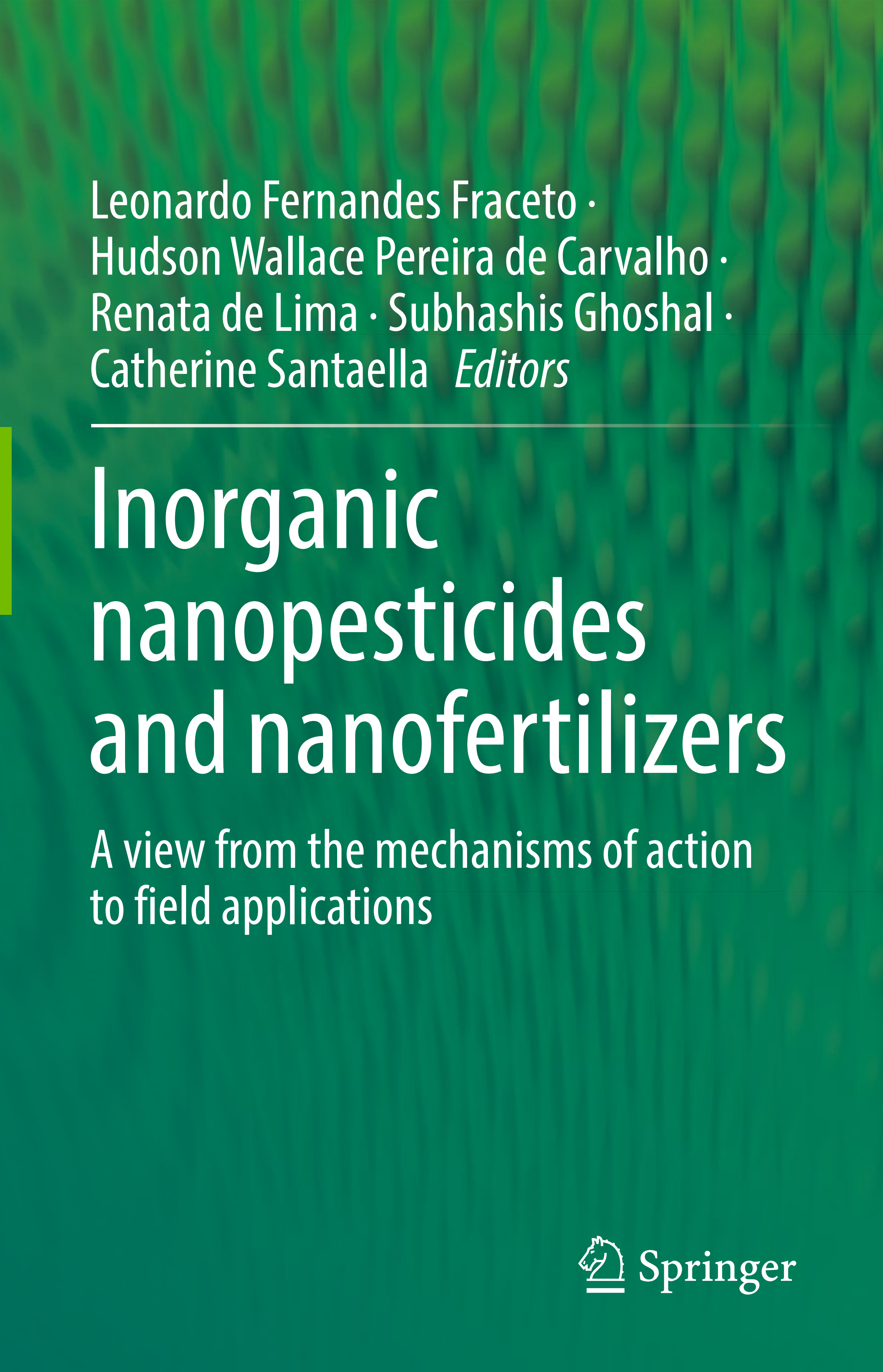

Leonardo Fernandes Fraceto ·
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Catherine Santaella *Editors*

Inorganic nanopesticides and nanofertilizers

A view from the mechanisms of action to field applications

Springer

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I would like to dedicate this book to Agda Fernandes Fraceto (my mom—in memoriam), for all your love, affection, and teachings. Stay in peace!

Leonardo Fernandes Fraceto

I offer this book to all those who fall in love with science every day and use it to support their truths.

Renata de Lima

To the memory of the agronomist Fernando Penteado Cardoso (1914–2021), a visionary and founder of the Agrisus Foundation-Sustainable Agriculture. According to him, "The land, as it has been said before, is a possession that we simply borrow from those who will succeed us."

Hudson Wallace Pereira de Carvalho

To all those who contribute to advance sustainability in agriculture.

Subhasis Ghoshal

To my mentors, collaborators, and students, who have contributed to make my scientific adventure challenging and exciting year after year.

Catherine Santaella

Foreword

The well-known role of fertilizers and pesticides in increasing the global food production in the past century has made them an integral part of modern agriculture. A wide range of formulations have been developed and used over time with a view to increase efficacy and reduce environmental impacts, but recent developments in nanotechnologies have opened up a brand-new window of opportunities in this area. Predictably, this has attracted the attention of many researchers, who have explored new nanoscale formulation of pesticides and fertilizers, and, as a result, several developments are understood to be at different stages of the innovation pipeline. This book is in fact a sequel to another recent book by Jogaiah et al., “Advances in Nano-Fertilizers and Nano-Pesticides in Agriculture,” published by Elsevier in 2021, and thus completes the picture by addressing the specific topic of inorganic nanopesticides and nanofertilizers. In this context, it provides another timely account of the state of the art on nanotechnology-derived innovations in this area and the outlook of nanopesticides and nanofertilizers for use in the global agriculture.

New formulations of agrochemicals, in particular of nanopesticides, that have been produced through a novel process, and are claimed for enhanced efficacy, inevitably also raise questions about their safety and environmental sustainability when used on food crops. It is therefore useful to note that this book has explored not only the beneficial and innovative sides of the technology, but also the potential harmful effects and impacts in terms of discussing the mechanisms of toxic action. This makes the book a comprehensive and balanced compilation that will not only inform the readers of the state of the art, but also invoke further interest into research and development in this area.

The book is comprised of 11 chapters that are written by a group of scientists renowned for their expertise in this field. It provides a detailed account of nanotechnology-derived inorganic pesticides and fertilizers, their expected benefits, potential hazards and risks, current gaps in knowledge, and future directions of R&D. The book is therefore likely to be of wider interest to academia, R&D scientists, industry developers, as well as regulators.

Chapter 1 discusses the likely benefits that inorganic nanoparticles can offer to agriculture and the potential adverse ecotoxicological impacts on the environment. It provides an overview of the beneficial and harmful effects in comparison to conventional formulations. It takes an account of the types and applications of nanofertilizers and nanopesticides and considers limitations in the current state of knowledge in relation to physicochemical properties, environmental behavior, potential exposure, and toxicity of inorganic nanoparticles in the environment. It also highlights the need for studies into the effects and impacts on nontarget organisms at various trophic levels, as well as any risk to human health.

Chapter 2 discusses the strategies to produce cost-effective fertilizer-based nanoparticles. It brings an industrial vision in terms of benefits and weaknesses of both bottom-up and top-down manufacturing approaches and compares their feasibility at the industrial production scales.

Chapter 3 discusses the effects of nanoparticles on seed performance. It discusses the basic aspects of physiology of seed germination and relates them to the potential effects of nanomaterials on the overall seed performance. Noting the current gaps in knowledge, it also highlights the need for further investigations to enable safe use of nanoparticles in seed treatments.

Chapter 4 explores the biological barriers, processes, and transformations that take place at the soil–plant–atmosphere interfaces and which drive uptake, translocation, and bioavailability of inorganic substances. It notes that nanoparticles interact with plants mainly through the root–rhizosphere and/or the atmosphere–leaf interfaces. Any transformation of nanoparticles taking place at these interfaces will effectively control bioavailability, absorption, and further translocation into the plants. The chapter also highlights the knowledge gaps and points to specific aspects that need further research.

Chapter 5 discusses the physiological and molecular aspects of plant biostimulation by nanomaterials. It provides a brief account of the pathways of entry of nanomaterials into plants, interactions at the plant-atmospheric interfaces, cellular uptake, compartmentalization, and transport of nanoparticles through plant tissues.

Chapter 6 discusses an example of copper-based nanoparticles for potential use as a pesticide. Copper is an essential element for plant growth, metabolism, and defense, and copper compounds are already used in agriculture as a fungicide. The chapter notes that copper nanoparticles can be produced by chemical, physical, and biogenic methods. It discusses the recent developments in the application of copper-based nanoparticles for agricultural pest management, their biogenic routes of synthesis, and phytotoxic activity.

Chapter 7 discusses the application of nanoparticles in the design of biosensors for use in the agri-food sector. There has been a growing interest in nano(bio)sensors because of their excellent analytical sensitivity, stability, specificity, and versatility. The potential applications therefore can range from field monitoring of crops to food processing, packaging, storage, and assessment of food quality and safety within the agri-food chain.

Chapter 8 discusses physicochemical properties and behavior of inorganic nanopesticides/nanofertilizers in aqueous media and tank mixtures. It takes an account of the global market for nanofertilizers and highlights the physicochemical properties of nanoformulations compared to conventional ones and their expected performance in field applications.

Chapter 9 discusses the role those inorganic nanoparticles can play in promoting crop health and growth in terms of disease suppression, nutrient uptake, and crop yield. It describes examples of sustainable application of nanomaterials for beneficial and sustainable impact on agricultural crops.

Chapter 10 discusses metal- and metalloid-based nanofertilizers and nanopesticides for agricultural applications. It takes account of the findings on metal- and metalloid-based nanoparticles/nanocomposites used as nanopriming agents, nanofertilizers, nanoinsecticides, as well as nanobiocides against viral, bacterial, and fungal pathogens of plants. It also discusses the mechanism of pesticidal/biocidal action and the potential use of zeolites and nanoclays as carriers of nutrients for use as slow-release fertilizers.

Chapter 11 discusses the use of porous inorganic nanoparticles as carriers for pesticides and nutrients. It provides a review of the key features that can increase the apparent solubility and mobility of poorly soluble pesticides and offers a means to control their release over time. It also reviews the role of physicochemical characteristics of nanoparticles that are important in relation to their uptake and translocation by plants and which can guide the rational design of nanoparticles that can respond to changes in pH, temperature, ionic strength, light, enzymes, or redox agents.

In summary, the book is a comprehensive single source of information on the application of nanotechnologies for the development of inorganic nanopesticides and nanofertilizers. It provides a balanced view of the beneficial and innovative aspects as well as the current limitations of nanoscale formulations for use in the agri-food applications. It is therefore highly commended to those who have an interest in this area from an academic, research, industrial, or regulatory perspective.

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Qasim Chaudhry

Preface

Registering and transmitting thoughts through written language is perhaps one of the most important communication tools that exist. Contemplating the final text makes us think of how many people will learn from and be motivated by the state of the art assembled within these pages. We are very much thankful to the leading scientists that accepted the challenge of sharing their expertise through this book.

The properties exhibited by matter at the nanoscale and the possibilities of applying these properties to change the environment around us for the better make nanoscience and nanotechnology fascinating fields of study. The interest in the topic can be seen in the growing number of journals, papers, books, and overall scientists that devote their time and material resources to nanoscience and nanotechnology.

This book addresses whether agriculture may benefit from or will be threatened by nanoengineered materials within the myriad of composition, shape, size, and possible applications. Despite more than 20 years of research, there is still no clear and straightforward answer to these questions (Chap. 1).

Perhaps the most apparent use of nanoengineered nanomaterials might be in plant nutrition. It is not difficult to conceive nanoscale oxide, carbonate, or phosphate particles being employed as fertilizers competing against micrometer materials or salts (Chap. 2). In principle, such nanoparticles could be broadcasted in soil (Chap. 4), sprayed on leaves, dispersed in hydroponic media, and employed in seed treatment (Chap. 3). Others propose the use of nanoengineered nanomaterials as pesticides against fungi, insects, bacteria, and viruses (Chaps. 6 and 10). Porous nanoparticles can also carry the plant nutrients and pesticides delivering them on demand (Chap. 11). Depending on the nanoparticle chemical composition, it could fulfill both functions simultaneously.

Less conventionally, nanoengineered materials may also be employed as plant growth regulators (Chaps. 5 and 9). The presence of exogenous substances may promote plant growth and stimulate their defense system. Plants experience such effects under the presence of hormones or signaling molecules produced by pathogens. If nanoengineered materials can mimic these molecular agents and trigger plant response, we may witness groundbreaking possibilities able to unleash productivity gains at rates comparable to what humankind experienced during the twentieth century.

Diagnosing plant health and nutritional status as well as the quality of food is also a challenge that can be met by nanotechnology. Nanoparticles may be employed as sensors revealing plant stress, presence of pathogens, and toxins before the human eye could notice it (Chap. 7).

However, despite so many possibilities, questions of utmost importance arise: (a) Will the benefits from the agricultural output surpass the costs of production of such new technologies? (b) What are the consequences of introducing nanoengineered materials in our food web?

How is this book different from the others? This book addresses different issues related to the use of nanotechnologies in agriculture, considering pragmatic issues, such as the behavior of nanomaterials in tank mixtures before their application to the field, to the interactions with the plant, and to the environment.

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Balancing the Benefits to Agriculture and Adverse Ecotoxicological Impacts of Inorganic Nanoparticles

Bruno Teixeira de Sousa, Jhones Luiz de Oliveira, Halley Caixeta Oliveira, and Vera Lúcia S. S. de Castro

Abstract Nutrient fertilization and use of pesticides in agriculture aid in the improvement of crop productivity and quality. However, their use may be harmful to environmental health. It is then needed an innovative alternative in agricultural cultivation, increasing fertilizers and pesticides' effectiveness, reducing its environmental impact, and improving food production. In particular, nanotechnology is emerging as a promising alternative. Inorganic nanoparticles can be used in association with active organic ingredients or as active ingredients. While nanofertilizers offer benefits in nutrition management, nanopesticides can increase environmental safety achieving better pest control. To that end, this chapter presents an overview of these materials' use and their beneficial and damage effects in relation to conventional compounds. It describes the main types of nanofertilizers and nanopesticides (such as nanoparticles of essential elements and polymeric nanoparticles containing these elements), giving examples of products and their applications in plants compared to conventional chemicals. In contrast, despite the advantages of using nanotechnology in agriculture, it is necessary to consider its limitations and understand its environmental behavior. The internalization and subsequent toxicity of inorganic nanoparticles in the environment depend on their physical–chemical characteristics. It is essential to understand the biological responses to their exposure in nontarget organisms at various trophic levels, which may pose a risk to human health. In conclusion, although use of inorganic nanoparticles in agriculture offer opportunities to

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improve crop yields, it is mandatory to make a risk prognosis due to their use before their market entrance to make decisions of agricultural practices.

Keywords Ecotoxicology · Nanotechnology · Environment · Fertilizers · Pesticides

1 Introduction

Nanomaterials (NMs) can improve crop productivity as fertilizers and pesticides. These materials can promote nutrient uptake by plants and suppress crop diseases by directly acting on pathogens through various mechanisms. Efficient use of NMs may complement or replace conventional fertilizers and pesticides, subsequently reducing the environmental impact of agricultural practices.

The nanotechnology uses for agri-food purposes are broadly conceived as a sustainable approach that is safer for human and animal consumption and for the environment, in addition to enhancing agricultural productivity. This technology will be a driving economic force to change the current agriculture practices. Novel delivery systems for crop improvement and productivity can decrease the use of bulk agrochemicals and provide more affordable solutions in the agriculture sector (Acharya & Pal, 2020). In the work of Kah et al. (2018), the authors make a critical assessment comparing nanopesticides and nanofertilizers against their conventional analogs. According to the authors, nanopesticides are more than 30% more efficient than nonnano analogs. However, the authors reinforce that biological and toxicological efficacy have not been confirmed for different target organisms/plants in many studies, which does not guarantee that this will be repeated in the field.

Before commercializing NMs used as fertilizers, phytological testing in both in vitro and in vivo setup must be carried out to ensure nutrient use efficiency with no or minimum material toxicity. Some NMs might be detrimental when applied directly and/or indirectly to the plants since they can sometimes readily aggregate or dissolute free ions in the immediate vicinity, which can cause tissue injury. The toxicity of nanoparticles (NPs) is dose, particle size, host plant, and plant growth-stage dependent. At higher doses, metal oxide NPs aggregate on root/seed surface due to physical attachment, electrostatic attraction, and hydrophobic interactions, causing local accumulation of ions released from the NPs to toxic levels. In this context, studies on uptake, translocation, internalization, and nutritional quality assessment must be carried out to understand NM–plant interactions (Pradhan & Mailapalli, 2017; Achari & Kowshik, 2018). Saleeb et al. (2019) found that the soil sorption of silver nanoparticles (Ag NPs) was significantly greater than Ag^+. According to them, the environmental impact of the citrate-coated Ag NP release may be determined mainly by the equivalent mass concentration of Ag^+. There is a considerable variation between plant species like spinach and silverbeet in Ag uptake that can accumulate sufficient Ag to pose a risk to human health.

Many NMs proposed for use in agriculture are made from metals known to be antimicrobial (Cu and Zn), photoactive (TiO_2), or redox-active (CeO_2). Their agriculture applications on a large scale may lead to toxicity risks that are not well understood. The impacts caused by these exposures can be the promotion of resistance in soil microbiome, bioaccumulation in plants and crops, and persistence in the environment, among others. The fate and subsequent consumption of NMs can cause human toxicity by ingesting an edible part of a crop where NM was translocated (Gilbertson et al., 2020). Understanding the potential toxicity and environmental impact of NPs requires that researchers study them at environmentally-relevant concentrations in complex, real-world systems. However, high metal concentrations of interest are present in every environmental compartment as well as many organisms. The successful development and application of various techniques that enable experimental designs reflecting the real environment will allow the determination of their toxicity mechanisms (Deline & Nason, 2019).

However, the synthesis protocols greatly influence the NM toxicity, and the use of toxic elements during the chemical synthesis process can lead to various health implications and environmental concerns. Hence, nowadays, there are efforts to synthesize NMs based on green principles by employing biogenic sources, as mentioned earlier (Baker et al., 2017). Once NPs are dispersed in the different environmental compartments (air, water, and soil), they suffer modifications through various physical, chemical, and biological transformation processes. Understanding the relationship between NM and critical ecosystem components as plants, pests, microbiomes, and livestock is essential. The agronomic and socioeconomic context and geographical differences that lead to some food deficit and an environmental impact should be considered to support the development of more viable and sustainable nano-innovations in agriculture (Kah & Kookana, 2020).

Nanotechnology offers potential solutions for sustainable agriculture, including increased nutrient utilization efficiency, improved pest management efficacy, mitigation of the impacts of climate change, and reduction of adverse environmental impacts of agricultural food production. However, for this technology adoption, it is necessary to use data and models that include sensitive endpoints for regulatory and safety concerns (Hofmann et al., 2020).

A significant challenge in nanotoxicology is establishing a comprehensive risk assessment framework for these materials since, after entering the environment, NMs can rapidly undergo surface modifications and chemical speciation changes. It is then necessary to assess potential environmental and human-exposure risks from NM fate, transport, and toxicity in environmental systems (soil and plants) and conditions relevant to agriculture fields (ultraviolet light, temperature, pH, and organic matter). In this scenario, this chapter examines the benefits of NMs used as pesticides and fertilizers and highlights critical challenges regarding their ecotoxicity, risk analysis, and regulatory issues to ensure safe application in agriculture viewing to achieve global food security.

2 Benefits of Inorganic Nanoparticles to Agriculture

2.1 Nanopesticides

Population growth, combined with environmental conditions changes, has put pressure on agriculture to increase food production (Bruinsma, 2017). Over time, agriculture has undergone countless revolutions, one of which is the so-called "green revolution." It was based mainly on the extensive use of pesticides and fertilizers and the mechanization of production (Shiva, 2016). It is noteworthy that these facts brought about a significant change in the agricultural sector, allowing greater productivity. However, over time, several organisms have developed resistance to pesticides. Numerous environmental problems have also emerged, such as contamination of soils, surface, and underground water, in addition to the damage to nontarget organisms (pollinators, among others) and agricultural producers (Shiva, 2016).

In this context, there has been a growing concern to protect crops from pest attack and reconcile environmental gains. In this way, numerous technological approaches have been explored. Nanotechnology has proven to be an important platform to achieve a dynamic balance between agricultural production and environmental sustainability. Advances in this area have allowed developing different systems based on NPs for agricultural applications, the so-called nanopesticides (Usman et al., 2020). Nanopesticides are generally based on organic molecular active ingredients, encapsulated in nanocarriers of different matrices, as well as nanoscale inorganic active ingredients complexed or not with organic carriers. Regardless of the type of formulation, nanopesticides aim to i) increase the solubility and stability of the active compounds; ii) release them slowly; iii) protect them against premature degradation caused by environmental factors; and iv) target the active ingredients more effectively, promoting a reduction in the amount of active ingredient used (Parisi et al., 2015). Therefore, these systems cause the active compounds to remain in an effective concentration range, thus increasing their efficiency and decreasing the toxicity and possible environmental contamination (He et al., 2019).

Concerning inorganic nanopesticides, these agents can act both in pest control and fighting diseases, such as those caused by viruses, bacteria, and fungi (Fig. 1). In the following subsections, we present some of the prominent examples in more detail, with Table 1 summarizing the literature's works.

2.1.1 Silicon Nanoparticles

Silicon (Si) is one of the most abundant metalloids on Earth. These compounds are characterized by their intermediate physical and chemical properties compared to metals and nonmetals (Blumenthal et al., 2018). Even though it is not considered an essential element, studies have described the application of Si in plants since it contributes to acclimation to different conditions of environmental stress (Abdel-Haliem et al., 2017; Cui et al., 2017). When on the nanoscale, this material has

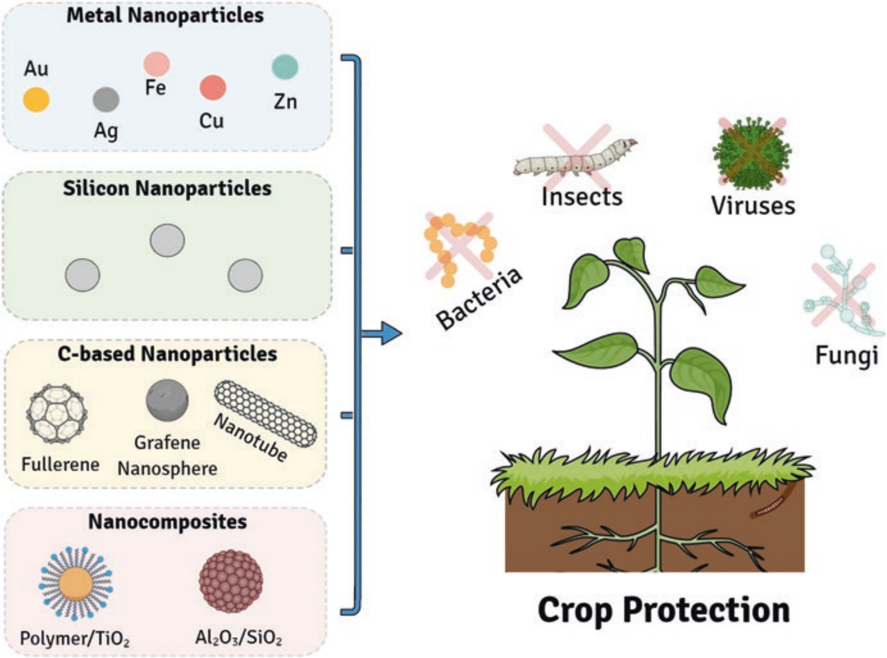

Fig. 1 Application of different inorganic nanoparticles, which include metal nanoparticles, silicon nanoparticles, and C-based nanoparticles and nanocomposites in crop protection. Such formulations have shown biological effectiveness against different agricultural pests (insects, bacteria, fungi, and viruses)

different properties compared to the bulk material; this is mainly due to its smaller size and surface area. Among the most commonly found compounds is silicon dioxide (SiO_2), also known as silica (Bera, 2019).

These Si-based NMs have been investigated for use in agriculture as nanopesticides and carrier agents for active biomolecules, such as organic pesticides, nucleotides, and proteins (Jeelani et al., 2020). El-Naggar et al. (2020) evaluated the insecticidal effect of silica nanoparticles (SiO_2 NPs) against four important pests that infect stored corn (*Sitophilus oryzae*, *Rhizopertha dominica*, *Tribolium castaneum*, and *Orizaephilus surinamenisis*). The results revealed that, when 0.25–2.0 g of SiO_2 NPs were applied per kilo of seeds, *O. surinamenisis, R. dominica*, and *T. castaneum* exhibited 100% mortality, while *S. oryzae* was more resistant and exhibited 93.3% mortality. Therefore, SiO_2 NPs have emerged as a promising insecticide during corn storage, with a minimal dose. In another study, Haroun et al. (2020) evaluated the conjugated effect of zinc oxide nanoparticles (ZnO NPs) and hydrophilic SiO_2 NPs against important storage pests (*S. oryzae*, *T. castaneum*, and *Callosobruchus maculatus*). The systems exhibited a significant toxic effect against *S. oryzae* and *C. maculatus* in the highest concentration (8 g/kg seed), while *T. castaneum* showed high resistance. The insects also suffered a reduction in the F1 progeny, indicating the system as a potential protective alternative for stored seeds.

Table 1 Examples of nanoparticles with potential use as nanopesticides

Nanoparticle	Active compound/ synthesis route	Target species	Main results	Reference
Mesoporous silica	Herbicide Diquat dibromide	*Datura stramonium* L.	Mesoporous silica nanoparticles (MSNs) were facilely fabricated by introducing sulfonate groups onto MSNs through a post-grafting method. The release of diquat dibromide from NPs was pH and ionic strength responsive, chiefly governed by the electrostatic interactions. The system exhibited good herbicidal activity, and the bioactivity was affected by the ionic strength of the release medium.	Shan et al. (2019)
	Botanical Insecticide Cinnamon oil	*Corcyra cephalonica* Staint.	The authors observed that pupation percentage, pupal duration, percentage of adult emergence, and adult longevity decreased in all treatments with cinnamon oil encapsulated in mesoporous silica NPs compared with the control. Furthermore, the protein profile of the treated larvae was evaluated to explain the mode of action of the tested compounds. Electrophoretic analysis of total proteins evaluated inhibitory action of the used compounds on the protein contents, as the appearance as well as the loss of specific protein fractions.	Attia et al. (2020)
	Insecticide Abamectin	*Plutella xylostella* L.	The mesoporous silica NPs containing abamectin was fabricated by simple operation, short preparation period, and remarkable drug-carrying capacity. The system presented a spherical shape, rough surface, uniform particle sizes, high loading efficiency (44.8%), and excellent photodegradation-reducing ability. The biological activity was maintained until the 15th day, with 70% mortality of the target insect.	Feng et al. (2020)
Hollow mesoporous silica	Insecticide Thiamethoxam	*Nilaparvata lugens* Stål	A temperature-responsive release formulation based on hollow mesoporous silica and thermoresponsive copolymer, poly(N-isopropylacrylamide-co-methacrylic acid) (P(NIPAM-MAA)), was prepared. The system can effectively protect thiamethoxam against degradation under UV irradiation and showed strong adhesion to rice leaves. The bioactivity results showed that the mortality of *Nilaparvata lugens* was positively correlated with temperature and mainly benefitted from the temperature-induced variation in the release rate.	Gao et al. (2020)

Nanoparticle	Active compound/ synthesis route	Target species	Main results	Reference
SiO_2	–	*Spodoptera littoralis* Bosid.	The larvae mortality rate was directly correlated with the increase in concentration. Also, the newly hatched larvae were more susceptible to treatments than the other tested instars. The observed developmental stages among survivals of test insects were also affected by the treatments.	El-Helaly et al. (2016)
		Plutella xylostella L.	The mortality percentage increased up to 58% and 85% 24 and 72 h after treatment, respectively (nanosilica applied at 1 mg cm^{-2}). In all bioassays, the mortality rate increased with both increased time after nanosilica exposure and increased concentration. The larval death was due to desiccation, body wall abrasion, and spiracle blockage.	Shoaib et al. (2018)
		Spodoptera frugiperda J. E. Smith	It was observed that the 14-nm NPs possess the highest toxic effect against *Spodoptera frugiperda* cells. Indeed, after 24 h, the viability of the cells exposed to the lower concentration of NPs (0.12 mg mL^{-1}) was about 40% of the value obtained for the control cells not exposed to NPs.	Santo-Orihuela et al. (2016)
		Callosobruchus maculatus F.	The treatment of pulse seeds revealed a significant reduction in oviposition, adult emergence, and seed damage potential. There was complete growth retardation of this beetle in the treated seeds. The soil microflora measured in colony-forming units was not affected by silica NPs upon its treatment with pulse seeds.	Arumugam et al. (2016)
		Rhyzopertha dominica F., *Tribolium confusum* Jacquelin du Val	The mortality of both species increased with increasing concentrations and time exposed to each concentration. *Rhyzopertha dominica* was more susceptible than *T. confusum*. SiO_2 NPs were more effective in wheat grains than barley. It can be used effectively in a stored grain integrated pest management program.	Ziaee and Ganji (2016)
Al_2O_3, TiO_2, and ZnO	Chemical	*Sitophilus oryzae* L.	The Al_2O_3 NPs presented a size range of 35–45 nm, TiO_2 NPs of 45–60 nm, and ZnO NPs of 50–350 nm. The results showed that more than 90% of *S. oryzae* died after 4 days of Al_2O_3 NP treatment at 1 g kg^{-1} dosage, and ZnO NP and TiO_2 NP treatment could attain this efficacy at 2 g kg^{-1} after 14 days.	Das et al. (2019)

(continued)

Table 1 (continued)

Nanoparticle	Active compound/ synthesis route	Target species	Main results	Reference
Cu	Chemical	*Fusarium equiseta, Fusarium oxysporum*, and *Fusarium culmorum*	Stable cu NPs were synthesized using cetyl trimethyl ammonium bromide and copper nitrate at room temperature. The antifungal activity was evaluated against three common crop pathogenic *Fusarium* spp. the Cu NPs synthesized have the maximum activity against *Fusarium equiseti* with a 25-mm zone of inhibition, followed by *F. oxysporum* (20 mm) and *F. culmorum* (19 mm).	Bramhanwade et al. (2016)
		Xanthomonas oryzae	The authors synthesized four different sized cu NPs in a narrow-size range (CuNP-1, 18 nm; CuNP-2, 24 nm; CuNP-3, 28 nm; and CuNP-4, 33 nm) by chemical reduction method. The antibacterial activity of the Cu NPs was found to be size and concentration-dependent. Among all the Cu NPs, CuNP-3 exerted the best antibacterial efficiency against *X. oryzae* due to the increased production of reactive oxygen radicals than the others.	Majumdar et al. (2019)
ZnO	Chemical	*Callosobruchus maculatus*	The authors studied the effect of ZnO NPs at different concentrations on pulse beetle in terms of different entomological parameters, adult mortality, and egg number. The highest mortality was found in treatment with 200 ppm (100% of mortality on 14th day). The number of eggs per 100 seeds was less in treatment T8 (3.33 eggs/100 seeds), and the highest was recorded in control with 27.33 eggs/100 seeds.	Lakshmi et al. (2020)

Nanoparticle	Active compound/ synthesis route	Target species	Main results	Reference
Ag	Biogenic Fungus *Trichoderma asperellum*	*Rhizoctonia solani, Fusarium oxysporum, Sclerotinia sclerotiorum*, and *Sclerotium rolfsii*	The Ag NPs had a size of 27.64 nm, a polydispersity index of 0.409, and negative potential of −1.34 mV. The fungicidal activity results showed that silver NPs at 100 ppm showed significantly greater efficacy in inhibiting pathogen mycelial growth than a commercial fungicide.	Kaman and Dutta (2019)
	Biogenic Fungus *Trichoderma viride* cell filtrate	*Fusarium oxysporum* and *Alternaria brassicicola*	Compared to chemically synthesized Ag NPs, it increased weight reduction by 20–48.8% of the fungal pathogens. The biochemical results showed that a higher generation of superoxide radicals occurred when treated with BSNP, leading to more significant fungal death. Electron microscopy images revealed that osmotic imbalance and disintegration of the *A. brassicicola* membrane after treatment are the leading causes of fungal cell death.	Kumari et al. (2019)
	Biogenic Bacteria *Streptomyces* spp.	*Fusarium verticillioides* and *Ustilago maydis*	The NPs showed a spherical shape with an average particle size of 16.4 ± 2.2 nm. The synthesized NPs are significantly active against phytopathogenic fungi. At 100 µg concentration, it inhibits the hyphal growth and conidia germination and shows ~42.85% reduction of ergosterol biosynthesis.	Marathe et al. (2020)
	Biogenic Plant Rice leaf extract	*Rhizoctonia solani*	The NPs were spherical, polydisperse; average size was 16.5 ± 6.2 nm and the zeta potential value was −27.4 mV. The results of antifungal activity confirmed effective hyphal growth inhibition, and percentage growth inhibition was dose-dependent. NP treatment (10 µg/mL) caused 1.3 and 1.5 times enhancement in seedling vigor index.	Kora et al. (2020)
ZnO	Biogenic Fungus *Aspergillus niger*	*Holotrichia* sp.	The NPs presented sizes ranging from 76.2 to 183.8 nm. The Fourier transform infrared spectroscopy (FTIR) confirmed the presence of various functional group interactions in the nanoparticle sample. The biologic activity against the first instar larvae of white grubs showed a 50% lethal dose of 12.63 ppm.	Shukla et al. (2020)

(continued)

Table 1 (continued)

Nanoparticle	Active compound/ synthesis route	Target species	Main results	Reference
Cu	Biogenic Fungus *Pseudomonas fluorescens*		The NPs presented a spherical aspect with size ranges from 10 to 70 nm, a polydispersity index of 0.227, and a zeta potential of −26 mV. The presence of alcohols, phenols, alkenes, and amines was confirmed by FTIR spectroscopy analysis. The biosynthesized NPs showed toxicity against the stored grain pest, where the LC50 value was 37 ppm after 5 days of treatment.	El-Saadony et al. (2020)
NiO	Biogenic Plant	*Callosobruchus maculatus*	The crystallite sizes varied from 9.42 nm (20 mL) to 4.89 nm (15 mL). The *C. maculatus* on black gram seeds with 5, 10, 20, and 40 ppm of NPs showed decreased fecundity and an increased developmental period in a dose-dependent manner.	Rahman et al. (2020)
CS-Cu	Chemical	*Rhizoctonia solani* and *Pythium aphanidermatum*	The physicochemical studies confirmed the size of 163.8 ± 13.3 nm and a zeta potential results of +25.6 mV. In vitro efficacy studies revealed up to 98% mycelial growth inhibition at 0.1% of NPs. An extracellular conductivity study of the mycelium showed cellular content leakage within 12 h of treatment. The system also exhibited growth-promoting activity with chili seeds by overcoming the limited germination rate of susceptible seeds.	Vanti et al. (2020)
CS-Fe_2O_3	Chemical	*Rhizopus stolonifer*	The synthesized NPs had various organic functional groups, spherical rod shape structure, ranging from 20 to 30 nm. The authors found that 1% of NPs showed a significant difference compared to 0.5% synthetic fungicide by effectively inhibiting microbial growth on fruit surface and reduced weight loss.	Saqib et al. (2020)

As previously described, SiO_2 NPs are also commonly used as carrier agents for biomolecules. Bapat et al. (2020) have functionalized SiO_2 NPs with the soybean trypsin inhibiting protein (STI) for smart delivery in tomato plants. The systems were synthesized in different sizes (20 and 100 nm), with no toxicity to plants. The functionalized NPs were absorbed by the plants through the roots and also through the leaf surfaces. The authors observed in in vitro tests that the NP-bound STI inhibited proteinase activity by 50% in the midgut of *Helicoverpa armigera* loopers. In addition, the second instar looper that ingested the systems (incorporated in artificial diet or leaves) showed significant growth retardation. Thus, the system proved to be a promising vehicle for the distribution of biomolecules to plants.

In another interesting work, a nanocarrier for the temperature-responsive insecticide imidacloprid was synthesized using mesoporous SiO_2 NPs. The system had approximately 100 nm diameter and had an ordered hexagonal mesoporous structure with a surface coating of approximately 6 nm. In vitro tests showed sustained release that was sensitive to temperature. Also, biological tests in *Aphis craccivora* showed that the insecticidal activity increased significantly with the increase in temperature, directly linked to the release of the insecticide (Yao et al., 2020).

2.1.2 Metallic Nanoparticles

Nanotechnology has helped in the development of different materials for agricultural applications, including the synthesis of metallic NPs. Concerning these inorganic NMs, the biological effect against pests and pathogens is directly related to their synthesis route and the material origin (Singh et al., 2018). There are different methods for synthesizing these NPs: biological, chemical, and physical methods. However, chemical and physical methods often do not have an attractive cost–benefit and often require toxic products for synthesis, bringing deleterious impacts on human and environmental health (Gouda et al., 2019).

On the other hand, biological methods have shown a lower cost and reduced toxicity. Besides, NPs synthesized through green routes can have different properties since biomolecules (proteins, peptides, amino acids, etc.) that act as reducing agents influence the characteristics of NMs such as size, polydispersity, and shape. Among the main biological sources for synthesizing these types of particles are plants, algae, and microorganisms (Chhipa, 2019; Akther & Hemalatha, 2019).

In recent work, Vargas-Hernandez et al. (2020) described the potential of metallic NPs to control viral diseases that affect agriculture. The authors carried out an exhaustive analysis of the characteristics of different metal oxide NPs and related these properties to the possible beneficial effects on plants and combat these pathogens.

Ag NPs were synthesized by chemical reduction and had an average size of 27 nm. Different bioassays were carried out with *T. castaneum,* including mortality tests, anti-feeding tests, oviposition deterrence, and repellent activity. The authors observed that the NPs showed significant activity in all parameters analyzed, and the joint use with the chemical insecticide malathion contributed to decreasing the resistance to the synthetic insecticide. (Alif Alisha & Thangapandiyan, 2019). In another recent study, Jameel et al. (2020) prepared and characterized a nanocomposite based on ZnO NPs and the insecticide thiamethoxam. The synthesized nanocomposite had an average size of 34 nm, and castor leaves impregnated with different concentrations (10–90 mg/L) were provided for fourth instar larvae of *Spodoptera litura*. The results of biological activity demonstrated an increase in larval mortality, in addition to malformation in pupae and adults, late emergence, and reduced fertility.

As previously mentioned, the biogenic synthesis of metallic NPs has also gained prominence. In the work of Alam et al. (2019), nanoparticles of iron oxide (FeO_2 NPs) were synthesized using the *Skimmia laureola* leaf extract. The NPs had sizes ranging from 56 nm to 350 nm. Biological tests showed that in vitro NPs (6 mg/mL) drastically inhibited the growth of the bacteria *Ralstonia solanacearum*. When the in-plant test was carried out, the severity of the disease was effectively reduced by treating the root zone with the same concentration of NPs. Sahayaraj et al. (2020) evaluated in laboratory conditions the antifungal activity of Ag NP prepared through the aqueous extract of dry leaves of *Pongamia glabra* against *Rhizopus nigricans*. The NPs had an average size of 29 nm, being able to drastically reduce the weight of the *R. nigricans* mycelia and the number of spores compared only to the crude extract.

In a recent chapter, Graily-Moradi et al. (2020) addressed the biosynthesis of gold nanoparticles (Au NPs) through different natural sources (plants, fungi, bacteria, actinomycetes, yeasts, and algae). The authors pointed out that Au NPs have different shapes and sizes and that enzymes secreted by microorganisms and plant metabolites act as reducing and stabilizing agents. Several works that show the potential agricultural applications of these systems have been published (Graily-Moradi et al., 2020).

The applicability of nanocomposites of inorganic NPs with different biopolymers (e.g., chitosan, gums) has been demonstrated. Ammar and Abd-ElAzeem (2020) synthesized copper oxide nanoparticles (CuO NPs) through fungal filtrates of *Aspergillus wentii*, which were then mixed in a polymeric gelatin matrix. The treatment with the conjugate allowed to reach higher values of larval and pupal mortality. Also, there was a significant decrease in the hatchability percentage and number of eggs. In a review article, Chouhan and Mandal (2020) addressed the use of hydrophilic polysaccharide chitosan in strategies for the synthesis of nanocomposites containing metallic NPs (silver, copper, zinc, iron, and nickel, among others). According to the authors, these systems are highly compatible, and chitosan has no toxic effects on the agricultural system. Several studies highlighting the applicability of these systems in the control of pests and pathogens of agricultural interest have been presented (Chouhan & Mandal, 2020).

2.2 Nanofertilizers

Many types of NPs have been developed aiming at agricultural applications, including those related to the supply of nutrients to plants (Fraceto et al., 2016). Nanofertilizers are structures in nanometric scale composed of or loaded with essential elements for plant development (Marchiol et al., 2019; Raliya et al., 2018). They are an efficient strategy for the delivery of nutrients directly to plants, allowing the reduction of the applied amount of fertilizers. In some cases, a gain of 100% can be achieved compared to conventional fertilizers, with positive impacts on crop growth, yield, and quality (Kalra et al., 2020; Nibin & Ushakumari, 2019; Qureshi et al., 2018).

The improved efficiency of nanofertilizers can be related to the gradual release of nutrient ions as well as to the enhanced dissolution in water or soil solution due to the high reactivity that results from the small particle size and the high superficial area (Liu & Lal, 2015; Kalra et al., 2020). In addition, nutrient availability may be increased due to the penetration of NPs through plant structures (e.g., stomata, trichomes, hydathodes, and cell pores), which improves nutrient uptake and reduces losses to the environment (Liu & Lal, 2015; Kalra et al., 2020; Nibin & Ushakumari, 2019; Mahil & Kumar, 2019; Ruttkay-Nedecky et al., 2017; Yaseen et al., 2020). In contrast, conventional fertilizers usually have a very low absorption efficiency resulting from processes like surface runoff, lixiviation, evaporation, hydrolysis, and microbiological degradation (Kalra et al., 2020; Marchiol et al., 2019; Preetha & Balakrishnan, 2017; Raliya et al., 2018). Thus, the production of nanofertilizers is an important alternative for sustainable agricultural production, as it could allow the increase of yield with reduced environmental impact (Yaseen et al., 2020).

According to Kah et al. (2018), nanofertilizers can be classified as macronutrient-based nanofertilizers, micronutrient-based nanofertilizers, and nutrient-carrier NPs. Liu and Lal (2015) also recognize as nanofertilizers plant growth-promoting NMs (i.e., elements that do not have a nutrient effect but promote plant growth by improving the use of nutrients or other physiological processes). Macronutrient nanofertilizers are composed of one or more essential elements that are required by plants in large amounts, like nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), and calcium (Ca). Micronutrient nanofertilizers are composed of those essential elements that are required in small amounts, like zinc (Zn), iron (Fe), copper (Cu), molybdenum (Mo), and manganese (Mn). Both macro and micronutrients can be encapsulated into polymeric NPs (Fig. 2). The applications of these three groups of nanofertilizers are summarized in Table 2 and presented in more detail in the following subsections.

Despite the benefits involved in the use of nanofertilizers, some factors can interfere with their efficiency, such as the method of application and characteristics of the plant that alter its interaction with the NMs (Raliya et al., 2018). The foliar treatment seems to result in a more effective uptake of the NPs than the soil treatments (Alidoust & Isoda, 2013; Raliya et al., 2015), as several soil properties can alter the nutrient availability to the plants (e.g., texture, pH, salt content) (Kalra et al., 2020).

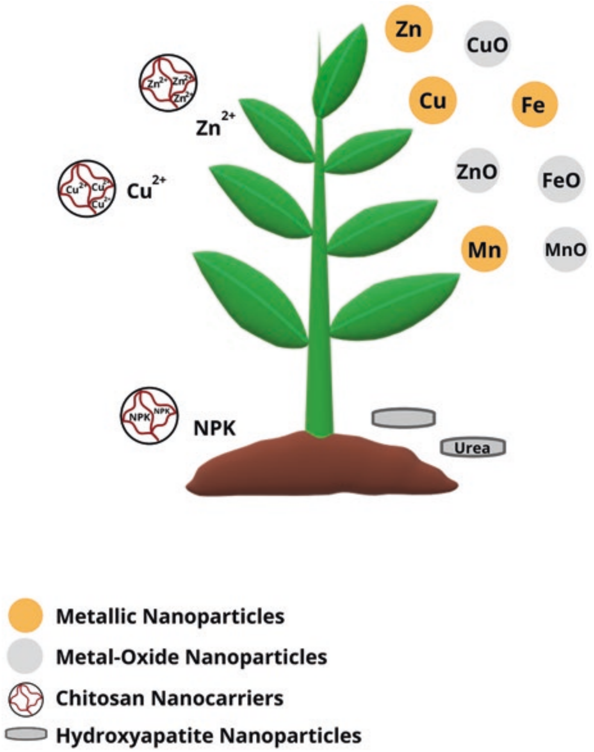

Fig. 2 The nutrients can be supplied to plants by metallic nanoparticles (Me), metal-oxide nanoparticles (MeO), polymeric nanoparticles (e.g., chitosan) loaded with nutrients allowing their gradual release, or inorganic nanoparticles composed of macronutrients (e.g., hydroxyapatite, composed of calcium and phosphorus), which can carry other nutrients (e.g., nitrogen in the form of urea)

Even when applied directly to the leaves, some problems might occur, including specific leaf characteristics, stomatal behavior, and potential phytotoxicity (Kalra et al., 2020). For the uptake and translocation of NPs by the plants, they can enter through different structures (e.g., stomata, cuticle, hydathodes, trichomes, lenticels, wounds, root junctions) with the need to surpass many barriers (Rastogi et al., 2017; Ruttkay-Nedecky et al., 2017). Thus, studies are necessary to improve the knowledge regarding the interactions of different types of nanofertilizers with plants, which would bring valuable information about the mechanisms involved in the nutrient delivery by these systems and allow the development of more efficient nanoformulations.

Table 2 Examples of nanoparticles with potential use as nanofertilizers

Nanoparticles	Plant species	Main results	Reference
ZnO	*Lactuca sativa* L. and *Daucus carota* L. subsp. sativus	Plants of both crop species grown in ZnO NPs showed a significant increase in biomass compared with control plants.	Song and Kim (2020)
	Glycine max (L.) Merrill cv. Kowsar	ZnO NPs as a nanofertilizer improved crop yield.	Yusefi-Tanha et al. (2020)
	Coffea arabica L.	ZnO NPs had a more positive impact on coffee growth and physiology than conventional Zn salts, increasing the fresh weight by 37% (root) and 95% (leaves) when compared to control, and increasing dry weight 28%, 85%, and 20% in roots, stems, and leaves, respectively. The net photosynthetic rate increased by 55%.	Rossi et al. (2019)
	Phaseolus vulgaris L.	ZnO NPs improved vegetative characteristics (plant height, internode length, root and shoot dry, and fresh weight), yield (pod number and seed weight), and quality (Zn content in seed).	Mahdieh et al. (2018)
	Zea mays L.	The highest germination percentage and seedling vigor index were observed at 1500 ppm of ZnO NPs; the yield was 42% more than control and 15% higher than 2000 ppm of $ZnSO_4$. Higher accumulation of Zn in grains was recorded with the application of 100 ppm and 400 ppm of ZnO NPs.	Subbaiah et al. (2016)
	Allium cepa L.	The plants treated with ZnO NPs showed better growth and flowered 12–14 days earlier than the control, and significantly higher values for seeded fruit per umbel, seed weight per umbel, and 1000 seed weight.	Lawre and Raskar (2014)
Cu	*Zea mays* L.	Application of Cu NPs enhanced the growth of maize plant in 51% in comparison to control and influenced different enzymatic activities.	Adhikari et al. (2016)
Fe	*Vigna radiata* L.	The uptake of Fe was more in seeds exposed to NPs. The radical length, biomass, and α-amylase activity were increased in seeds exposed to Fe NPs than the ions.	Raju et al. (2016)
	Spinacia oleracea L.	The nanofertilizer causes a 58% and 47% increase in wet weight and maximum leaf surface index, respectively, comparing to the use of no fertilizer.	Moghadam et al. (2012)

(continued)

Table 2 (continued)

Nanoparticles	Plant species	Main results	Reference
FeO	*Arachis hypogaea* L.	Fe_2O_3 NPs increased root length, plant height, biomass, and SPAD values.	Rui et al. (2016)
	Triticum aestivum L. cv. Pishtaz	FeO NPs increased spike weight, 1000 grain weight, biologic yield, grain yield, and grain protein content.	Bakhtiari et al. (2015)
	Glycine max (L.) Merrill	Fe_2O_3 NPs produced a significant positive effect on root elongation and significantly enhanced photosynthetic parameters.	Alidoust and Isoda (2013)
	Glycine max (L.) Merrill	FeO NPs increased chlorophyll levels with no trace of toxicity.	Ghafariyan et al. (2013)
Mn	*Vigna radiata* L.	Increased in photosynthesis and enhancing the net flux of nitrogen assimilation through NR-NiR and GS-GOGAT pathways.	Pradhan et al. (2013, 2014)
MnO	*Carthamus tinctorius* L.	Mn_2O_3 NPs enhanced leaf water content, chlorophyll content index, and ground green cover, leading to an increase in plant height, branches per plant, and capitols per plant.	Ghassemi-Golezani and Afkhami (2018)
Mo	*Cicer arietinum* L.	Treatment with Mo NPs increased the number of nodules per plant by two times.	Taran et al. (2014)
HA	*Brassica oleracea* L. var. Italica	HA NPs surpassed calcium superphosphate by 14.2–17.8% for leaf area and 13.6 to 15.8% for total head yield.	Shams and Abbas (2019)
	Glycine max (L.) Merrill	Application of the NPs increased the growth rate and seed yield by 32.6% and 20.4%, respectively, compared to those of soybeans treated with a regular P fertilizer, and biomass productions were enhanced by 18.2% in shoot and 41.2% in root.	Liu and Lal (2014)
$Mg(OH)_2$	*Zea mays* L.	$Mg(OH)_2$ NPs showed improved seed germination and growth. Similarly, the enhanced shoot height (44.2 ± 1.6 cm) and root length (29.2 ± 1.3 cm). Chlorophyll *a* fluorescence measurements revealed that plants treated with $Mg(OH)_2$ NPs showed maximum performance index and minimum dissipation compared to control and plants treated with bulk Mg.	Shinde et al. (2020)
CS-Zn	*Zea mays* L.	CS-Zn NPs promoted seedling growth, strengthened plant innate immunity by elevating antioxidant and defense enzymes, and enhanced lignin accumulation. In the field, seed treatment and foliar application of NPs increased grain yield from 20.5% to 39.8% and enriched the grain with Zn.	Choudhary et al. (2019)
	Triticum durum L.	Foliar application of CS-Zn led to grain Zn enrichment in wheat grown in the Zn-deficient environment.	Deshpande et al. (2017)

Nanoparticles	Plant species	Main results	Reference
CS-cu	*Glycine max* (L.) Merrill	CS-Cu NP treatments promoted growth in terms of plant height, root length, root weight, nodule number, nodule weight, and number of pods per plant.	Swati and Joshi (2020)
	Zea mays L.	In CS-Cu NP treatments, higher shoot length, seedling vigor index, and fresh and dry weight were observed. Moreover, the increased activity of α-amylase and protease was reported.	Choudhary et al. (2017)
		Higher values of percentage germination, shoot and root length, root number, seedling length, fresh and dry weight, and seed vigor index were obtained of CS-Cu NPs compared to water and $CuSO_4$. Moreover, CS-cu NPs induced the activities of α-amylase and protease enzymes.	Saharan et al. (2016)
	Solanum lycopersicum L.	CS-Cu NPs showed substantial growth promotion effect on seed germination, seedling length, and fresh and dry weight.	Saharan et al. (2015)
CS-NPK	*Solanum tuberosum* L.	Foliar application with CS-NPK NPs significantly increased all the growth and yield parameters, photosynthetic pigments, chemical constituents of potato tuber at harvest, and macronutrients in potato leaves and tubers as compared with the control treatment.	Elshamy et al. (2019)
	Coffea sp.	The nanofertilizer improved enhanced uptake of nutrients, and total chlorophyll content increased up to 30.7% and 71.7% of photosynthesis net rate. Also enhanced leaf number, plant height, and leaf area of the seedlings.	Ha et al. (2019)
	Triticum aestivum L. cv. Egypt 1	Treatment of plants with nano CS-NPK fertilizer induced significant increases in harvest index, crop index, and mobilization index of the determined wheat yield variables, as compared with control yield variables of plants treated with normal nonfertilized and normal fertilized NPK.	Abdel-Aziz et al. (2016, 2018)

2.2.1 Micronutrient Nanoparticles

Although required by plants in small amounts, micronutrients play essential roles in plant metabolism (Bisquera et al., 2017). They are usually applied to crop fields in the form of salts, a significant part of which is not used by the plants, thereby contaminating the environment (Deshpande et al., 2017). Many metals have been manipulated in nanoscale to act as nanofertilizers (Yaseen et al., 2020). Metallic or metal-oxide NPs show physicochemical properties that differ from the bulk materials, showing improved efficiency (Rastogi et al., 2017).

Zn, both in ionic or oxide (ZnO) forms, has been widely used in the last decades for the development of NPs (Liu & Lal, 2014). This micronutrient is essential for membrane integrity, seed development, and plant reproduction (Sturikovaa et al., 2018; Deshpande et al., 2017). Zn-based nanofertilizers show greater and faster dissolution than bulk materials, allowing lower dosages (Milani et al., 2012). Moreover, they have limited mobility in the leaves and are kept attached to the leaf surface, where Zn ions are gradually released and then translocated, improving the use of this nutrient by the plant (Kopittke et al., 2019; Rossi et al., 2019). The positive effects of Zn and ZnO NPs have been reported to occur when applied to plants in different developmental stages, leading to the improvement of biomass accumulation, crop yield, and seed quality (Bisquera et al., 2017; Lawre & Raskar, 2014; Mahdieh et al., 2018; Rossi et al., 2019; Song & Kim, 2020; Subbaiah et al., 2016; Yusefi-Tanha et al., 2020). The biological effects of Zn and ZnO NPs depend on their size, morphology, and concentration, as observed by Yusefi-Tanha et al. (2020) in soybean plants. It is also noteworthy that Zn phytotoxicity is lower when this element is applied as NPs compared to the ionic form.

Cu is another metal with several agricultural applications, as it is a constituent of many plant enzymes (Adhikari et al., 2016; Rastogi et al., 2017; Ruttkay-Nedecky et al., 2017). In the soil, CuO NPs can provide this micronutrient to the roots in a slow and sustained manner (Spielman-Sun et al., 2018). CuO NPs have also been shown to improve plant growth, regulate enzymatic activity, and have antifungal properties (Adhikari et al., 2016; Ruttkay-Nedecky et al., 2017).

Many plant metabolism processes require Fe, including chlorophyll biosynthesis, nitrogen fixation/assimilation, and redox reactions (Drostkar et al., 2016). Most studies applying iron nanoparticles (Fe NPs) have reported the increment of chlorophyll levels and photosynthetic activity, with the consequent increase of plant growth and yield (Alidoust & Isoda, 2013; Bakhtiari et al., 2015; Drostkar et al., 2016; Ghafariyan et al., 2013; Moghadam et al., 2012; Raju et al., 2016; Rui et al., 2016). Also, the application of iron oxide nanoparticles (FeO NPs) has been considered a strategy for food biofortification (Siva & Benita, 2016).

Other micronutrient-based NPs (as Mn, MnO, and Mo) have been shown to benefit plant growth and physiology, with the improvement of photosynthesis and nitrogen fixation (Ghassemi-Golezani & Afkhami, 2018; Pradhan et al., 2013; Pradhan et al., 2014; Taran et al., 2014).

2.2.2 Macronutrient Nanoparticles

P-based nanofertilizers have been developed aiming at the promotion of the controlled ion release and at the increase of P mobility in the soil, which would allow an improved uptake and usage of this macronutrient by the plants (Kopittke et al., 2019). Hydroxyapatite [$(Ca_{10}(PO_4)_6(OH)_2$] nanoparticles (HA NPs) have been considered the main alternative to conventional P fertilization (Kottegoda et al., 2017). In addition to providing Ca, they efficiently deliver P to plants, thus reducing eutrophication risk. The beneficial effects of HA NPs have been attributed to their higher and more persistent availability in the soil than conventional P ions, which are rapidly adsorbed to soil colloids (Liu & Lal, 2014; Maghsoodi et al., 2020). Moreover, HA NPs did not induce phytotoxic effects on the germination and initial development of tomato seedlings (Marchiol et al., 2019).

Due to its low efficiency and high production cost, N fertilization has also arisen great interest in the development of nanotechnology-based solutions. Urea can be coated to HA NPs, as the large surface area of this NM allows the binding of many urea molecules (Kottegoda et al., 2017; Gunaratne et al., 2016; Kottegoda et al., 2011). This association decreases urea solubility (that is very high), yielding a slower N release. Another multinutrient nanofertilizer, composed of amorphous calcium phosphate, K, and N (nitrate and urea), was recently formulated (Ramírez-Rodríguez et al., 2020). Due to the gradual nutrient release, this nanofertilizer avoided losses to the environment and decreased by 40% the applied amount of nutrients compared to conventional fertilizer. Another advantage of this nano-NPK was the presence of two N forms with different release kinetics in its composition. Magnesium nanoparticles (Mg NPs) have also been developed and shown to promote the growth of maize plants, which was related to the increment of chlorophyll content (Shinde et al., 2020).

2.2.3 Nutrient-Loaded Polymeric Nanoparticles

The use of polymeric NPs as nutrient carrier systems can provide a safe strategy for the delivery of fertilizers to the plants, decreasing the environmental impacts. Moreover, the nanoformulations can be adjusted to allow a gradual nutrient release, which improves the nutrient availability and its use efficiency by the plants (Chen et al., 2013; Guo et al., 2018). A variety of polymeric matrixes have been used to prepare NPs, including chitosan, a chitin-derived polysaccharide that can promote per se benefits to plants (Chen et al., 2013). For example, the treatment with chitosan oligomers induced nutrient uptake, the biosynthesis of photosynthetic pigments, and the growth of coffee plants (Dzung et al., 2011). Chitosan nanoparticles (CS NPs) have been demonstrated as an excellent alternative for the nanoencapsulation of both micro and macronutrients, as they show characteristics as biocompatibility, biodegradability, low phytotoxicity, high adsorption, gradual nutrient release, and protection of biomolecules against adverse environmental conditions (pH, light, temperature) (Chen et al., 2013; Kashyapa et al., 2015; Mujtaba et al., 2020).

In association with Zn^{2+}, CS NPs stimulated the germination, initial growth, and defense system of maize plants, as well as increased the yield and promoted the biofortification of wheat and maize grains (Choudhary et al., 2019; Deshpande et al., 2017). As Cu^{2+}-carrier systems, CS NPs induced α-amylase activity and storage mobilization, yielding improved germination and growth of maize and tomato seedlings (Saharan et al., 2015; Saharan et al., 2016).

In addition to micronutrients, CS NPs have been used to encapsulate NPK fertilizers, enhancing the growth of potato and coffee plants (Elshamy et al., 2019; Ha et al., 2019) and wheat yield (Abdel-Aziz et al., 2016; Abdel-Aziz et al., 2018). However, the mechanisms involved in the positive effects of NPK-loaded CS NPs have not been completely elucidated, as they can be related to the gradual nutrient release or the direct internalization of the NPs by the plant, followed by the posterior release (Guo et al., 2018).

3 Adverse Ecotoxicological Impacts of Inorganic Nanoparticles

The small size of NPs, which gives immense benefit for their use, also contributes to their toxicity issues with several adverse effects. NPs react with various environmental components due to their high surface area. They are highly dynamic and reactive; various physical, chemical, or biological transformations may occur in the environment. Then, the use of nanoproducts in pest control is subjected to various environmental risks. These effects range from environmental hazards to human and animal health in general. The toxicity and responses of materials used in the delivery system may be species-dependent driven by a series of factors, including the NM itself and the environmental and physiological conditions on which they are applied (Vega-Vásquez et al., 2020). NM-induced toxicity could be changed by environmental factors such as sunlight irradiation, natural organic matter, and mineral particles. Because of the uncertainties on environmental concentrations and ecotoxicity, there are significant challenges in understanding the environmental risks of NMs (Zhao et al., 2020a).

Engineered NMs may adversely impact human health and environmental safety by nano–bio–eco interactions not fully understood. Their interactions with biotic and abiotic environments are varied and complicated, ranging from individual species to entire ecosystems. Biological, chemical, and physical dimension properties, the so-called multidimensional characterization, determine interactions. Intermediate species generated in the dynamic process of NM transformation increase the complexity of assessing nanotoxicity (He et al., 2018). Dispersion and dosing of NMs are critical aspects of nanosafety studies since the environmental concentration is the potential dose to that an organism can be exposed. Also, the fate and behavior of NMs are determined by transformations during and following their dispersion in biological and environmental media. In complex environmental media, where natural nanoscale particles and colloids with plenty of positive and negative charged moieties are present, NM heteroagglomeration is the dominant process. Thus, NM heteroagglomeration rather than homoagglomeration or freely dispersed NMs are expected under environmentally relevant conditions (Wigger et al., 2020).

The physicochemical transformations suffered by NM can result in different characteristics leading to the formation of transformed NM functional fate groups. Transformation, especially speciation changes, results in reduced potency. Further reactions at the surface, such as ecocorona formation and heteroagglomeration, may also reduce NM potency. Different NMs that suffered transformation in the environment may have their hazard reduced in the same way, leading to similar actual hazards under realistic exposure conditions (Spurgeon et al., 2020).

Bio–nano interactions between proteins and NMs lead to the formation of the protein corona. Corona formation has proven to be critical for cellular uptake, intracellular localization, and toxicity arising from NMs. Even if the aquatic factors remain consistent, the intrinsic physicochemical properties of multifarious NMs (e.g., metallic and polymeric NPs) may produce unique characteristics in their acquired coronas. The most altered environmental corona interactions appear to be membrane adhesion, membrane damage, cellular internalization, and oxidative stress responses induced by NMs. When natural organic matter (NOM) or expanded polystyrene (EPS)-coated NMs enter the organisms or cells, the macromolecules in the surrounding medium will change into proteins, lipids, and nucleic acids. However, it is not clearly understood whether the adsorbed NOM or EPS macromolecules will be covered or replaced by other biomolecules and form an evolutional corona inside cells or organisms (Xu et al., 2020).

Biomolecule affinities for NM surfaces can change the corona composition. It was recently shown that the chronic (reproductive) ecotoxicity of Ag and TiO_2 NPs to *Daphnia magna* is reduced by environmental aging of the NPs in media of different ionic strengths and natural organic matter contents (Ellis & Lynch, 2020). Then, corona determines how organisms' cells interact with NMs, and its proteins confer a biological identity to NMs, influencing the uptake by cells. However, the role of metabolite corona is not fully understood. Metabolites are orders of magnitude smaller than proteins (typically below 1000 Da), whereas proteins are measured on the kDa scale, and metabolites are typically reactants, intermediaries, and products of enzymatic activity. These coronal metabolites are beginning to gain interest since they influence NM impacts on molecular signaling and adverse outcome pathways (Chetwynd & Lynch, 2020).

Consequently, these processes change the properties of NMs, thereby affecting transport in soil, uptake, and translocation in the plant, and their toxicity to organisms (Fig. 3). The released metal ions can be accumulated by the plant directly or as complexes with other components from the environment. Also, aggregation and agglomeration may occur, modifying NM surface charge and chemistry and influencing subsequent behavior and bioavailability. The various kinds of nanopesticides, from emulsion to nanodispersion, have diverse environmental interactions due to the difference in the chemical components and preparation method. Thus, the safety evaluation of the developed NMs has increasingly become important. A clear understanding of the environmental safety and fate of nanopesticides and their

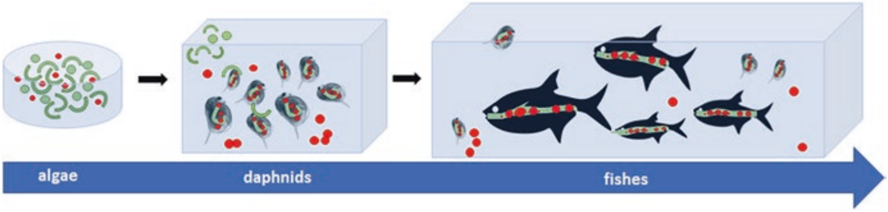

Fig. 4 Example of transfer of NPs (in red) at different trophic levels in an aquatic environment. It can occur biomagnification in the food chain between algae and daphnids, resulting in NP transfer to higher trophic levels such as fish. This transfer among organisms leads to an environmental risk

active ingredients is mandatory before commercial application (Acharya & Pal, 2020; Zhang et al., 2020a).

Coatings on NP surfaces play a crucial role in dictating their behavior in the environment. The fate of NPs as ligand displacement reactions will modify the stability of these NPs during their transport in the environment, NP agglomeration, and their interactions with biological systems. Corona formation of environmental or biological molecules on the surface of these NMs could occur, which either accelerates or slows the dissolution. For metal oxide NPs, the physicochemical processes of dissolution, aggregation, and reactivity are all impacted by surface coatings. The relative binding affinity to the surface depends on the ability of different functional groups to interact with the surface and through nonspecific surface interactions that become important for species with higher molar mass (Wu et al., 2019). So, physicochemical parameters for NP–protein corona formation are frequently derived from protein corona fingerprints, and NPs and protein can suffer aggregation or disaggregation (Falahati et al., 2019).

3.1 Interactions of Nanoproducts and Ecosystem

Current agricultural practices pose unintentional and adverse effects on environmental health, highlighting the need for more sustainable agriculture strategies. Excessive use of conventional chemical fertilizers and pesticides has been increasing toxicity in ground and surface water reservoirs, which has adverse effects on environmental and human health. Some of these agricultural practices can humiliate soil quality and is responsible for the eutrophication of water bodies. Although nanotechnology is of significance for different agricultural applications, further research is needed to explore their applications' effects. Thus, nanotechnology use risks should be carefully examined to guarantee a correct and safe application of NMs in agriculture (Yadav et al., 2020).

NP properties and environmental conditions govern environmental transformation processes and ultimately alter their fate and behavior. Environmental fate assessment remains a critical aspect of studies to understand NM behavior in the environment and the nature and concentrations of the materials that do not damage human and environmental species. Environmental factors such as pH, ionic strength, salts, and sunlight can play a role in the degree of toxicity, and effects resulting from a combination of these factors will undoubtedly be dynamic and complex.

In the aquatic environment, NM agglomeration trends in aqueous systems are controlled by the water chemical properties, most importantly, ionic strength, the valence of the electrolytes, and pH. These parameters largely determine the surface charges/zeta potential of the particles. Then, aggregation refers to strongly bonded or fused particles where the resulting external surface area is significantly smaller than the sum of the individual components' surface areas. In contrast, agglomerates refer to weakly or medium strongly bound particles where the resulting external surface area is similar to the sum of the individual components' surface areas. Thus, NM agglomeration and the formation of a surface coating are closely linked and depend on the surrounding matrices (Wigger et al., 2020).

A major concern arises when commercialized metal-based NMs come into contact with the aquatic ecosystem since their ion dissolution mechanisms and release kinetics into the water are highly unpredictable. Because NMs can readily dissolute and aggregate in many cases, the released ions can be potentially harmful to living systems (Pradhan & Mailapalli, 2017). The fate of nano-TiO_2 in the aquatic environment depends on their aggregation and sedimentation rates, transport in water and sediments, and interactions with the living and nonliving components of the ecosystem (Luo et al., 2020). Also, irradiation by ultraviolet (UV) light is a factor that is of particular concern for photocatalytically active metal oxides such as TiO_2 NPs and ZnO NPs. Under these conditions, there is reactive oxygen species (ROS) formation. Then, the illumination of these NMs in surface waters results in the formation of reactive intermediates, consequently altering the ecotoxicological potential of co-occurring organic micropollutants, including pesticides, due to catalytic degradation (Lüderwald et al., 2020).

Clemente et al. (2013, 2014) showed the importance of considering the experimental conditions in nanoecotoxicological tests. They evaluated the effects on fish exposed to different TiO_2 NP concentrations and illumination conditions by observing the organisms' survival, together with biomarkers of biochemical and genetic alterations. Also, prolonged fish exposure (21 days) to two different TiO_2 NP crystal phases (anatase and a mixture of anatase 80% and rutile 20%) were evaluated at the same light conditions. Similarly, the occurrence of sublethal effects was influenced by the TiO_2 NP crystal phase and illumination condition. Pure anatase caused more oxidative damage without co-exposure to UV, while the mixture anatase:rutile caused more sublethal effects when exposure occurred under UV (Clemente et al., 2015). Nowadays, it is well known that light conditions play an essential role in the dissolution processes of NPs as Ag NPs and ZnO NPs (Odzak et al., 2017). Besides, the behavior of Ag NPs is influenced by environmental factors (including pH, dissolved oxygen, sunlight, temperature, and NOM), which alter their bioaccumulation and toxicity. There are driving processes and potential sources that show correlations between Ag NPs concentrations and biogeochemical parameters, like dissolved organic carbon concentration and divalent cation concentrations. The trace element dissolved in environmental compartments should be considered in material flow analysis and toxicity models since it is the most reactive (Wang et al., 2020a).

Consequently, their bioavailability and potential ecotoxicity are associated with these environmental factors, and Ag NPs can exert different toxic effects depending on the environment and the surface properties (Yang et al., 2018a; Zhang et al., 2018a; Zhang et al., 2019). Moreover, Ag NPs can interact with metal and metal oxide particles/NPs, and their biological effects may not only be limited by NP concentration or particle size but also on the amount and species of products yielded from chemical interactions between Ag NPs and other variables (Sharma et al., 2019).

Similarly, the interaction of NPs with NOM alters the NPs' persistence and toxicity (Abbas et al., 2020). The NOM levels found in most natural waters have been reported to influence the fate and transport of NMs (De Marchi et al., 2018). NOM adsorbed onto NM surfaces alters their surface properties. Humic acid can increase the suspension stability of TiO_2 NPs, diminishing the bioavailability (Luo et al., 2020). More than that, humic acid in a concentration of 20 mg/L (realistic for surface waters) was able to disperse NPs during periods of 24 h or more (Pradhan et al., 2018). Different aquatic sources of NOM can result in differential toxicity, and different concentrations of humic acid can affect aggregation state and toxicity (Ong et al., 2017). However, the combined impacts of UVA, photoactive NMs such as TiO_2 NPs, and NOM on co-occurring pollutants toxicity seem not easily predictable (Lüderwald et al., 2020).

Moreover, NMs can suffer transformations by environmental factors such as climate change and soil moisture. Interactions between nano-sized chemicals and the various climatic stresses in the agro-ecosystem are possible and may result in synergistic, antagonistic, or susceptibility to adverse environmental effects and their combinations. The evaluation of environmental fate, uptake by plants, aquatic and terrestrial ecosystems, and changes in test methodology should form research priorities. Therefore, the ideal situation is analysis of nanopesticides for some of the fundamental molecular and physicochemical aspects that determine their efficacy, stability, and environmental and/or human safety (Kranjc & Drobne, 2019; Gahukar & Das, 2020).

Terrestrial environments are expected to be the largest repository for environmentally released NMs from agriculture and facilitate NM exposure of soil microorganisms, such as plant growth-promoting rhizobacteria. In the soil, NMs can interact with microorganisms and compounds, facilitating or hampering their absorption. NMs can lead to severe effects on soil microbial communities and diversities, soil enzyme activities, carbon and nitrogen cycling, etc., depending on the soil physicochemical spatial heterogeneity at different microenvironments in areas such as the rhizosphere (Zhang et al., 2020a). For example, metal NP nanopesticides can target pathogens through several mechanisms such as the generation of ROS, binding to metabolites, and penetration of cells and spores. The NPs of plant essential and nonessential elements act by diverse mechanisms to elicit beneficial activity to plants in microbes. In its turn, plant beneficial microbes participate in NP transformations in rhizosphere/soil and mitigate toxic effects on plants of specific NPs. However, this NP action is nonspecific and can also benefit pathogenic microbes in the plant rhizosphere (Achari & Kowshik, 2018).

The toxicity of NMs to various soil bacteria has been investigated using various toxicity end-points and experimental procedures. NP toxic effects are due to their uptake by the microbial cells, their chemical nature and concentration in the soil and within the plant roots, ions released interactions between NPs and cellular biomolecules, protein expression, and cell membrane stability alterations, among others (Achari & Kowshik, 2018). The employment of microbial ecoreceptors can highlight NM–bacteria interactions in complex, environmentally relevant media in the future and contribute to nanotoxicological research (Lewis et al., 2019).

The microbial composition and enzyme activities show great potential to indicate NP environmental risks since the soil is an essential sink for NMs due to applications of nanoagrochemicals. Some critical pathways implicating soil enzymes are good indicators of the quality of the soil ecosystem and are likely to be affected by NPs. For example, environmental concentrations of Ag NPs affected microbial biomass but had little impact on microbial diversity and may have little effect on the soil biogeochemical cycles mediated by extracellular enzyme activities (Oca-Vasquez et al., 2020). Functional properties of antioxidant enzymes may affect the stability of NPs and vice versa and that NPs could affect the enzymes' reactivity (Liu et al., 2020). Then, NMs may affect agricultural systems through modifications in nutrient cycling and soil fertility. However, whereas soil enzyme activity measurements are likely to provide critical information on NP effects on soil function in a risk evaluation, there is a need to further research to validate their use as an internationally accepted environmental indicator (Galhardi et al., 2020; Zhang et al., 2020b). An application of the nanoinformatics approach can help understand NM complex transformation processes in the soil–plant environment (Zhang et al., 2020a).

After NM exposure, soil organic matter (SOM) and exudates from roots or rhizosphere microbes can interact with the surface of NMs and change their physicochemical characteristics as hydrophobicity and charge. Soil organic matter may exhibit contradictory effects on the mobility and stability of NMs depending upon their nature. Soil colloids and minerals, mainly clay and Fe minerals, are considered an important sink for NMs. Thus, the surface coating can increase the bioavailability of NMs by decreasing the heteroaggregation of NMs with soil particles and increasing the interaction between NMs and plants. Dissolved organic carbon concentration may control dissolved metal concentration as Cu from CuO NPs in calcareous soil pore waters varying in organic matter concentration. Also, exudates from the root and microorganisms in the rhizosphere can affect physicochemical processes such as the NM heteroaggregation and dissolution in the soil. Root exudate in the rhizosphere could assist the dissolution of metal species as Cu and increase the contact possibility between particle surfaces and plant cells, both likely resulting in higher toxicity of CuO NPs to plants. Besides, the activities of soil fauna could also modify the physical and biochemical environment of rhizosphere soils. Earthworms can also increase the bioavailability of NMs, influencing the physical, chemical, and biological soil environment (Shang et al., 2019; Hortin et al., 2020; Usman et al., 2020; Wang et al., 2020b). Considering all environmental interferences, an in-depth evaluation of the effect of nanoagrochemicals in soils with different physicochemical properties is necessary to recommend a specific one for a specific crop and soil type (Zulfiqar et al., 2019). In this regard, a deeper understanding of the interactions between root exudates and NPs can enhance our knowledge on NP toxicity to plants and promote the effective and safe use of NPs as antimicrobial agents in agriculture.

Furthermore, NPs have their entrance into the environment facilitated by plant functions as a significant route for the bioaccumulation of the NPs into the food chain. The physicochemical properties of NPs and plant physiology significantly contribute to the interaction between NPs and plants, as well as the application method. Several tissues and barriers must be crossed before reaching the vascular tissues, depending on the entry point (roots or leaves). The cell wall barrier mostly restricts the access of NPs in the plant body. Plant cells can either enlarge the pore diameter or generate new pores in the cell wall to enhance NP uptake. Also, NP can enter the cell, crossing the membrane via transport carrier proteins or ion channel mechanisms. NMs can move up and down the plant (Pérez-de-Luque, 2017; Acharya & Pal, 2020).

In the aquatic environment, invertebrates serve as food for higher trophic level organisms, such as fish. Fish are broadly used to assess the strength and health of aquatic environments. For example, TiO_2 NPs are released into the aquatic environment from multiple sources and can promote cytogenetic and hematological alterations in African catfish *Clarias gariepinus* and are relevant to biodiversity and aquatic health management (Ogunsuyi et al., 2020).

NPs that reach the aquatic environment will likely accumulate in sediment where they may be available for uptake by invertebrates (Kim et al., 2016). CuO NPs associated with sediment can enter the aquatic food web, and their chemical and biological processes can result in NP transformation. Depending on the organisms studied, the uptake, fate, and biological effects of CuO NPs and dissolved Cu are different. In this way, transfer of CuO NPs from benthic invertebrates (*Tubifex tubifex*) that serve as food for higher trophic level organisms as fish (*Gasterosteus aculeatus*) may be limited compared to dissolved Cu (Lombi et al., 2019). Also, different NP uptake mechanisms take place in oysters. Ingestion of particles dominated the uptake of 60-nm Ag NPs, whereas dermal uptake and ingestion contributed equally to 15-nm Ag NPs (Shao & Wang, 2020).

Depending on the environmental fate of NMs, feeding groups may be differentially exposed to NMs. For water exposures of single-celled and small multicellular species suspended, it is necessary to separate the suspended NMs from small organisms not to overestimate bioaccumulation. It is important for multicellular organisms to distinguish between the NM adsorbed by external surfaces or by the digestive tract and the amount absorbed by the epithelium. As for multicellular plants, the main considerations include the interactions between the route of exposure and the effect of the rhizosphere on measuring its absorption. Invertebrates can potentially accumulate NMs actively via ingestion and consecutive uptake across the epithelium in the body and to a lesser extent by anal uptake, or passively via uptake through body surfaces or body openings. Then, quantifying uptake and elimination bioaccumulation of NMs is a step toward understanding the potential for NM trophic transfer and biomagnification, both of which are essential concerns in ecotoxicology (Petersen et al., 2019). However, very little is known about the accumulation capacity and coping mechanisms of organisms in NM-contaminated soil due to its release in the terrestrial environment. In this way, Courtois et al. (2020) observed that *Eisenia fetida* bioaccumulates Ag but in a limited way. The Ag location in the organism, the competition between Ag and Cu, and the speciation of internal Ag suggest a link between Ag and metallothioneins, which are key proteins in the sequestration and detoxification of metals.

Consequently, there is a need to characterize actual exposure and quantification of NP bioaccumulation and toxicokinetics to understand toxicological effects. Despite that, tissue concentrations were generally quantified as the total metal content (NP and ions). Since dissolution is considered a crucial reaction for the study of the toxicity of metal NPs, more studies are needed to confirm it as an essential paradigm for assessing metal NP uptake in soil organisms. This understanding is vital to a more accurate risk assessment of NMs (Baccaro et al., 2018).

In aquatic environments, suspension feeders will be exposed predominantly to waterborne NMs, while deposit feeders will be exposed mainly to NMs following sedimentation. Once taken up by organisms, NMs can be retained in the body or excreted. Accumulation of NMs in organisms depends on their availability in the exposure medium and on the physiological traits of the species evaluated. The kinetics of uptake and elimination of metal-based NMs, or derived metal ions, vary among organisms and determine their accumulation patterns. Besides, uptake and elimination kinetics of metal NMs may also be form-dependent; the same organism can use different uptake and depuration pathways for NMs and ions. The fate of NMs in the body will depend on the NM manufactured material and their transformations while aging. For metal-containing NMs that dissolve, it is possible for the free metal ion to be taken up and subsequently incorporated into a metal storage granule inside the organism. The organism's physiology influences the metals and NM elimination rate from organisms, beyond other parameters such as medium, NM characteristics, and the exposure route. NM elimination may involve several different processes among aquatic and terrestrial invertebrates (van den Brink et al., 2019). Also, fish developmental stage-dependent toxicity can affect the profiles of metal oxide NPs as seen in the zebrafish embryo and larvae that emphasize the importance of considering developmental stage differences when evaluating safety assessment of NPs when using living organisms (Peng et al., 2018).

Thus far, with the increasing application of metal NPs, metal ions will accumulate in the environment to threaten the ecosystem (Wang et al., 2020b). Although TiO_2 NPs were initially classified as a biologically inert material, there is growing evidence of toxicity to humans and nontarget organisms requiring further research and improved regulatory practices. Mechanical stress due to the interactions of cells with TiO_2 NPs can impair the cell membrane integrity and affect ion homeostasis and activity of the membrane-associated receptors and enzymes. Intracellular accumulation of TiO_2 NPs leads to DNA damage, whereas altered gene expression affects the induced oxidative stress and inflammation (Luo et al., 2020).

Concerning Ag NPs, sodium (Na) ion channels are involved in the uptake of ionic Ag in freshwater fish rainbow trout. Primarily intact NPs enter tissues through the endocytosis pathway in respiratory or digestive system epithelial tissue. Ions released as a result of NP dissolution are internalized in the cell through transporter proteins or ion channels. Primary NP toxicity induction modes include the release of ions with particle dissolution, oxidative stress, cellular protein injury, and membrane and DNA damage, among others. Also, physicochemical characteristics of NPs such as shape, size, charge, crystalline phase, and coating materials could influence their bioactivity and toxicity (Abbas et al., 2020). In addition to particle size, surface area, and charge, NP surface coating or intentional surface modification are essential determinants to NP translocation in organisms. However, the age of the healthy animal seems not to affect it. The particle properties may also affect the time-course of translocation and clearance mechanisms (Raftis & Miller, 2019).

In addition, bioaccumulation of chemical compounds is the first step toward inducing toxic effects in aquatic organisms. The bioaccumulation kinetics and tissue distribution of Ag NPs in aquatic organisms are affected by NOM since NOM molecules are adsorbed on the surface of Ag NP. This fact increases the particle sizes and negative charges and suppresses the dissolution of Ag NP. As a result, the uptake by zebrafish via dissolved Ag and ingestion of Ag NPs was reduced. Also, NOM inhibited the cell membrane crossing by Ag NPs and promoted the depuration of Ag NP from the fish body, alleviating the bioaccumulation of Ag NPs in zebrafish (Xiao et al., 2020).

Surface chemistry can be used to alter multifunctional properties in metal oxide NPs, leading to broader use of NPs in agriculture, for example, as adjuvants for agrochemicals. Any use evaluation of NMs must address the diverse nature of their shapes (size, shape, organic coating), states (free versus embedded in the matrix, monodispersed versus clustered), and behavior (dynamic transformations that affect shape and state) immediately before entering the environment and after a while (Svendsen et al., 2020; Zhao et al., 2020b).

In their turn, the dissolution of ceria NPs at the nano–bio interface can lead to cytotoxicity as other easily ionized NPs. For that, NPs could bypass the cellular membrane and release high levels of toxic ions in cells after their internalization (Xie et al., 2019). NM biotransformations result from NM–biota interactions and alter the behavior and fate of engineered nanomaterials (ENMs) in the environment. NM biotransformations include dissolution, redox reactions, and chemical reactions with surrounding molecules. NM dissolution appears to be a significant driver of toxicity due to the increased bioavailability of ions, and biotransformation of undissolved NMs does not appear to occur (Kranjc & Drobne, 2019).

Whereas ions released by dissolution can diffuse more freely toward biological receptors and transfer across cellular boundaries, the NM arrival in organisms may be limited by transformations or attachment to other surfaces in the environment. NM heteroagglomeration and dissolution and subsequent chemical speciation in organisms are extremely important in studying their exposure since they affect their uptake. Indeed, during laboratory tests, the attachment efficiency of NMs to organisms is a good predictor of their uptake potential and subsequent toxicity (Klaessig, 2018; Svendsen et al., 2020).

The heteroaggregation between Ag NPs and other particles, such as microbial colloids and mineral particles, can reduce effective Ag NP exposure. Hence, it is essential to study the interactions between ions and solid environmental matrices to predict Ag NPs' fate and risk in the environments. Dong and Zhou (2020) observed distinct mechanisms in heteroaggregation of Ag NPs with mineral and organic particles. While metal ions enhance the attachment of Ag NPs to kaolin, humic acid prevents Ag NP–kaolin attachment at low concentrations. In contrast, lowering pH or adding metal ions inhibited Ag NP–cell attachment associated with the solubility product of metal salts. Although humic acid has little impact on Ag NP–cell attachment, it may complex with metal ions and reduce their effective solution concentrations. As a consequence, metal ion's competition for Ag NP adsorption by bacterial cells can be mitigated. Besides, chronic exposures to NMs may allow vertebrate microbiota to adapt to the xenobiotic presence, resulting in the development of a new bacterial community with a modified composition, which may change microbiota–host signaling and physiological regulation (Zhang et al., 2020c).

As seen, NMs that enter into the environment are often harmful to the living systems. So, safer NP development is essential to cope with the need for more secure and safe NMs. Due to their toxic effects, metal NPs should be given proper care in the production and application process, mostly the chemically synthesized metal NPs. An ideal nanodevice for use in agriculture should be nontoxic and environmentally safe and avoid further contamination problems and a negative perception of consumers. Besides, its synthesis and production must be easily up-scaled, involve low-cost materials, and be affordable to farmers. The establishment of collaborative and interdisciplinary research could assess NM risks and benefits, allowing for better exploration of their potential (Vurro et al., 2019).

NP shape-based toxicity differences could be due to increased uptake of NP of specific shapes by plants and differences in their stability or dissolution patterns in soil (Achari & Kowshik, 2018). Nevertheless, little information is available on the role of properties such as shape and charge of NPs in bringing about beneficial or toxic effects in plant systems (Achari & Kowshik, 2018). In a safer-by-design perspective, the environmental risk related to NMs may be mitigated by lowering the hazard or the exposure potential. Controlling the shape of NMs, as their surface reactivities, could be an option to increase their applicative potential while reducing their potentially harmful effects once released in the environment. Indeed, it was observed an Ag NP shape-dependent impact under such environmentally relevant exposure conditions. From an environmental risk perspective, Ag NP shape can predict which ecological niches of a lotic ecosystem would be more impacted since it was observed a dependent biological response by this characteristic (Auffan et al., 2020). Also, NP aggregates with larger sizes may not be taken up, eliminating the toxicity, or restricting it to the root surface (Achari & Kowshik, 2018).

Furthermore, atrazine (ATZ) and atrazine-loaded poly-ε-caprolactone nanocapsules (ATZ NP) have distinct adverse effects on the nontarget rhizosphere bacterial communities of plants after long-term exposure. Long-term exposure to high concentrations of ATZ NPs was found to act more effectively and gave more microbial community impacts (decreased the community metabolic capacity and shifted the community structure and composition to a greater extent) compared to the same amount of ATZ. The ATZ NP surface modification may solve this effect and promote benefits from other promising properties of these materials (Monikh et al., 2020).

Falinski et al. (2018) proposed a framework for sustainable NM selection and design based on performance, hazard, and economic considerations. This framework's development and implementation can facilitate promising applications, prevent unintended consequences, and support a proactive regulatory action. The final goal is to contribute to nanotechnology governance, having faster, cheaper, effective, and safer nanoproducts on the market for users and the environment (Kraegeloh et al., 2018). The collaboration between regulatory risk assessors and academia helps regulators keep up with novel materials and techniques and support regulatory preparedness (Soeteman-Hernández et al., 2020). Regulatory barriers to the use of nanotechnology in agriculture require careful selection of starting materials, as well as a comprehensive and holistic analysis of the associated risks, fate, and impacts. In a recent publication, Hofmann et al. (2020) explored these barriers: efficient delivery on a field scale, regulatory and safety issues, and consumer acceptance. These authors also proposed ways to overcome these barriers and develop effective, safe, and acceptable nanotechnologies for agriculture. A network of sentinel sites can generate the data needed to understand any associated risks, and more advanced analytical tools are needed to identify and quantify these NMs in natural environments (Hofmann et al., 2020).

Bringing this awareness, biological methods may be the safer, cost-effective, and eco-friendly option than chemical synthesis and allow the synthesis of NPs at physiological pH, temperature, and pressure (Chaudhry et al., 2018; Souza et al., 2019). Some studies have indicated that NP containing Ca, Mo, Mg, and mineral nanoconjugates of chitosan exhibited limited adverse effects on plants after soil application (Achari & Kowshik, 2018). Biogenic NPs are comparatively safer and less toxic than the chemically synthesized ones (Girilal et al., 2015). Although green synthesized NPs can induce harmful effects as oxidative stress, they are milder than the chemically synthesized ones (Krishnaraj et al., 2016; Shobana et al., 2018; Yaqub et al., 2019). Due to the lack of toxic chemicals during their synthesis and their high adaptability, green NMs have a vast application domain (Bartolucci et al., 2020). In this context, nanotechnology interest in agriculture use is today mainly turned to green production of NMs, slow and sustained delivery of nutrients from nanofertilizers, and active ingredient delivery from nanopesticides. For example, contrary to chemically synthesized Ag NPs, biogenic Ag NPs at lower concentrations can be a promising option for many applications in both industrial and environmental areas. However, it is still crucial to understand the interaction between these Ag NPs with living organisms and their potential environmental toxicity (Ottoni et al., 2020).

3.2 Bioaccumulation and Trophic Transfer of NPs

Another critical issue to consider is the bioavailability of the accumulated NPs to the next trophic level since NPs can reach different environmental compartments and their organisms. Chae et al. (2016) showed that the transfer of NPs through a model terrestrial food chain consisting of the yeast, the collembolan, and the pill bug indicated the potential hazards of released NPs for organisms at different trophic levels. Furthermore, Skjolding et al. (2014) observed the trophic transfer of ZnO NPs from daphnids (*Daphnia magna*) to zebrafish (*Danio rerio*). Nemati et al. (2019) found that CuO NPs can be transferred from one trophic level to the next level, as verified after diet-borne exposure of *Amatitlania nigrofasciata* larvae for 21 days to *Artemia salina* nauplii pre-exposed.

NM trophic transfer to the next level depends upon NM stability and surface properties (Pradhan & Mailapalli, 2017). Tangaa et al. (2016) defined four processes that influence the trophic transfer of metal NPs: environmental transformations of metal NPs, uptake and accumulation in the prey organism, internal fate and localization in the prey, and the digestive physiology of the predator. Additionally, in aquatic food webs, they suggest that the NP association with sediments may be a process that results in the transfer of intact particles. However, other possible co-existing effects of contaminants may also interfere with nano-toxicity. There are some potential routes for NP increasing bioaccumulation of co-exposure contaminants. Then, NP can absorb other contaminants, serve as carriers for the contaminants, bind with contaminants, facilitate the formation of more reactive metabolites, and cause cellular damage. Also, few studies have investigated the joint toxicity of NP mixture. These studies focused on mixtures of metal-based NP as plant fertilizers, ZnO and CuO NPs, since there may be effects of interactions between dissolved ions, dissolved and particulate NPs, and particulate NPs (Du et al., 2018).

Several organic and inorganic contaminants are distributed in the natural environment, and NPs act as carriers to transport these environmental contaminants into the cells of living organisms due to their enormous sorption capacity. NP surface can adsorb contaminants that have synergistic or antagonistic effects on the toxicity of them to different organisms depending on the contaminant surface charge and NPs' zeta potential (Abbas et al., 2020). For example, a mixture of NPs and metals can lead to decreased ingestion and filtration rates of copepods leading to an alteration of their metabolic responses. Then, combined lead (Pb) and TiO_2 NPs exposure may negatively impact the physiology of aquatic biodiversity and food chain dynamics in freshwater ecosystems (Matouke & Mustapha, 2018). Also, Yang et al. (2018b) observed that the increased transfer of algae by the food chain to *A. salina* of arsenic (As) in the presence of nano-TiO_2 can be explained by adsorption of As onto nano-TiO_2 in contaminated food (algae).

Indeed, there is limited information regarding what extent metal NPs could accumulate in biota and magnify along the food chain in real natural aquatic environments. Baudrimont et al. (2018) verified some effects of Au NPs from periphytic biofilms to the crustacean *Gammarus fossarum* due to transfer and bioaccumulation of Au NPs along with the food web. Moreover, Ag NPs and TiO_2 NPs may endanger phytoplankton via inducing oxidative stress and compromising photosynthetic activities. For invertebrates, sediment served as the main reservoir and a vital exposure source of Ag NPs and TiO_2 NPs. Chironomid larvae, which are associated with benthic substrates and link primary producers to secondary consumers, can be considered the entry point for the Ag transference to the higher trophic levels. Also, chironomids seem to play a critical role in enhancing Ag bioaccumulation due to their feeding habits in macrophytic zones (Williams et al., 2018). In turn, the potential great bioaccumulation and biomagnification of Ag NPs in benthic invertebrates (e.g., shrimp, shellfish) and fish species highlight the risks of aquatic food product consumption. However, the potential of metal NP accumulation in organisms depends on the material. For instance, Ag NPs showed stronger bioaccumulation than TiO_2 NPs and biomagnified in fish food webs (Xiao et al., 2019).

In addition, NP interaction with biota at one trophic level may alter the biological response at the next trophic level in a way that is dependent on the delivery scenario (Fig. 4). That is, direct exposure to CuO NPs can cause significantly higher *Daphnia magna* mortality relative to feeding exposure, whereas neonate production from adult daphnids exposed indirectly to CuO NPs was significantly reduced. Besides, exposure to $Cu(OH)_2$ nanopesticides showed a significant effect on the expression of genes related to detoxification and the reproductive system in *D. magna*. Short-term (24 h) exposure to the nanopesticide reduced the expression of genes associated with detoxification, but its expression increased significantly after 48 h of exposure. The expression of genes related to the reproductive system changed with concentration and time-dependent manner. These results show the role of genes related to detoxification and the reproductive system in response to $Cu(OH)_2$ nanopesticides. These facts show the importance of evaluating potential ecological impacts of NMs in more relevant, complex exposure scenarios and stress the importance of considering dietary uptake as a pathway for NP exposure (Majumdar et al., 2016; Wu et al., 2017; Aksakal & Arslan, 2020).

Only a few studies evaluated the NM transfer along food chains, including predatory fish as a secondary consumer. TiO_2 NPs are among the most studied. For example, Wang et al. (2016a) studied the trophic transfer of TiO_2 NPs in a marine benthic food chain from clamworm to juvenile turbot. The authors reported trophic transfer but no biomagnification of TiO_2 NPs between trophic levels. Also, only a few studies are assessing the dietary uptake of nanoparticulate Cu in fish. However, some information on NP transfer from invertebrate prey organisms to fish can be inferred from studies that examined intestinal uptake and accumulation of metal oxide NPs from artificial diets (Lammel et al., 2020).

Two arthropod species with different exposure routes to soil contaminants (isopod *Porcellio scaber* and springtail *Folsomia candida*) accumulated Ag when exposed to pristine Ag NPs, suggesting a risk for food-chain Ag accumulation. In contrast, no Ag bioaccumulation was detected in the case of the poorly soluble Ag_2S NPs, which is the more environmentally relevant form of Ag NPs. From this study, it is verified that soil pH and soil texture are the strongest predictors of Ag bioavailability, respectively, to isopods and springtails and is evidenced the dominant role of dissolution in Ag NP bioavailability (Talaber et al., 2020).

Given that, NP adverse effects, including its transfer through the food chain risks, have to be studied to ensure both the safe use and social acceptance of nanotechnology. In the heterogeneous environment, NP ecotoxicity monitoring is a challenging task as this process is considered dependent on both abiotic and biotic factors. Mammals, including human beings, are the ultimate recipient of the NPs through dermal absorption, inhalation, or ingestion of contaminated food (Abbas et al., 2020). So, the use of more complex experimental systems may evidence routes of exposure that are poorly or not estimated in classical standardized tests based on single-species assessments (Wang et al., 2016b).

4 Risk Analysis and Legislation

Nature-derived biopolymeric NPs such as chitosan and cellulose can be safely incorporated into the food matrix without affecting their sensory properties (Valencia et al., 2019). Therefore, the production of nanofertilizers should focus on the slow release of mineral ions entrapped in NPs of biodegradable, natural polymeric materials, such as chitosan, carboxymethylcellulose, hydroxyapatite, mesoporous silica, etc. Biopolymer–mineral nanoconjugates can be formulated with greater stability, biodegradability, and reduced toxicity (Achari & Kowshik, 2018). Biocompatibility, biodegradability, and low toxicity make chitosan an effective nano-delivery system since it is stable, has low toxicity, and requires simple preparative methods, which make it a versatile and user-friendly drug delivery agent (Chandra et al., 2015).

In the agricultural sector, polymer-based NPs help the local delivery of fertilizers and pesticides without polluting soil and air. Polymers are widely employed for the nanoencapsulation of pesticides. Several studies have also demonstrated the benefits of polymeric nanocarriers to reduce the toxicity of synthetic pesticides toward nontarget crop species. The significant advantage of natural polymers is that they can be degraded by soil microorganisms resulting in environmentally nontoxic products compared to their nondegradable synthetic counterparts. However, the potential ecological and safety benefits of nano-formulations conferred through the reduction in cytotoxicity or ecotoxicity of the active ingredient or reduced proliferation of antibiotic-resistant organisms should also be considered (Siracusa, 2019; Shakiba et al., 2020; Zhao et al., 2020b).

Although polymeric NPs can minimize ecological impacts, vital information on the toxicity of inorganic NMs like TiO_2, ZnO, and SiO_2 and organic NMs like carbon nanostructures are still lacking. From a safety and regulatory standpoint, proper legislation has to go through more studies and improvements. On the other hand, exposure to NMs may be harmful to the consumer and the environment and might increase risk potential. Risk assessment of NMs is still a controversial and extensive topic because of the lack of sufficient scientific data. The properties, physiological and chemical interactions, and toxicity of NPs under different environments are important considerations before they are commercialized for use in the market. Quality control is also an essential factor to be considered, and product shelf life and stability are important aspects. The cost would be another mitigating factor (Shakiba et al., 2020; Svendsen et al., 2020). Furthermore, products should be tested under relevant field conditions, mainly if they aim to improve production in regions where practices are inadequate and where pedo-climatic conditions are unfavorable and variable. Also, both technological development and improvement of agronomic practices should be considered concurrently, aiming at the reduction of currently used agrochemicals that have lower reliance (Kah & Kookana, 2020).

There is a need to develop proper methods to quantify NMs worldwide since the detection and identification of NMs is very challenging. Furthermore, a reasonable correlation between nanocompounds and toxicology is not yet well explored. For risk management, we should take a systems innovation approach for scaling up from laboratory to industrial level, which is not merely about changes in technical products but also about policy, user practices, infrastructure, and industry structure (Liu et al., 2018). Indeed, there is a lack of scientific data for different regulatory agencies to assess and provide risk management guidelines. It is needed to enhance the knowledge and awareness of nanotechnology applications in agriculture. Advances in these directions will contribute to the fast nanotechnology expansion.

Additionally, more research is needed to apply nanotechnology in different environmental systems and their interaction with organisms and biomolecules (Dasgupta et al., 2015; Abbas et al., 2020). No method dominates in applicability and use over the others, within all contexts. One option is governance using holistic, multi-criteria approaches, which comparatively review risks, benefits, and other implications of nano-enabled products against conventional alternatives (Trump et al., 2018).

The development of standardized testing protocols is needed to allow stakeholders to efficiently and consistently parameterize exposure models (Singh et al., 2019; Svendsen et al., 2020; Xiarchos et al., 2020). As an alternative to analytical methods*,* the potential NM environmental concentration in a given region can be estimated by in silico modeling approaches (Wigger et al., 2020). Although traditional risk management frameworks for agriculture have largely been deemed adequate for the task, there are several characteristics unique to nanotechnologies that need attention as physical, chemical, and biological properties of NMs that may differ in important ways from the properties of single atoms, molecules, or bulk materials. These proprieties interfere in identifying any direct, indirect, and/or cumulative impacts of NMs and nanotechnologies. Besides, some concerns related to subtle changes in the method of preparation can lead to significant alterations in the physicochemical properties and morphologies of the resulting NPs (Mitter & Hussey, 2019).

For this reason, evaluation of the potential risks resulting from the interaction of NMs with biological systems, humans, and the environment need more studies before commercialization (Sadeghi et al., 2017). Consumer acceptance of foods produced using nanotechnologies is essential for their widespread adoption, and public attitudes toward nano-enabled agriculture would likely vary by area of application. Consumer perception and acceptance will then decide the success or failure of nanotechnologies in agriculture (Hofmann et al., 2020).

Further research on socioeconomic aspects would be ideal while recommending nanopesticides in crops and stored grains. Thus, the commercial use of NMs requires thorough investigations into the screening and optimization of the NMs for different plant species (Usman et al., 2020). The need for adequate regulation to support nanosecurity is critical as its continued advances are quickly translated into new commercial products. Consequently, the lack of validated protocols and a need for regulatory approval before using any new technology have led to a delay in its adoption (Lombi et al., 2019).

The agricultural applications of nanotechnology are affected by several factors, including technological feasibility, cost-effectiveness, regulatory requirements, and consumer acceptance. Since agriculture is, and always has been, a socioecological system, the assessment of new technologies entering it requires integrating different forms of knowledge. To overcome any agri-nanotechnology doubts, it is vital to perform comparative toxicological studies, engage the public and stakeholders in research and innovation, and contribute to developing a transdisciplinary risk governance framework for nanotechnology (Lombi et al., 2019).

To be safely introduced to the market, the risk assessment of these nanoproducts demands establishing the proposed use pattern (Walker et al., 2018). For nanotechnology implementation in agricultural practices, it is necessary to evaluate changes of NM properties in the environment and make an ecotoxicological risks diagnosis due to their use. As a result, nanotoxicology has become a significant concern for all areas. The information obtained may be used by regulatory agencies to assess the potential NM risks throughout different stages of the product life cycle. The effects of using ENMs in agricultural practices cascade throughout their life cycle and include effects from upstream-embodied resources and emissions from ENM production as well as their potential downstream environmental implications. These analyses are important for the agriculture sector due to the relationship between food production, global health, and prosperity (Gilbertson et al., 2020).

Nanoformulations are challenging to implement due to their production costs, legislative uncertainties, and public opinion challenges (Nehra et al., 2021). From the perspective of researchers and stakeholders in agriculture, public understanding can lead to greater security to decide which technological solutions are a priority. Public perception of safety and regulatory concerns surrounding the use of engineered NMs in food production must be addressed to ensure safety and assist the acceptance and adoption of plant nanobiotechnology approaches (Lowry et al., 2019).

5 Conclusion and Perspective

NM applications raise some concerns about their impact on human health and the environment. These concerns emerge because a reliable risk assessment in nanotechnology is yet to be achieved. The reasons for such a shortcoming are the inherent difficulties in characterizing NMs properties (Xiarchos et al., 2020). Understanding NM environmental behavior and the time needed to track them in natural systems is challenging (Wigger et al., 2020). There are uncertainties concerning the use of NMs appropriately in an ethical way to preserve the sustainability of the environment. Nanotechnologies should be considered to ensure intergenerational and ecological equity. Ethics plays a role in protecting our environment from the NM risks and involves identifying and assessing potential risks in the environment. For that, values and actions need to be considered to protect ecological systems (Besha et al., 2020). The incorporation of ethics into a scientific decision support framework for risk governance of NMs is essential.

On the other hand, there is no platform where all stakeholders can meet and discuss these issues. Ethical dilemmas cannot easily be accommodated in an appropriate balance between precaution and innovation as it depends on cultural differences. However, it is important to consider conflicting values and worldviews and place them in historical contexts (Malsch et al., 2020). There is a long way to be covered to produce commercially successful, eco-friendly, and safe nanopesticides. Further studies on environmental fate and bioaccumulation of nanoformulations are still required to develop environmentally friendly and sustainable methods to avoid the excessive use of pesticides (Nehra et al., 2021).

Environmental risks of NMs have mainly focused on the characterization and quantification of their hazards, using standard toxicity assays or slightly adapted procedures to cope with the unique properties of NMs. Dose–response relationships may be derived from nominal exposure concentrations. However, the use of measured concentrations is difficult to obtain with the present methods, and the biological matrices present many challenges to NM detection inside organisms (van den Brink et al., 2019). Then, additional studies are needed for investigating transformation and its related toxicity at environmentally relevant concentrations. Further research is needed to elucidate the influence of transformation processes on NM toxicity and their transformed products (Zhang et al., 2018b). In the agriculture sector, the adoption of a technology is commonly driven by favorable economic tradeoffs. Targeted applications, as a soil amendment, seed coating, or foliar spray, will prevent the excessive release of NM to the environment, which will reduce costs to promote crop production and the potential adverse environmental implications as the fate and subsequent consumer exposure potential of NMs (Gilbertson et al., 2020).

As demonstrated throughout this chapter, nanopesticide and nanofertilizer research and development can provide new tools that support the sustainable growth of agriculture, directly impacting the present scenario as in the coming decades. However, despite these advances, it is still necessary to overcome some barriers to the consolidation of these materials. Among these barriers, we can highlight the lack of more specific regulatory protocols for these compounds and the intensification of studies on the fate and behavior of these NMs in the environment. Overcoming these barriers will allow a better understanding of these materials' effects on nontarget organisms, leading to greater security.

Therefore, more effective collaboration among universities, companies, and government agencies will be needed in order to strengthen and secure these products on the market. In addition, research will be required under more realistic conditions and on larger scales to provide important data for the real assessment of the advantages of these systems. Future research priorities may include developing methods to detect and characterize NMs in complex matrices and determine their transformations in such environments. Furthermore, to assess NM nanosafety, the experimental design must also consider adequate calibration, method validation, accurate dosimetry, and the availability of reference materials (Johnston et al., 2020). More strategic and interdisciplinary research is thus urgently needed to support technological innovation that will help achieve more environmentally sustainable food production (Kah & Kookana, 2020) and reduce the NM input per agricultural area. Biosynthesized NP-based fertilizers and pesticides should be explored further as a promising technology to improve yields while achieving sustainability.

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Strategies to Produce Cost-Effective Fertilizer-Based Nanoparticles

A. L. E. Fattobene

Abstract Population increase, the need to increase the productivity of crops per unit of agricultural land, and a considerable market share in the case of special fertilizers bring the need for new technologies. Nanofertilizer production is through two technological approaches: bottom-up and top-down. Both production methods have their benefits and weaknesses. While bottom-up brings better process control and smaller particles, top-down is more widely used in industry because it is cheaper and simpler to apply.

The main idea of this chapter is to bring an industrial vision that contemplates all the steps and procedures of the development and production of nanofertilizers within industry, dealing with the main points, their motivations, and possible consequences. The processes described and exemplified here are part of everyday industrial life. However, many are clearly only summarized, may vary from company to company, and should be used only as a guide. Equipment for development, production, and quality control and raw material, additive, and formulation characteristics are described.

Keywords Fertilizer · Nanotechnology · Industrial process · Production · Particle size · Nanosuspension

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1 Introduction

The definition for fertilizers, according to the International Fertilizer Association (IFA), is: “Fertilizers are any solid, liquid or gaseous substances containing one or more plant nutrients” (IFA, 2021). However, the definition of fertilizers is broad and should include other characteristics, such as growth of crops, reduction in productivity loss, improvement in food quality, and keeping the levels of contaminants within the current rules for environmental protection.

The world fertilizer market is estimated at approximately USD $186.0 billion considering the numbers of macronutrients—USD $151.4 billion (International Fertilizer Association (IFA), 2019), secondary macronutrients—USD $30.86 billion (Markets and Markets, 2018), and micronutrients—USD $3.5 billion (Fortune Business Insights, 2018a, 2018b). Within these numbers, there is a market for specialty fertilizers, which is estimated at USD $22.92 billion (Fortune Business Insights, 2018a, 2018b). This categorization is one of several ways to categorize specialty fertilizers and includes controlled-release fertilizers, water-soluble fertilizers, agricultural micronutrients, and customized fertilizers. Microsuspension fertilizers make up one of the segments within those specialty fertilizers.

There are several companies that produce microsuspension fertilizers. Table 1 shows some of these companies and their websites.

Table 1 Microsuspension fertilizer companies

Company	Website
AdFert™	http://www.adfert.com/products/suspension_product.html
Agrichem™ Australia	https://agrichem.com.au/
Agrichem™ Brazil (Nutrien)	https://www.agrichem.com.br/
Agrigento™	https://agrigento.com.br/en/products
Agromila™	https://www.agromila.com/en/npk-suspension-brfertilizer-group-c11
Compo Expert™	https://www.compo-expert.com/product-groups?country=global
IFTC™	https://iftcjo.com
Infert™	https://infert.com.jo/liquid-and-suspension-fertilizer/
Jiangsu Hanling Fertilizer™	http://www.hanling-fertilizer.com/
Liquid Grow™	https://www.liqui-grow.com/blog/what-are-liquid-suspension-fertilizers/
MAPCO Fertilizers™	http://www.mapcofertilizers.com/
Omex™	https://www.omex.com/
Prime Agro™	https://primeagro.com.br/prime-nutre/
Santa Clara Fertilizantes™	http://www.santaclaraagro.com.br/
Sonic Essentials™	https://sonicessentials.com/icon-range/
Vittia Fertilizantes™	https://vittia.com.br/
Wuxal™	https://www.mywuxal.com/en/product-finder?step1=3
Yara™	https://www.yara.co.uk/crop-nutrition/fertilizer/micronutrient/

Despite the secrecy of the manufacturing processes, it is possible to infer that most companies use the top-down manufacturing process for their microsuspension fertilizers. These processes yield larger particle sizes and higher concentrations than do bottom-up processes, while the latter is still mostly retained in academic research due to the high cost of equipment and raw materials, long processing times, and the complexity of these new technologies when referred to an industrial scale.

Microsuspension fertilizers tend to have high density (usually above 1.3 g/cm^3 to 2.2 g/cm^3), medium to high viscosity (800–4000 cP at Brookfield, Spindle 3, 20 rpm, 25 °C), high nutrient content, normally sparingly soluble (oxides, carbonates, and some hydroxides), and a particle size distribution (PSD) normally below 8 μm (most commonly d90 < 4.0 μm).

From the fertilizer industry standpoint, for the medium-term horizon, the production of colloidal dispersions might continue to rely on a top-down strategy since current equipment can be adapted. However, the lower limit of the technology is currently around d50, 30 nm (zirconium beads of 0.03 mm). In order to really achieve smaller particles, bottom-up technologies must be scaled up for the market in the long term.

Companies still show a certain resistance to move toward nanotechnology because they do not know definitively how the market and production methods (in this case, the production of crops through the application of fertilizer) will develop. One reason is that there are still few companies in the world working with micronized fertilizers. Thus, some companies that have the technology to produce nanofertilizers prefer to wait to innovate until a more opportune market time.

According to the Nanotechnology Products Database (NTC, 2021), there exist 102 nanofertilizers from 41 companies located in 17 countries. Just two of them have certification, which does not necessarily mean that others do not have the technology.

Many countries do not have regulations, certifications, or special registration for nanotechnological products. Therefore, it is essential to separate actual nanotechnological products from those that take advantage and just use the word "nano" as a marketing strategy.

The main idea of this chapter is to bring an industrial vision that considers all the steps and procedures of the development and production of fertilizers within the industry, dealing with the main points, their motivations, and possible consequences. The processes described and exemplified here are real. However, many are clearly summarized and may vary from company to company and thus should be used only as a guide.

2 Bottom-Up

In the bottom-up approach, the particles are synthesized under specific reaction conditions to control the resulting PSD. With current technologies, this approach can deliver smaller particle sizes than the top-down approach. Below, a brief explanation and some studies of each process are presented that demonstrate how the nanoparticles of that particular nutrient (oxide or carbonate) are obtained.

2.1 Sol-Gel Synthesis

The sol-gel method involves a precursor, a solvent, and a medium (water or organic phase) (Hasnidawani et al., 2016) and, in general, can be described in these five steps: hydrolysis, polycondensation, aging, drying, and thermal decomposition (Parashar et al., 2020). $CaCO_3$ was reported by Ghiasi and Malekzade (2012), CuO by Dörner et al. (2019), and MgO by Lopez et al. (1991), and in their review, Parashar et al. (2020) reported the sol-gel synthesis of ZnO by different research groups.

2.2 Reduction

The basis of the reduction method for the formation of nanoparticles is the dissolution of a soluble salt in a liquid medium and, through a reducing agent and specific reaction conditions, controlling the bonding between atoms forming metallic oxide and carbonate nanoparticles, as can be seen for $Cu–Cu_2O$ (Khan et al., 2016), MgO (Moorthy et al., 2015), $MnCO_3$ (Wang & Li, 2003), and ZnO (Preeti & Vijay, 2017).

2.3 Precipitation

The precipitation method involves the addition of a soluble salt to a liquid medium, and, after dilution, the addition of an alkaline agent to promote precipitation. In this way, it is possible to control the size of the particles formed. Precipitation methods are described for $CaCO_3$ (Widyastuti & Kusuma, 2017), CuO (Mohsen, 2016), MgO (Vijayalakshmi et al., 2016), $MnCO_3$ (Lei et al., 2009), and ZnO (Raouf, 2013).

2.4 Hydrothermal/Solvothermal

Solvothermal synthesis takes place when the precursors are dissolved in a solvent and, after being closed hermetically, the container is brought to temperatures above the boiling point of the solvent. As the temperature and pressure increase, the chemical reaction, or decomposition of the precursors to the desired material, occurs. When the solvent used is water, this synthesis is referred to as hydrothermal. The following works indicate the synthesis of $CaCO_3$ (Sun et al., 2016), CuO (Titirici et al., 2006), MgO (Hadia & Mohamed, 2015), $MnCO_3$ (Yang et al., 2009), and ZnO (Xu et al., 2009).

2.5 Flame Spray Pyrolysis

A solution of the nutrient salt of interest is sprayed into a flame. While the solvent is decomposed or evaporated, the salt is transformed into the oxide/carbonate of that nutrient through pyrolysis and collected on a substrate. The PSD obtained is the result of controlling the agglomeration of the formed oxide/carbonate molecules that occur during the deposition on this substrate.

Flame spray pyrolysis procedures are presented for $CaCO_3$ (Huber et al., 2005), CuO (Chiang et al., 2012), MgO (Boningari et al., 2018), and ZnO (Wallace et al., 2013).

3 Top-Down

In theory, a top-down methodology is basically defined as breaking down a system so that its subsystems are known. An overview of the system is initially formulated but does not specify any details of the first level of the subsystems. Each subsystem is then refined in greater detail, sometimes at many levels of supplementary subsystem, with the entire specification being reduced to an elementary basis.

In the case of fertilizer nanosuspensions, for dry or wet grinding methods, the particle size reduction process takes place in three steps:

- De-agglomeration of lumps.
- Separation of aggregated primary particles.
- Breakdown of primary particles.

As Fig. 1 shows, primary particles can be defined as the individual, crystalline, or amorphous parts generated in the material manufacturing process and difficult to grind. These primary particles are usually aggregated, that is, strongly bonded over a large surface area. These aggregates form clusters that are various aggregates or primary particles that are weakly connected.

Note that there are spaces within these clusters that contain air. When de-agglomeration starts, the PSD decreases, and the surface area increases significantly. The surfactant will bind to these hydrophobic regions bringing balance to the formulation. The real breakdown of the primary particles will only occur in the advanced stages of grinding, with the change to a smaller set of beads.

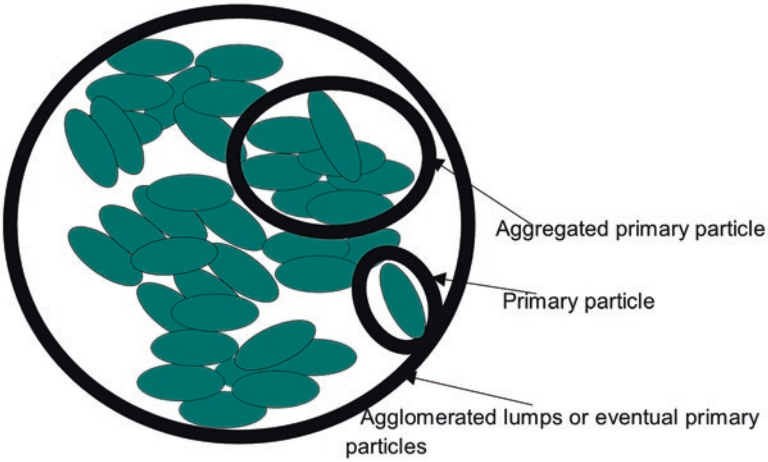

Fig. 1 Scheme showing primary particles, aggregated particles, and agglomerates

3.1 Development of Nanosuspension Fertilizers

For the successful development of any fertilizer, including nanosuspensions, the flow of information is vital. The choice of raw materials and other components of the formula are closely linked to the initial information and decisions about the product. Which crop, which mixtures, which nutrients, which cost target, and which functions are expected are some of the questions that must be answered before the development process starts, as seen below**.**

3.1.1 Raw Materials

The production of a stable, high-quality nanoparticle fertilizer in accordance with the needs of the customer begins with the choice of raw materials and additives, which must have specific characteristics for each fertilizer considering their purity, physical-chemical properties, and the interaction between the various components of the formulation.

The following are the other aspects that must be considered when evaluating a raw material:

The grade (food, pharmaceutical, industrial, technical). Obviously, the higher the purity of the raw material and additives, the higher the price and the lower the levels (ppm or ppb) of heavy metals (As, Cd, Cr, Hg, and Pb), remembering that fertilizers will be applied to plants that will produce food for human consumption. Also, the greater the level of contaminants, the greater the risk of undesirable interactions.

The supplier should be a business partner (and a great deal of time is necessary to build this), be ethical, have production capacity, and be sustainable.

The lead time for each raw material and additives should be considered. Having a known schedule makes it possible to buy at lower prices since it is possible to avoid market speculation.

Whenever possible, it is better to formulate using raw materials and additives whose production is not very specific (alternatives will be easier to find in the market).

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Tip The eventual cost increases of the finished product due to the price of high-quality raw materials compared to cheaper, lower-quality raw materials will no doubt deliver future savings in terms of product returns and reprocessing. Obviously, it is important to approve more than one supplier of a raw material to gain strength in negotiations and reduce the risk of shortages. It is also important to be watchful of the market to find new suppliers and to reduce costs, but cost should never be put before quality.

For micro- and nanosuspension fertilizers, there are soluble and insoluble solid raw materials. The most common soluble ones are urea, sodium molybdate (Na_2MoO_4), monoammonium phosphate (MAP), diammonium phosphate (DAP), potassium hydroxide (KOH), potassium chloride (KCl), and potassium carbonate (K_2CO_3). The insoluble ones are carbonates and oxides of alkaline earth (Mg and Ca) and transition (Co, Cu, Fe, Mn, Mo, Ni, and Zn) metals.

Tip Plants can only use Mn^{2+} as a nutrient.

Boric acid (H_3BO_3) and disodium octaborate ($Na_2B_8O_{13}$) can be considered soluble or insoluble depending on the concentration.

Tip Boron-containing raw materials should be used with care as they bring instability to suspensions.

3.1.2 Determining the Components and Nutrients

The information for creating a product can come through benchmarking, scientific work, process improvement proposed by the industrial area, company strategy, customer information, and fieldwork. After an initial development request, each company has its own workflows and information systems. In Fig. 2, an example is given of the information flow in the development of a new product.

Once the product information, such as suggested guarantees, pH, and its commercial viability has been determined, the chemical development begins.

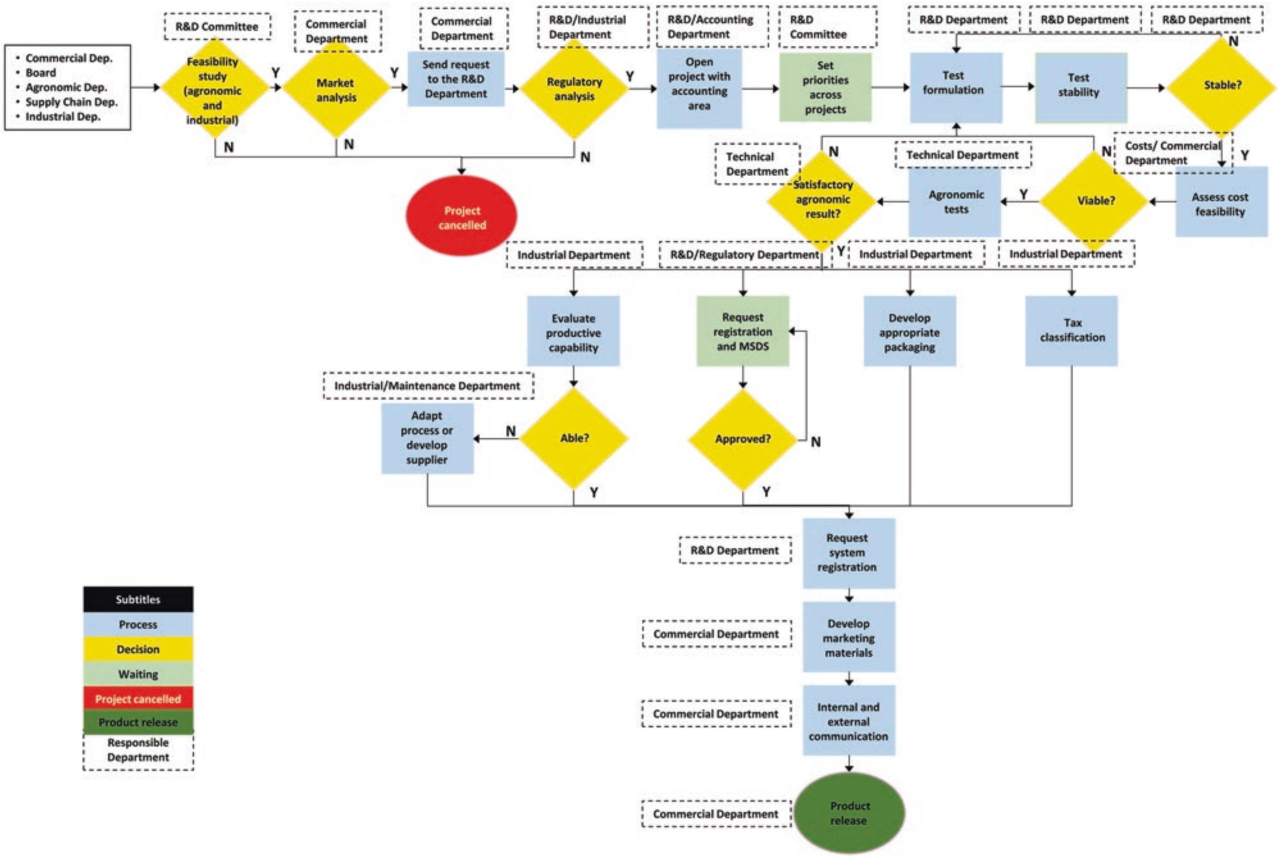


Fig. 2 Flowchart example

Usually, the nutrient content is presented in w/w and w/v, and it can be calculated by Eq. 1:

$$\left(\frac{w}{w}\right) = \frac{(m \cdot nc)}{d \cdot v} \tag{1}$$

where *w/w* is the weight/weight content (%), *m* is the raw material mass (kg), *nc* is the nutrient content in the raw material (%), *d* is the suspension density (kg/dm^3), and *v* is the volume to be produced (dm^3).

In this way, it is possible to calculate, for each raw material, the correct quantity to include to guarantee the amount of nutrient in the product formulation.

A high-suspension nanoparticle formulation has the following components:

Water- or Oil-Based

Water-based microsuspension fertilizers are the more common, but there has been some research into oil-based formulations in the industry (cobalt and molybdenum formulations, for example). From now on, the discussion will concern only water-based formulations except when otherwise stated.

With Surfactants

There are many surfactant options available on the market, from simple and cheap but functional, to more complex and expensive, which can confer other desirable characteristics (Fig. 3) to the products in addition to their main function (discussed in Sect. "Surfactant").

According to Lv et al. (2015), ZnO nanoparticles are solubilized and enter the leaves as Zn^{2+} and accumulate in the form of phosphate. The nanosuspensions are diluted in the application solutions. Therefore, the smaller the particles, the greater

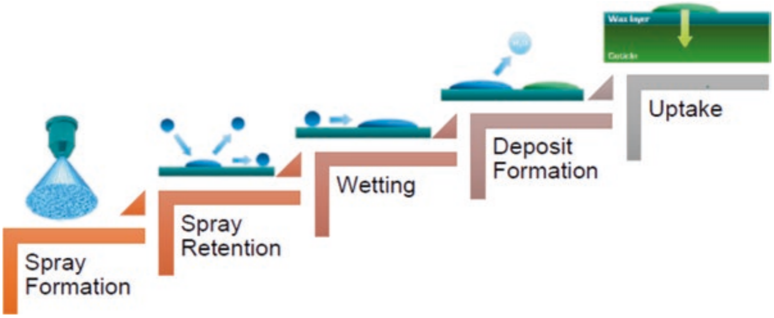


Fig. 3 Diagram showing the desirable functions of a fertilizer where surfactants work in sequence. Image reproduced by permission of Croda

their solubility. When the drop touches the leaf, Zn^{2+} ions are absorbed. As the drop spreads on the leaf, evaporation increases, and the particles start to settle on its surface, adhering thanks to the surfactant.

At night, with the dew, these deposited particles are re-suspended and the smallest particles again solubilized, entering the leaf in the form of Zn^{2+}. The surfactant is responsible for maintaining the particle size and allowing re-suspension.

The example of Zn was mentioned here, but the same applies for any nutrient. And so, day after day, the ions are absorbed and there is a gradual release of nutrients.

Anti-drift (Fig. 4) and/or increasing coverage by reducing the contact angle between the applied spray and the hydrophobic surface of the leaves (Fig. 5) are greatly affected by the addition and type of surfactant.

Many variables influence the choice of surfactant, such as pH, conductivity, the particle size of the raw materials and the final product (and the surface area, which is closely linked to the particle size), and chemical affinity. Table 2 shows a list of surfactant suppliers and their websites.

Tip Test the surfactant with the raw materials before starting product testing. That way, it is possible to exclude some incompatibilities before starting.

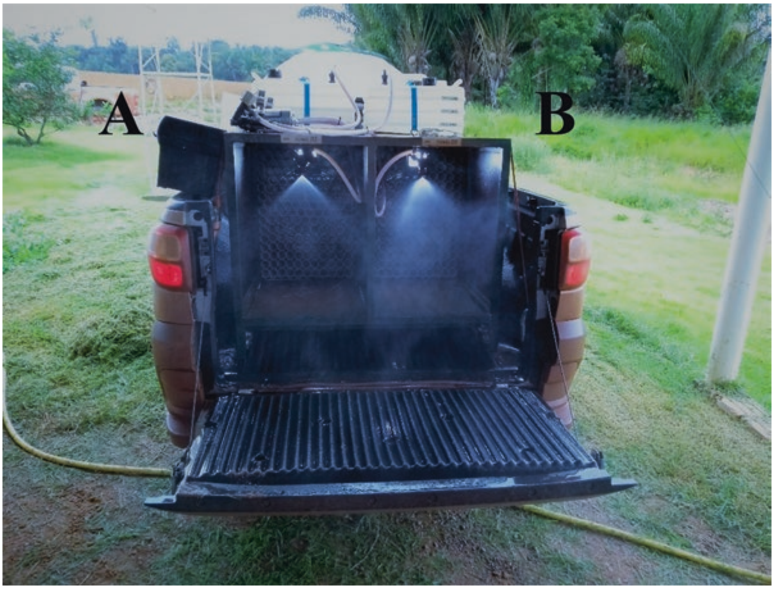


Fig. 4 Anti-drift test: (**a**) water with added surfactant, and (**b**) water without added surfactant. It is possible to verify that the cone in **a** is much more defined and the mixture reaches the bottom, while in **b** much of the mixture is lost due to drift. Photo by Maickon Balator

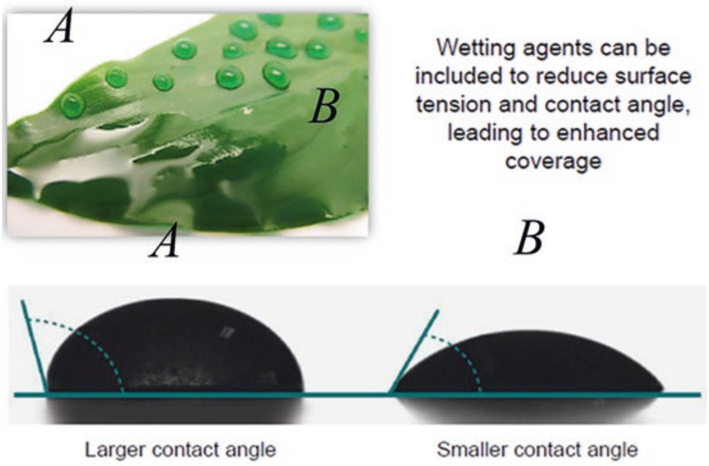


Fig. 5 Comparative coverage and contact angle in an application: (**a**) without surfactant, and (**b**) with surfactant. Image reproduced by permission of Croda

Table 2 Surfactant manufacturers

Company	Website
ARKEMA™	https://www.arkema.com/global/en/products/
BASF™	https://www.basf.com/global/en.html
CLARIANT™	https://www.clariant.com/pt/Corporate
CRODA™	https://www.croda.com/en-gb
Dow™	https://www.dow.com/en-us
ELKEN™	https://www.elkem.com/
EVONIK™	https://corporate.evonik.com/en
HUBTSMAN™	https://www.huntsman.com/
INNOSPEC™	https://innospec.com/
LANKEM™	https://www.lankem.com/
MOMENTIVE™	https://www.momentive.com/en-us
NOURYON™	https://www.nouryon.com/products/anionic-surfactants/
OXITENO™	https://www.oxiteno.com/
Sasol™	https://products.sasol.com/pic/products/home/index.html
Solvay™	https://www.solvay.com/en/solvay-around-the-world
STEPAN™	https://es.stepan.com/

With Thickener

As for the surfactant, the choice of thickener is influenced by the same variables and will be different for oil-based and water-based formulations (their function will be discussed in Sect. "Viscosity").

They can be natural, usually derived from polysaccharides, such as xanthan gum and guar gum, or synthetic, usually an acrylic polymer or cellulosic derivative, such as carboxymethylcellulose (CMC) and hydroxyethyl cellulose (HEC).

Other Additives

Depending on the industrial process or application in the field, additives can be included in the formulation for better results, such as defoamers, chelates or complexing agents, nutrient carriers, block co-polymers, spreaders, encapsulants, anti-crystallizing agents, antifreeze, preservatives (especially if the thickener is any of the gums), and antioxidants. However, it must be considered that each of these additives removes some water from the medium and, in some cases, can make particle dispersion more difficult. The use in the formulation must follow the dose and recommendations of the supplier.

3.1.3 The Suspensions Tripod

There are several factors that influence the stability of a suspension. By altering three of these factors during the development of the formulation, it is possible to solve in practice the intrinsic difficulties of this type of formulation. This is called the suspension tripod.

Two elements were studied by Stokes in his law for small rigid beads (Eq. 2):

$$V = g{d_p}^2\left(\rho_p - \rho\right)/18\mu \mathrm{Re}_\mathrm{p} < 0.1 \tag{2}$$

where V is the terminal settling velocity (m/s), g is the acceleration of gravity (m/s^2), d_p is the particle diameter (m^2), ρ_p is the particle density (kg/m^3), ρ is the density of surrounding fluid (kg/m^3), μ is the fluid viscosity (Pa s), and Re_p is the Reynolds Number (−).

For now, it is important to understand that if terminal settling velocity is high, the sphere takes less time to reach the bottom and two variables have a direct influence on that: sphere diameter and viscosity.

The larger the diameter of the sphere, the higher the terminal settling velocity, and the higher the viscosity, the lower the terminal settling velocity.

However, Stokes' work considered just one sphere (Fig. 6). When talking about a nanosuspension, there are millions of suspended particles and, because of that, several interactions between them.

Fig. 6 Scheme of the Stokes experiment

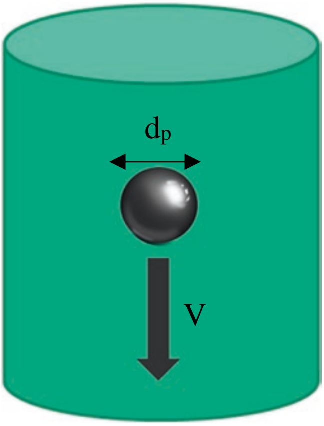
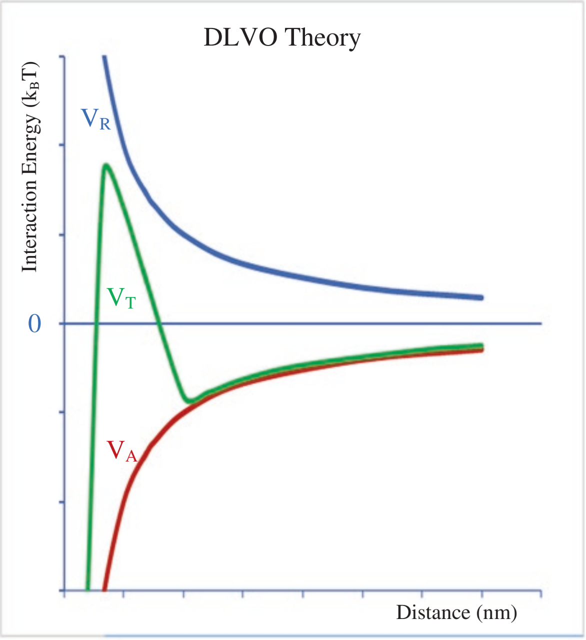


Fig. 7 DLVO theory diagram where V_T is the total interaction energy, V_A is the energy due to van der Waals (attractive) forces, and V_R is the energy due to repulsive electrostatic forces



Hence, by Stokes' law, there are viscosities, particle diameters, and PSDs as that it is possible to consider approximations for a nanosuspension.

The other variable comes from studies from the 1940s. Two pairs of scientists, Derjaguin and Landau (1993, but first published 1941—URSS) and Verwey and Overbeek (1948) simultaneously studied interactions in a colloidal suspension (Fig. 7).

The classic DLVO theory states that the energy resulting from all interactions (V_T) is the sum of the energy due to van der Waals forces (attractive forces, V_A) and

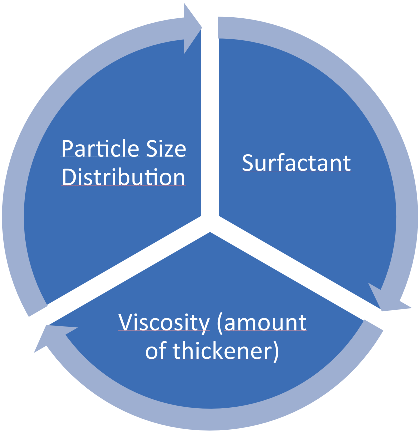


Fig. 8 Tripod of suspension stability interdependency

the energy due to double-layer forces (repulsive forces, V_R) varying according to the distance between the particles (Israelachvili, 2011), as shown in Eq. 3:

$$V_T = V_A + V_R \tag{3}$$

It is easy to understand that the interaction forces have a greater influence on smaller particles. In order for two particles to not clump together, the repulsion between them must prevail over the attraction.

Knowing these interactions in depth, it is possible to achieve the desired repulsion by adjusting these forces of interaction between particles with surfactants. They are the last part of the tripod. These surfactants, which generally consist of a hydrophilic head and a hydrophobic chain, are adsorbed on the surfaces of the particles through the hydrophobic part of the chain and preventing the particles from being electronically attracted by others and exerting a steric effect.

Although treated separately, these three variables are interdependent in relation to product stability, as shown in Fig. 8. The smaller the size distribution, the greater the number of particles and number of interactions, requiring more surfactant, which will affect viscosity.

Particle Size Distribution

As seen previously, the smaller the particle size, the slower the deposition speed. However, if there are more particles, there are also more interactions between them and longer process times.

Some materials show a significant natural increase in viscosity when they reach a certain size, requiring more surfactant, a change to a more powerful one, or even the addition of a second surfactant.

The greater the homogeneity of the PSD curve, the easier it is to find the ideal quantity of surfactant and viscosity in the formulation.

The reduction in particle size directly affects the surface area, considerably improving the quality of the application and increasing and homogenizing the coverage on the applied leaves.

In addition to the size distribution itself, three parameters are usually considered:

- d10: the volume of particles with diameters smaller than this value is 10%.
- d50: the volume of particles with diameters smaller than this value is 50%.
- d90: the volume of particles with diameters smaller than this value is 90%.

These parameters bring, numerically, a way of quality control to analyze batch by batch if the product is in conformity or not.

Tip During development or in further studies, it is also necessary to analyze the PSD graph since it is possible to have large variations in the curve even though the parameters d10 and d50 are close in value.

Figure 9 presents three normal distributions to exemplify d10, d50, and d90. Particle size distributions commonly do not follow normal distributions and may even have more than one peak depending on the structure of the crystal or agglomerate, as shown in Fig. 10, or, in the case of mixtures, with more than one component.

Tip There are fertilizers that contain mixtures of materials of different hardness. It is important to adjust the process and the surfactant(s) to ensure less variability in size distribution.

Viscosity

Viscosity can be defined simply as the resistance of a liquid to flow after a mechanical stress is applied.

Most of the fertilizers discussed here can be defined as non-Newtonian fluids, dependent on time and with thixotropic characteristics, meaning that at a constant shear rate the viscosity decreases over time until reaching a constant final residual viscosity.

It is reasonable to state that the deposition velocity is inversely proportional to the viscosity of the suspension and directly proportional to the particle size.

Two factors of the formulation affect viscosity in micro- and nanosuspensions. One is the particle size. As particle size reduces, the viscosity of the product tends to increase, due mainly to the increase in the surface area and the number of particles in contact with the surfactant and water. At this stage, an adjustment is usually necessary by adding a surfactant or even water.

The other is the thickener. The stability of the system must be controlled by adding thickener, which basically increases viscosity, forming an associative network

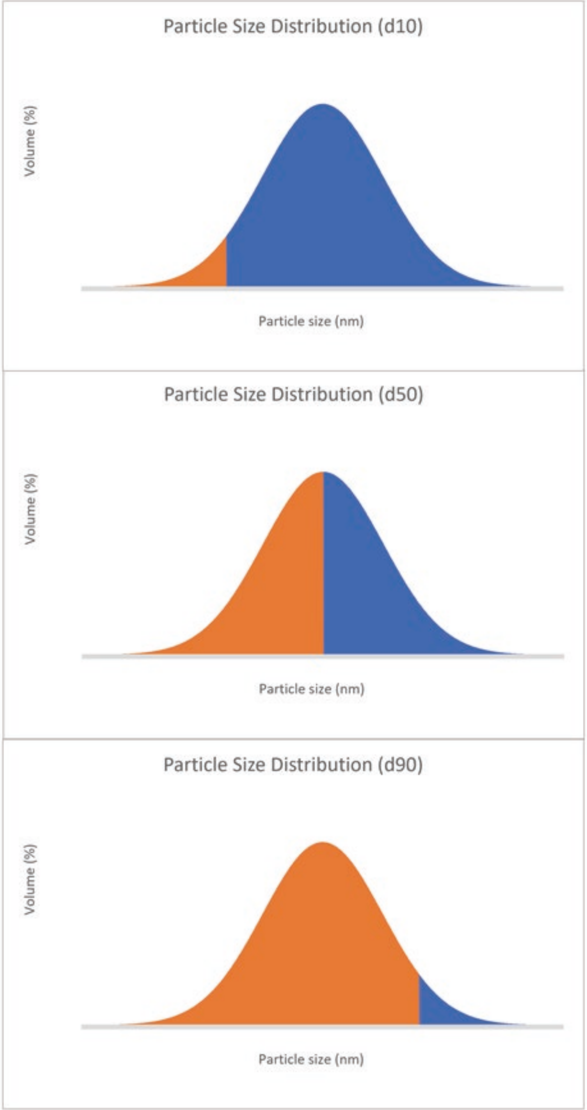


Fig. 9 Example diagrams of d10, d50, and d90

and raising a physical barrier to the liquid phase, therefore reducing the deposition velocity.

Surfactant

The surfactant will be essential during the first mixing and for the final stability.

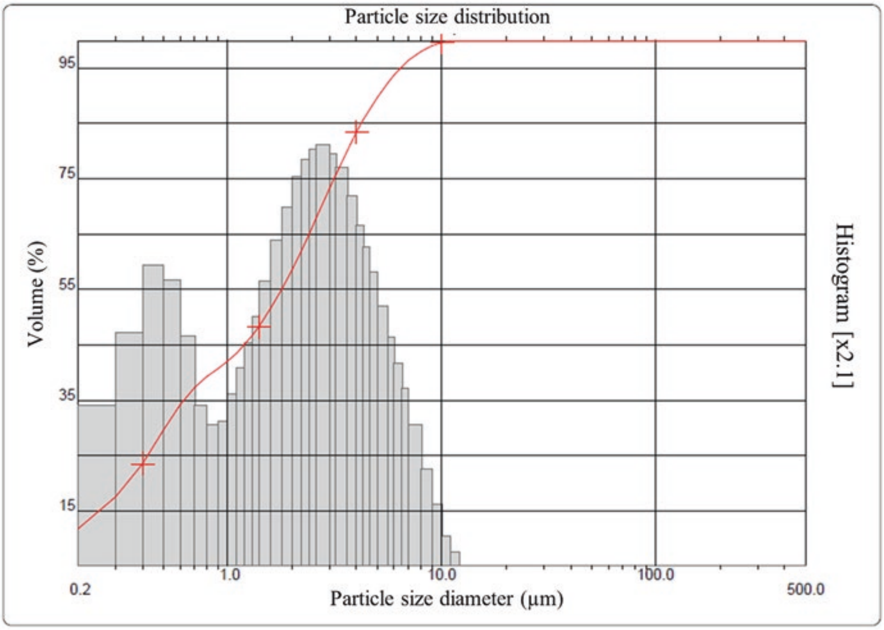


Fig. 10 Example of PSD of $CuCO_3$ by dynamic light scattering

In the first part of the process where solid (extremely hydrophobic) raw materials are added to the water, if the surfactant is not first added, much larger (and more expensive) equipment would be needed to achieve greater agitation speed (adding much more energy to the system), and the process would be significantly slower and more expensive.

Regarding stability, during grinding and size reduction (if there is induction charge generation), there is a consequent increase in the number of particles and the surfactant will bind these particles, reducing the attractive van der Waals forces and resulting in a steric effect.

Surfactants are also important in the application of these fertilizers, facilitating penetration into the leaf, adhesion, the rebound effect, and reducing drift. In addition, they may allow other products to be added to the application mix without chemical incompatibility.

3.1.4 Preparation of the Fertilizer

There are different sequences for adding the materials that make up a nanosuspension; these can vary from manufacturer to manufacturer and from product to product. Below is a suggested test sequence that can be adjusted as needed:
Add water.
Turn on the impeller.

Add urea (if used) or another soluble raw material (except boron-containing).
Add surfactant.
Turn on the chiller.
Add insoluble raw material (turn on the mill immediately after adding 25 kg).

Tip When there is more than one insoluble raw material of very different input particle size and hardness, add the harder and larger ones first. As the softer materials grind more quickly, adding them first will cause an anomalous size distribution that will be difficult to correct during the process.

After the addition of all raw materials, let them grind to the desired size (recirculation or multiple-pass will be discussed in Sect. 3.2.1), noting the time for future analysis and monitoring of the process.

When reaching the specific PSD of the product, measure the density, and start the product viscosity adjustment step by the addition of thickener.

Tip If there is boron-containing raw material, add it after the end of the grinding process and before the adjustments.

Sample to quality control to confirm the viscosity, density, pH, and nutrients content.

Send for filling.

Tip Any grinding after the addition of thickener may deteriorate the product due to the breakage of its chains. Therefore, avoid any grinding after its addition. If more grinding is really necessary, carry it out with caution and with prior tests to ensure stability. However, other solutions, such as batch mixes, can produce better results if there is space and, mainly, time available.

This is the suggested sequence for the development of the formulation. Obviously, it can vary with new developments and experiences and as new technologies appear.

It is important to note that the sequence defined here will later be used in the production process. Therefore, when the production process is dealt with in the next sections, the predetermined sequence is the one described here.

3.1.5 Quality Control during the Development Tests

The analyses related to quality control are described in Sect. 3.3. However, the analyses will be cited on the basis of their importance in the development and in which phase.

Density, pH, and nutrient content analyses will certify that the formula is balanced and the levels are in accordance with the initial specifications.

The following analyses ensure that stability has been achieved according to the suspension's stability tripod:

The first is the analysis of PSD, the second is the viscosity analysis, and finally the zeta (ζ) potential analysis, which is closely linked to the DLVO theory and, by approximation, connected with the action of the surfactant to predict the stability of the system. However, the analysis of zeta (ζ) potential is still not widespread in companies, due either to the cost of the equipment or because the technology is not understood. Therefore, in order to analyze stability in general, aging tests should be performed.

The aging test alone brings a great deal of information showing what will happen to the product in the future. But it is also a powerful tool when used in conjunction with PSD and viscosity measurements because it is possible to understand which of the variables may be affecting instability.

Except for the analysis of content, PSD, and, eventually, zeta (ζ) potential, it is suggested that analysts in the research and development department carry out the other analyses to monitor closely any variations during the development of the formulation (mainly the aging test).

It is important to perform a prior cost analysis of the product at this point to ensure that it is within the market price expectation after the company adds its profit margin.

Tip A good practice is to repeat all the stability analyses on samples that have reached 30 days of age, on other batches of raw material, and, if possible, by another analyst or laboratory operator. If the samples still show stability, the robustness of the formulation is attested at the laboratory level.

3.1.6 Compatibility Tests

Compatibility tests are carried out on products that have already undergone advanced stability tests. The tests are performed using the commercial doses of product in mixtures that are usually applied in farms. In addition to water and the fertilizer itself, adjuvants are added to adjust the pH and reduce foam and drift, and usually herbicide, fungicide, and/or insecticide depending on the time of application.

The procedure is to verify that there will be no incompatibility in these mixtures that would affect their application.

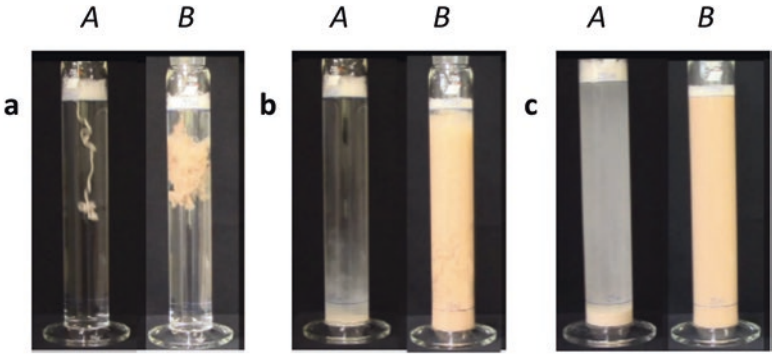


Fig. 11 Manganese carbonate suspension in mixture with glyphosate (Roundup Transorb™), at (**a**) immediately after addition, (**b**) a few minutes after addition, and (**c**) a few hours after addition; *A* without Croda's Atlox PN-100™; and *B* with Croda's Atlox PN-100™. Image reproduced by permission of Croda

For example, a mixture of manganese and glyphosate is known to be problematic due to the chelating power of glyphosate, which, when specifically added to manganese carbonate suspensions, can cause incompatibility problems not only with manganese carbonate but with other components of the suspension. Other surfactants can be used in the fertilizer formula or be added directly to the mixture to eliminate unwanted reactions. Figure 11 shows the mixture of a $MnCO_3$ microsuspension with glyphosate Roundup™ with and without Croda's Atlox PN-100™ adjuvant at three different times:

The difference goes beyond the visible. In a real application, the decanted usually clogs the filter/sieve or the spray nozzle, requiring the cleaning of the entire system. After a few attempts and several cleanings, the farmer usually abandons one of the products in the subsequent mixtures, causing problems with the crop.

This decanted is usually fully agglomerated, and the particle size can reach millimeter size. With the additive, it is possible to see the homogeneity of the mixture and it is possible to guarantee that the clogging problems mentioned above will not occur.

So, the function of compatibility tests is, ultimately, to show if there is anything that needs to be changed in the formulation itself or whether it can be corrected with the addition of some adjuvant (containing surfactants) at the time of farm tank mixing, to correct any problems that could not be addressed for some reason in the formulation of the product (space for other chemicals, untested mixtures, changes in the formulation of the other components of the mixture, and other possible cases).

3.1.7 Scale-Up, Field Trials, and Other Regulatory Processes

After the new product is approved by the quality and compatibility tests, it is time to increase the scale to ensure product stability at a pre-industrial level with a greater volume of raw materials and a number of process variables. If there is no equipment of intermediate volume, at least one test must be carried out directly with industrial volumes and all analyses and aging tests performed again before the product is launched. Often, situations unforeseen in the laboratory environment arise, and it is necessary to adjust the formulation and/or processes to achieve an effective, high-quality, and, where possible, low-cost process.

Once approved by all internal processes, it is time for the product to be tested in the field. Samples are sent to determine dosages and the method of application. The product will be tested in benchmarking tests against other products from the company itself and from other companies to ensure its functionality in the real production situation of the target crops. This step will not be dealt with in depth in this text because it is not the focus of the discussion, but it is relevant for the success of the product in the market.

At this point, it is already possible to request product registration from the Competent Authorities (if any), start assembly of the artwork for the label according to the specifications and standards of each country, and perform the product registration in the internal systems (production, quality control, commercial, supply chain, and taxation).

If the results of all the steps and analyses are positive, it is possible to proceed with the commercial launch of the product and, from that moment on, it becomes part of the production process to be discussed in the following sections.

3.2 Process and Equipment

The process and equipment are as important as all the chemistry involved and described earlier.

Having a balanced formulation with the right components in the right quantities alone does not guarantee obtaining a nanofertilizer.

The topics below will discuss the variables, the equipment, their characteristics, and some physical variables that allow the production of the nanofertilizer.

3.2.1 Wet Grinding Process and Equipment

Wet grinding starts with the dispersion of particles of insoluble materials in water inside the reactor (the suggested sequence of the main production process was described in Sect. 3.1.4).

In this step, just as important as the energy input into the system through the motor, is the guarantee that this energy will be used efficiently in dispersing the raw material, making the first breakdown, and enabling the action of the surfactant.

The better the homogenization of the raw material in the mixture of water and surfactant (and other soluble nutrients), the simpler and more efficient the grinding will be, resulting in a product with stability and superior quality.

After the mixing process, the product enters the mill, and other variables enter the scene. The stress energy, the stress intensity, the stress number (or requests), the effective specific energy, the residence time distribution, the mode of operation (recirculation or multiple-pass), the type of mill and its characteristics (size, model, and materials of the chamber, disks, or pins, etc.), and the beads (material, hardness, and diameter) have a direct influence on the distribution of particle size, product quality, and process time.

Besides that, as already mentioned in Sect. “Viscosity”, the reduction in particle size increases the viscosity of the product. In addition, the grinding of a poorly dispersed product, in addition to influencing viscosity, significantly changes the quality of the product, reducing its stability and increasing phase separation.

For that, the two main items of equipment are the reactor and the mill, but additional equipment will also be necessary, such as a chiller and pumps.

The reactor must have a high level of dispersion in both processes: the addition of the raw material (which, in the final product, can reach 75–80% solids) and the addition of the thickener in the final stage of the process.

The mill must be aligned with the volume of the reactor and with the desired process time, which are closely linked to productivity. It must also be equipped with disks (or pins) and chambers resistant to the type of fertilizer to be produced and with a ball set in accordance with the inlet and outlet PSD specifications.

The chiller will be necessary to cool the mill chamber and, if the reactor has a jacket or external coil, to cool the product in the reactor.

Tip The product must not exceed 50 °C during the dispersion and grinding process to ensure that components such as surfactants do not degrade (check the specification of each material to confirm the maximum temperature and carry out some stability tests to confirm before using them in the formulation). Furthermore, a high temperature can also damage the mill and the pump (check temperature specifications for both pieces of equipment).

The pump regulates the flow between the reactor and the mill and the return to the reactor. This flow will be responsible for the residence time of the product inside the grinding chamber.

Tip Do not use pumps that cause strong pulsations, such as diaphragm pumps, to move products to the mill. These pulses cause rapid sieve clogging by increasing the pressure in the grinding chamber. This pressure increase can reach the maximum indicated, causing the automatic stop of the equipment by a safety device to protect the mechanical seal.

Reactor

The reactors must be designed according to the type of fertilizer to be produced.

It is important to perform tests by companies that specialize in agitation systems to reach the best working and agitation conditions.

Many variables influence the dispersion of a product inside the reactor, starting with the ratios between its dimensions, as shown in Fig. 12:

The shape of the reactor's base also directly influences agitation and must be chosen in conjunction with the type of impeller. Figure 13 shows the types of reactor bases.

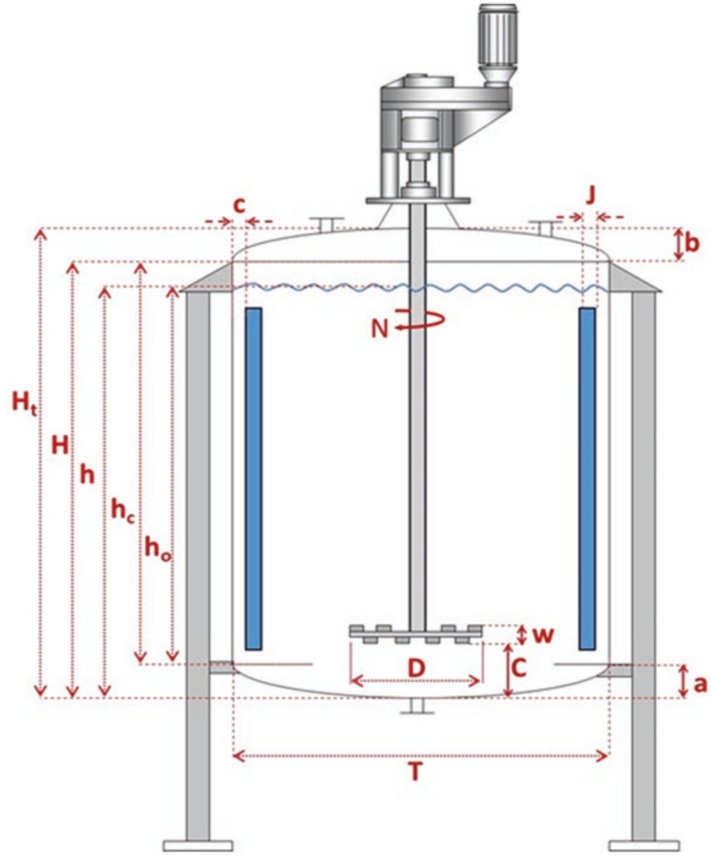


Fig. 12 An example of a reactor and its dimensions: H_t, the total height; H, the useful height; h, the occupied height; h_c, the total height of the cylindrical part; h_o, the occupied height of the cylindrical part; T, the reactor diameter; a, the height of the ellipsoidal base; b, the height of ellipsoidal cover; c, the deflector spacing; D, the disk diameter; J, the deflector width; W, the disk height; and N, the direction of rotation. Reproduced with permission of Prof. Dr. Murilo Daniel de Mello Innocentini

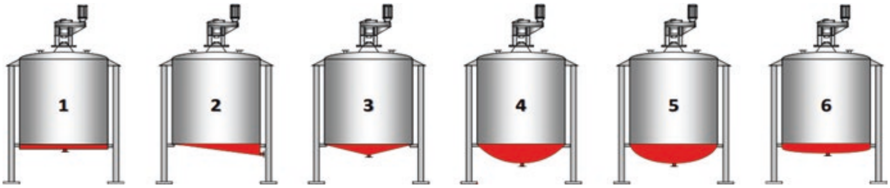


Fig. 13 Types of reactor bases. Reproduced with permission of Prof. Dr. Murilo Daniel de Mello Innocentini

Table 3 Benefits and limitations of the types of reactor bases

Parameter	1. Flat	2. Inclined	3. Conical	4. Hemispherical	5. Ellipsoidal	6. Torispherical
Drainage of liquids	–	+	+	+	+	+
Mixture homogeneity	–	–	+	+	+	+
Pressure resistance	–	–	–	+	+	+
Ease of construction	+	+	+	±	±	±
Stagnant regions	–	–	+	+	+	+
Occupied volume	+	+	+	–	±	+
Fixing of the shaft to the bearing housings	+	–	±	±	±	±
Routing for the discharge pipe	+	–	+	+	+	+

Table 3 shows the benefits and limitations of each type of reactor base in the total drainage of liquids, homogeneity of the mixture, pressure resistance, and other important variables that must be considered during the planning stage.

The diameter and height (in relation to the base of the reactor) of the impeller are directly related to the diameter and height of the reactor. Figure 14 shows a reactor where the ratio between height and diameter is near 1 and the ratio is near 1.5.

The massive study to determine the type of impeller used will give the product more stability and waste less energy. The energy transfer from the motor to disperse and mix the hydrophobic raw material in the mixture of water and dispersant is performed by the impeller. Those most used for nanosuspensions are the high-shear types and their variations. However, there are countless types of impeller and new technologies appear every day (Fig. 15).

Mill

The modern history of mills began with ball mills, used mainly in the ceramic industry between 1896 and 1958. The principle of operation is a cylindrical container filled with stones, taken from rivers because they were more rounded in shape, later replaced by ceramic balls of varied sizes but an average of 50–80 mm in diameter. As a working principle, cranks were initially used, and later, motors

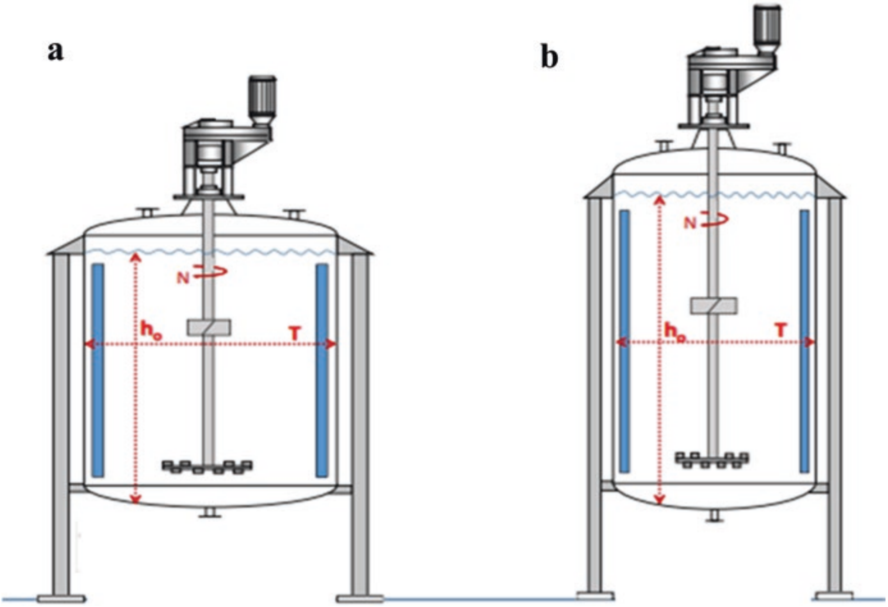


Fig. 14 (**a**) Height to diameter ratio 1. (**b**) Height to diameter ratio 1.5. Reproduced with permission of Prof. Dr. Murilo Daniel de Mello Innocentini

that rotated the container on its transverse axis. However, these motors could not be used at very high speed, or the balls were deposited at the bottom of the container due to inertia and did not perform well. It was then found that the ideal speed for carrying out the work was such that the balls rose to approximately 70% of the diameter of the container and descended by gravity, performing the grinding. In this type of mill, the production was by batch, and at each end of the process, the product was removed together with the balls and, after separation by sieving, everything required cleaning before charging with the new product. The balls were inspected individually and the damaged ones changed. Figure 16 shows a ball mill.

In 1958, with the creation of the Attritor mill, Fig. 17, the size of the balls was reduced to 5–10 mm and the energy was introduced to the product through an axis with pins. By reducing the size of the balls, it was possible to attain smaller particle sizes and thus reduce the grinding time. However, the production of this mill was still in batches, and the balls were removed with the product and had to be cleaned with each product change. The inspection was still carried out manually.

In 1963, continuous grinding was introduced. The procedure is very similar to the Attritor mill, but with the difference of not having to remove the beads after each production, as shown in Fig. 18. These are added to the grinding chamber and the product pumped into the bottom of the chamber. At the top of the chamber, there is a sieve to separate the product from the beads. The size of these beads is in the order of 6 mm. Grinding is used in other applications such as for chocolate, paints, and varnishes, among others. Bead sizes smaller than 6 mm have already been tested,

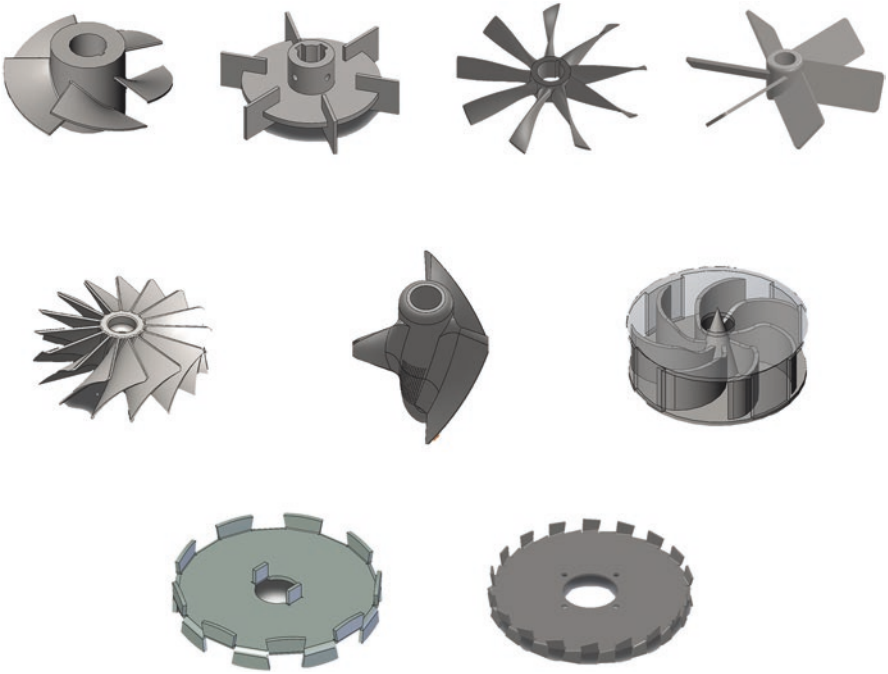


Fig. 15 Different types of impeller. The last two are high-shear models. Reproduced with permission of Maurício Villanova do Amaral

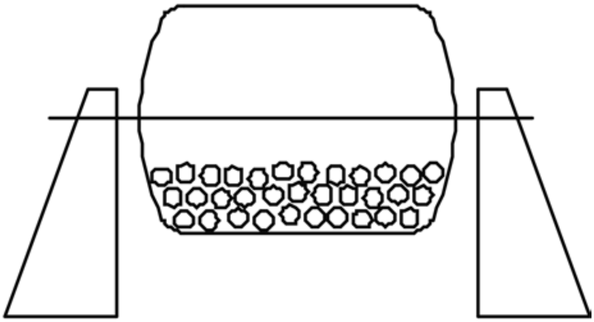


Fig. 16 Ball mill. Image reproduced permission of Netzsch

but only for research purposes. One of the main limitations of this type of mill is the inability to apply pressure, as the beads are then dragged to the separation screen causing overflow.

In 1974, there was a significant change in grinding technology through the creation of the mechanical seal for mills. Therefore, it was possible to supply energy through movement inside a pressurized chamber, positioned horizontally. Due to these two factors, flow rates and productivity have increased considerably. In that same period, there were already beads of 2–3 mm and glass beads had already been created. Figure 19 shows two different technologies for horizontal mills:

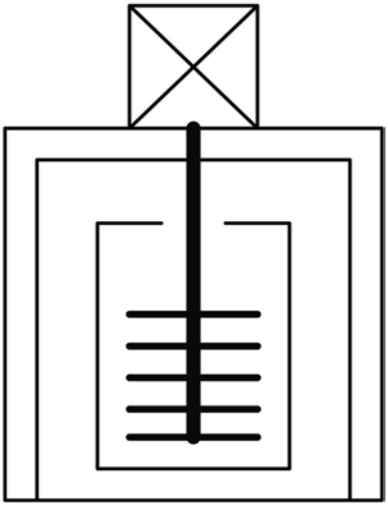


Fig. 17 Attritor mill. Image reproduced by permission of Netzsch

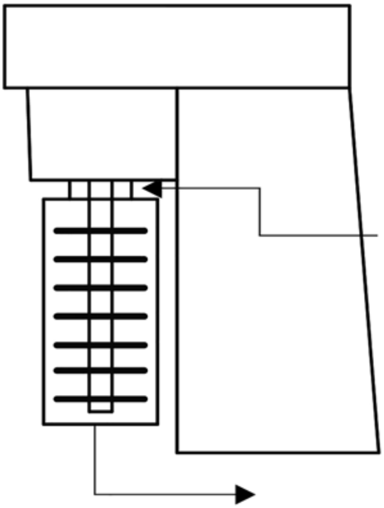


Fig. 18 Continuous grinding Attritor mill. Credit: Image reproduced by permission of Netzsch

Tip Choose mills with speed adjustment for both pump and shaft. During the cleaning process, it is important to set the shaft speed as low as possible while keeping the beads in motion. The speed must neither be so large that the beads abrade themselves and the internal components of the grinding chamber, nor so low so that the product remains between and below them due to the difference in density between the products and water.

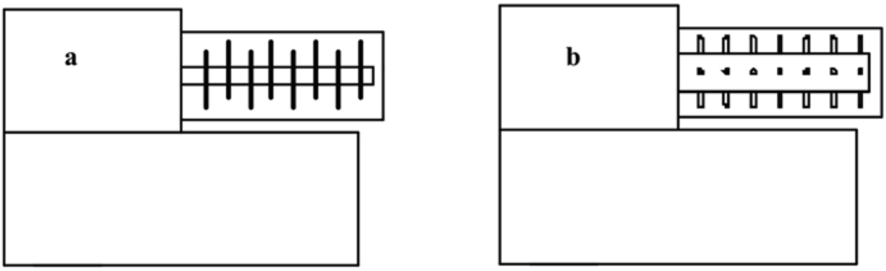


Fig. 19 Horizontal mill. (**a**) Disc agitator. (**b**) Pin agitator. Images reproduced by permission of Netzsch

Between the 1990s and 2000s, detailed refinements to mills made all the difference to production capacity. The shape of the disks and pins, the sieve that prevents the beads from leaving, the size and shape of the chamber, and the possibility of passing coolant inside the shaft were studied. Materials for pins, shaft, and chamber were developed to confer greater durability to the equipment (Fig. 20).

Figure 21 shows the increase in power per liter (kW/L) supplied to the grinding chambers of these types of mill with the evolution of the capacity (L) of the chamber. With the increase in the power supplied, the reduction in particle size became faster and faster, even for smaller grinding chambers, thus accelerating production processes.

For the movement of the mill shaft that produces the movement of the grinding media, the disks, and the material to be milled, power is required, which can be calculated by Eq. 4 (Gupta & Yan, 2016) as developed by Bond. The dimensioning of the engine, and, obviously, of the mill, is possible due to the following equations:

$$P_M = 1.341 \bullet M_b \left[15.6 \bullet D^{0.3} \bullet \varnothing_C \left(1 - 0.937 \bullet J_B\right)\left(1 - \frac{0.1}{2^{(9-10\varnothing_C)}}\right)\right] \tag{4}$$

where P_M is the power required by the mill (wet grinding) (HP), M_b is the mass of beads (t), D is the useful inner diameter of the mill chamber (m), J_B is the fraction of ball filling of the mill (−), and $\varnothing_C$ is the fraction of critical speed (−).

This equation is suitable for mills with a diameter of ≥2.4 m and for a maximum bead diameter of 45.7 mm. For beads smaller than 45.7 mm, it is necessary to use a factor introduced by Bond (Gupta & Yan, 2016), defined as a slurry factor in Eq. 5, which, in this case, must be subtracted from Eq. 4:

$$F_s = 1.102 \bullet \left(\frac{45.72 - d_{MAX}}{50.8}\right) \bullet 1.341 \bullet M_b \tag{5}$$

where Fs is the slurry factor (HP), d_{MAX} is the maximum ball diameter (mm), and M_{b} is the mass of beads (t).

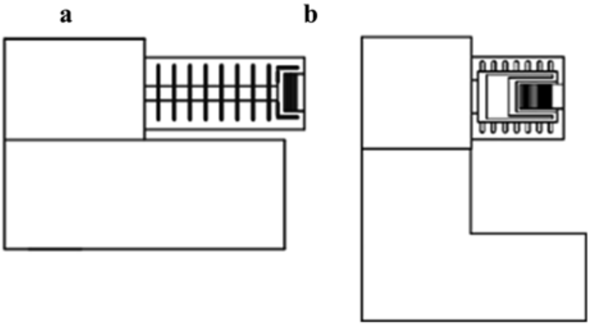


Fig. 20 Evolution of the horizontal mills. (**a**) Disk agitator. (**b**) Pin agitator, as shown in Fig. 19. Image reproduced by permission of Netzsch

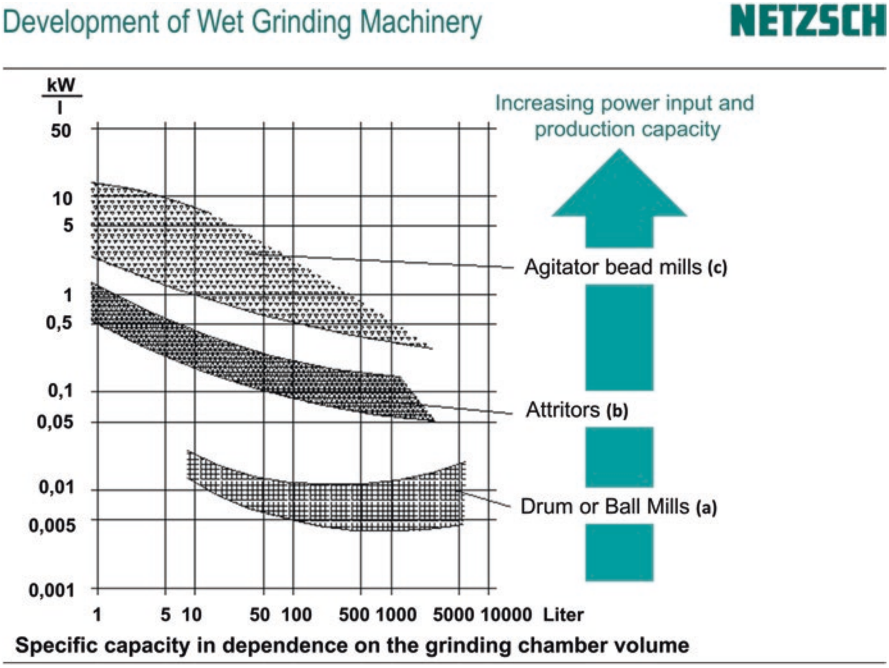


Fig. 21 Increase in power per liter (kW/L) inserted in the grinding chamber for (**a**) ball mills, (**b**) attritors, and (**c**) agitator bead mills. Image reproduced by permission of Netzsch

For mills with a diameter less than 2.4 m, Eq. 6 (Gupta & Yan, 2016) has been described in the work by Austin et al.:

$$P_M = 1.341 \bullet M_b \left[\frac{13.0 \bullet D^{0.5} \bullet \left(\varnothing_C - 0.1\right)\left(1 - 0.937 \bullet J_B\right)}{\left(1 + 5.95 \bullet J_B^5\right)\left(1 + \exp\left[15.7\left(\varnothing_C - 0.94\right)\right]\right)} \right] \bullet 1.07 \qquad (6)$$

where P_M is the power required by the mill (wet grinding) (HP), M_b is the mass of beads (t), D is the useful inner diameter of the mill chamber (m), J_B is the fraction of ball filling of the mill (−), and $\varnothing_C$ is the fraction of critical speed (−).

The technological developments mentioned above, the increase in power per liter (or kg) supplied to the grinding chamber, and the possibility of reducing bead size to the 0.1-mm range made it possible to produce nanosuspensions.

Until now, beads have been mentioned several times. In the next section, the specifications of this component, so important for the grinding process, will be presented.

Beads

As previously mentioned, in the first mills, river stones and then ceramic balls were used as grinding media. Subsequently, glass, steel, aluminum, and a multitude of other beads appeared for use as grinding media depending on the application. In better-quality fertilizer suspensions, zirconium silicate and zirconium oxide (ZrO_2) beads are used. The latter is used for nanosuspensions because it offers greater hardness and less wear compared to other beads. They can be stabilized with yttrium ($Y\text{-}ZrO_2$) or cerium ($Ce\text{-}ZrO_2$), with the yttrium beads being slightly more durable. The ZrO_2 beads have sizes of 0.1–30 mm. For fertilizer microsuspensions, sizes of 0.8–1.2 mm are commonly used, and for fertilizer nanosuspensions, sizes of 0.1–0.3 mm, as shown in Fig. 22.

Regarding the bead diameter, according to the manufacturers' data, it is important that they are in the order of 20 times the d97-value (largest size reached by 97% of the volume of particles) of the input particles (raw material or fertilizer in process). The d50-value (largest size reached by 50% of the particle volume) attainable is in the order of 1/1000 of the diameter of the grinding beads. Therefore, two or more sets of beads of different sizes are usually required to reduce the particle size to nanometric sizes.

Equation 7 (Gupta & Yan, 2016) is used to calculate the mass of beads to be added to the mill:

$$M_B = \frac{\pi D^2}{4} \cdot J_B \cdot L \cdot \rho_b \left(1 - \varphi\right) \tag{7}$$

where M_B is the mass of beads (t), D is the useful inner diameter of the mill chamber (m), J_B is the fraction of ball filling of the mill (−), L is the mill length (m), ρ_b is the bead density or specific gravity (kg/m^3), and φ is the porosity of the grinding media at rest (usually 35–40%) (−).

Now that the beads have been defined and their mass calculated, it is time to add them to the mill chamber. In addition to the beads, other variables act within the chamber and are responsible for grinding. That is the subject of the following sections.

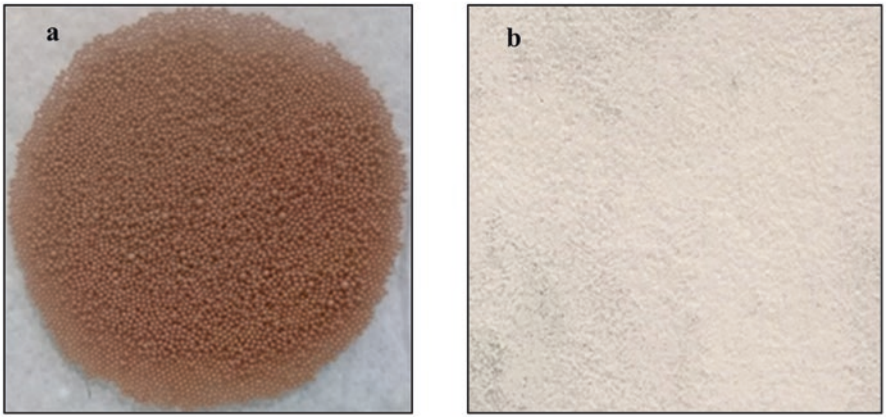


Fig. 22 (**a**) 0.8–1.0-mm ZrO_2 beads and (**b**) 0.1-mm ZrO_2 beads

The Stress Energy of the Grinding Beads and the Stress Intensity on the Particles

Each collision between two beads with one or more agglomerates or particles is called a stress event. Each of these collisions transfers kinetic energy from the beads to the agglomerates or particles. This energy is called the stress energy and is proportional to the stress energy of the beads (Kwade & Schwede, 2007). This energy obviously comes from the mill through tangential velocity (v_t) and the beads themselves, through their density (ρ_{GB}) and diameter (d_{GB}), as shown in Eq. 8:

$$SE \propto SE_{GB} = d_{GB}^3 \cdot \rho_{GB} \cdot v_t^2 \tag{8}$$

where SE is the stress energy (J), SE_{GB} is the stress energy of grinding beads (J), d_{GB} is the diameter of grinding beads (m), ρ_{GB} is the density of grinding beads (kg/m^3), and v_t is the tangential velocity (m/s).

Following the example of two beads that collide, as mentioned above, with a specific grinding energy (explained in the next section) capable of de-agglomerating or, in the case of the particle, breaking it, means that the energy is effectively transferred to the agglomerate or particle. The measure of how effective this transferred energy is in reducing particle size and product quality is called stress intensity (Kwade & Schwede, 2007).

While the stress energy of the grinding beads is constant throughout the grinding process, as it depends only on the tangential speed, diameter, and density of the grinding beads, the stress intensities on the particles vary according to the grinding time due to the reduction of their sizes (Kwade & Schwede, 2007).

The Number of Stress Events

The number of stress events, or stress number (SN), Eq. 9, is directly linked to the reduction in PSD. It is defined as the product of the number of shocks between beads, the probability of effective shock with a particle or agglomerate, and by the number of agglomerates/particles that can be dis-aggregated/broken (Kwade & Schwede, 2007):

$$SN = \frac{N_c \cdot P_s}{N_p} \tag{9}$$

where SN is the stress number (−), N_c is the number of bead contacts (−), P_s is the probability that a particle is caught and sufficiently stressed when contacted by a bead (−), and N_p is the number of the particles to be caught inside the mill (−).

There is a relationship between the SN and the ratio of the particle size to the grinding media size, the grinding time, and the rotational speed of the mill axis when the input flow and the solids' concentration are constant, as shown by Eq. 10. This is the called reduced stress number (SN_r) (Kwade & Schwede, 2007):

$$SN \propto SN_r = n \cdot t \cdot \left(\frac{x}{d_{GB}} \right)^2 \tag{10}$$

where SN is the stress number (−), SN_r is the reduced stress number (−), n is the rotational speed of the mill axis (s^{-1}), t is the grinding time (s), and x/d_{GB} is the ratio between particle size and grinding media size (−).

The stress energy of the grinding beads and the total SN are parameters in the calculation of the specific effective energy, which is the parameter that directly influences particle size, as can be seen below.

The Specific Grinding Energy

Specific grinding energy can be defined as the energy introduced into the grinding chamber (Kwade & Schwede, 2007).

An important decision must be made during development, but it has its implications here. What is the best grinding strategy to choose? Single-pass, multiple-pass, or recirculation? Figure 23 shows a scheme of these modes of operation:

The mode of operation (single-pass, multiple-pass, and recirculation) and hence the specific energy input affects the residence time (discussed in the next section) and, as a result, the particle size (as shown in Fig. 24) and the width of the PSD.

Figure 24 above shows a specific example and should be considered carefully. In this specific case, for the same flow, the multiple-pass shows an advantage over recirculation until the fifteenth pass, where the d95-values are equal. Several points affect this choice between multiple-pass and recirculation modes, such as the availability of reactors, for example. A study can be carried out to compare recirculation

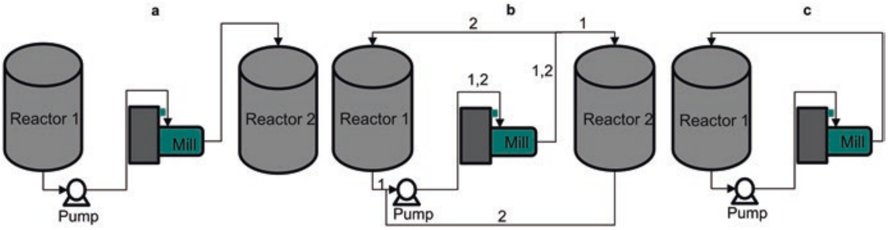


Fig. 23 Scheme demonstrating the modes of operation: (**a**) single-pass mode, (**b**) multiple-pass mode, and (**c**) recirculation

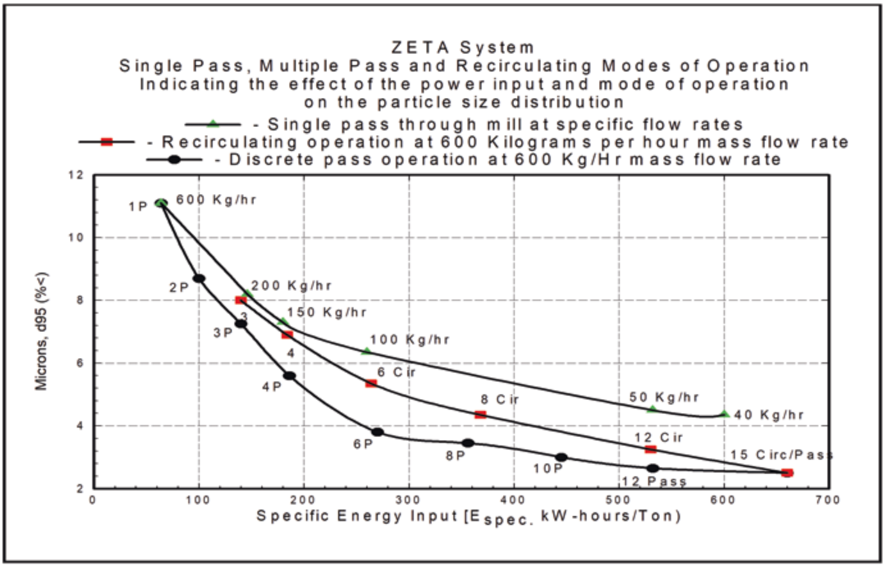


Fig. 24 Effect of the mode of operation and the specific grinding energy on the particle size (d95) (Way, 1997). Reprinted/adapted by permission from [**Springer Nature Customer Service Centre GmbH**]: [**Springer Nature**] [**Particle size reduction of pigments using a small media mill**] by [**H. W. Way**] [**© Chapman & Hall**] (1997)

at maximum flow to the multiple-pass at median flow. This makes sense because in the recirculation mode the particles must pass through the grinding chamber many times (with a shorter residence time) and in multiple-pass the idea is that the particles pass a few times, reducing the process time but with a longer residence time.

To support the decision, it is possible to calculate the specific grinding energy (E_m) for each type of process (recirculation: Eq. 11, or multiple-pass: Eq. 12):

$$E_m = \int_0^t \frac{\left(P_{(t)} - P_0\right)dt}{m_{FS}} \text{ for recirculation} \tag{11}$$

where E_m is the specific grinding energy (J/kg), t is the grinding time (s), P is the power draw of the motor (W), P_0 is the no-load power (W), and m_{FS} is the mass flow rate of the product (kg/h).

$$E_m = \sum_{i=1}^{n} \frac{P_{Stat} - P_0}{m_{FS}} \quad \text{for multiple} - \text{pass} \tag{12}$$

where E_m is the specific grinding energy (J/kg), n is the number of passes (−), P_{stat} is the power draw at stationary operation (W), P_0 is the no-load power (W), and m_{FS} is the mass flow rate of the product (kg/h).

Pay attention that for recirculation the specific grinding energy is calculated for the entire grinding time, while for multiple-pass the energies of each pass are added.

The effective specific energy (E_{Sp}) is proportional to the product of the stress energy of the grinding beads $\mathrm{SE}_{\mathrm{GM}}$, the ratio of the overall number of stress events $\mathrm{SN}_{\mathrm{tot}}$, and the stressed overall mass of the product m_{FS}, as shown in Eq. 13 (Kwade & Schwede, 2007):

$$E_{Sp} \propto SE_{GM} \cdot \frac{SN_{tot}}{m_{FS}} \tag{13}$$

where E_{Sp} is the effective specific energy (J/kg), SE_{GM} is the stress energy of grinding beads (J), $\mathrm{SN}_{\mathrm{tot}}$ is the overall number of stress events (−), and m_{FS} is the stressed overall mass of the product (kg).

As seen above, this energy is responsible for the reduction in particle size and, depending on process mode, for the width of the PSD. Because of this, it is the most important parameter while scaling-up the production process.

The Residence Time Distribution

Residence time can be defined as the time that the product and, of course, the agglomerates or particles remain inside the mill for the entire grinding time.

In continuous-flow mills, even considering the internal turbulence promoted by the disks/pins and beads, there will be a speed gradient according to the *Poiseuille flow*. This gradient will cause a distribution in the residence time and also in the number of requests, following the same pattern as the displacement of the product.

Eq. 14 is used for the mean residence time ($\bar{t}$) calculation for recirculation and multiple-pass process (Kwade & Schwede, 2007):

$$\bar{t} \approx t \cdot \frac{V_{GC-}V_{GM}}{V_{Susp}} \tag{14}$$

where $\bar{t}$ is the mean residence time (s), t is the grinding time (s), V_{GC} is the grinding chamber volume (m^3), V_{GM} is the overall solid volume (m^3), and V_{susp} is the suspension volume (m^3).

When the residence time, the intensity, and the SN are the same in two or more processes with the same material and input particle size, the result of the distribution of particle sizes in the final product will be the same.

These four last sections demonstrate, without going into too much detail, what happens inside the grinding chamber and what are the energies and variables involved. The next section will present another strategy for nanometric raw materials.

3.2.2 Dry Nanoscale Raw Materials

It is possible to source raw materials already pre-ground or manufactured via any of the bottom-up or top-down processes and of nanometer size. However, when mixed with the components to form a concentrated suspension and analyzed by DLS (dynamic light scattering), parameters such as d50 and d90 often appear at the micron scale.

The primary particles are actually on the nanometer scale but agglomerated. In this way, even the strong agitation of a reactor cannot perform de-agglomeration, and high-energy grinding is necessary.

The grinding time is generally considerably shorter, but, as a disadvantage, the level of difficulty in stabilizing these suspended raw materials when compared to the process with normal raw materials is much higher due to the high level of settling and re-agglomeration.

The costs of nanosuspensions must be considered because raw materials have both an effectively higher price and more complex molecules (and with a higher price) that need to be stabilized.

Therefore, a study must be carried out for each case, analyzing the gains, benefits, losses, and disadvantages of each process.

3.3 Quality Control

Quality control is an extremely important area in the production of a nanosuspension.

Before (raw material analysis), during, and after manufacture, samples will be taken to check various product parameters such as pH, electrical conductivity, density, viscosity, PSD, and element content (nutrients and contaminants).

The point of collection of these samples must be studied for each product and for each analysis mentioned above, thus ensuring stability and compliance with the product specifications.

While the analysis of content, pH, electrical conductivity, and density apply to all fertilizers, viscosity and PSD are specific to concentrated suspensions, including nanosuspensions.

3.3.1 Process Analysis

There are some parameters that are analyzed during the production process. At this stage of the process, practically all the parameters analyzed can be corrected without major consequences for the final product, obviously with all the necessary attention and care. The analyses of these parameters are described below without further details, which can, if necessary, be found in analytical manuals.

Particle Size Distribution

The measurement of PSD is performed by different forms of equipment and methodology. For nanosuspensions, the two most common are DLS and the measurement of size by scanning electron microscopy (SEM).

For DLS, the most used equipment has its own software installed that can provide the graph (Fig. 25) and the compiled information that can be customized depending on the user's needs.

There is also software that comes with SEM equipment. However, it is customary to use external image software, such as ImageJ™ (Abramoff et al., 2004) (Fig. 26).

For each measurement in the image, the information is sent to a database that can be exported to any spreadsheet software for analysis (Fig. 27).

Viscosity

As with the PSD, there are several methods and types of equipment for measuring viscosity. In industry, dynamic viscosity reading is more common. However, more important than the result is to maintain the same conditions and method for the

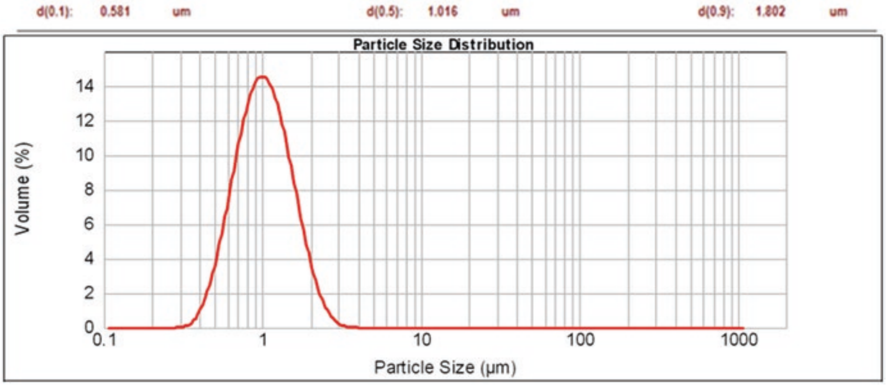
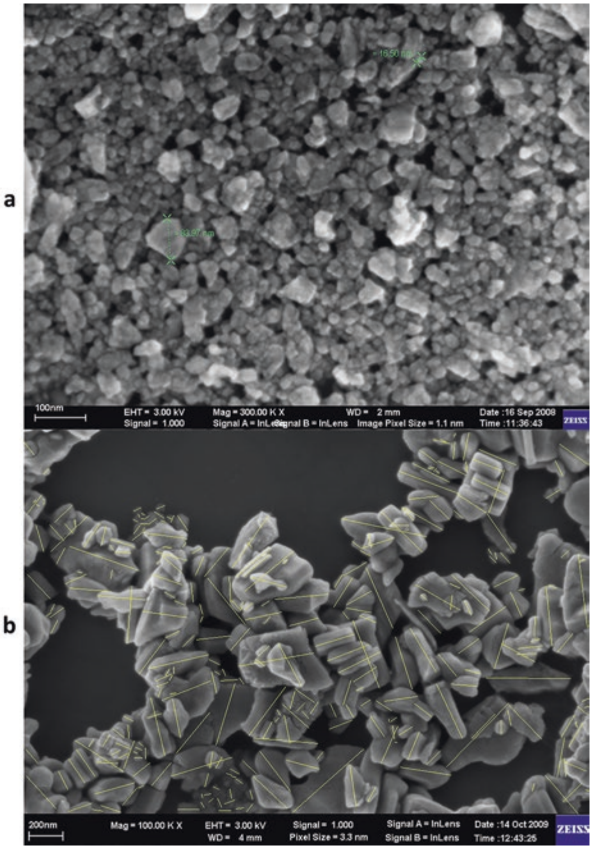


Fig. 25 ZnO microsuspension PSD by DLS

Fig. 26 Zinc oxide nanosuspension micrographs: (**a**) magnification 300 KX; (**b**) measured micrography with magnification 100 KX



different samples. The viscosity is influenced by the temperature and time of the rest of the sample, the measuring equipment, the rotation, and the size of the spindle, if there is one. So, it is easy to understand that without a well-described and carefully followed method, the information may be lost due to the instability of the product.

> **Tip** Determine equipment, method, and conditions in product development and implement in quality control. In this way, the particle size and viscosity distribution information for the different batches will be consistent with the tests.

pH

For nanosuspensions, pHs are usually alkaline (8–12), with the exception of molybdenum trioxide products (2–3). In general, it is not necessary to change the pH of the final product. However, pH plays a role in achieving better stability because it directly affects the zeta (ζ) potential.

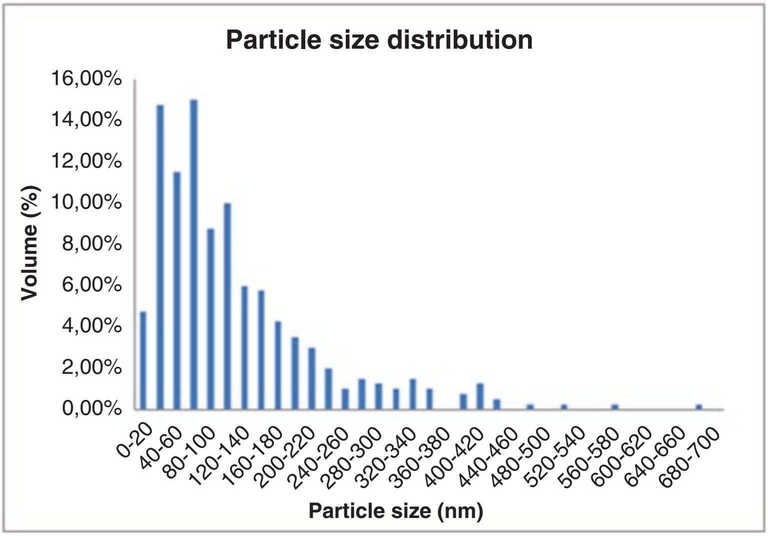


Fig. 27 Particle size distribution resulting from the analysis of Fig. 26**b**

Density

There are several methods for determining density. The most common are the densimeter and the pycnometer. The density of nanosuspensions ranges from 1.0 to 2.0 g/cm^3, depending on the solid concentration and if the medium is water.

3.3.2 Final Analyses

These analyses show us if the product is within the standards pre-established by the R&D and agronomic areas of quality control and certify that the fertilizer is ready to be sold.

Small adjustments can still be made in the formulations, but if the process is carried out according to the production order with the raw materials specified, as a rule no adjustment is necessary, and the product is released for packaging.

In case of any problems or if major adjustments are required, whether in nutrient content, viscosity, density, or even in particle size, a study is needed to determine which path to follow in reprocessing the batch showing the variation.

Tip The most common methods of reprocessing are mixing two batches (50/50) to form a new one, mixing a percentage (1–30% by weight) of the batch out of specification with several new batches, or by adjusting the batch itself depending on the parameter that is out of specification in this sequence.

Nutrient Content

For nutrient content, the most common analyses are by X-ray fluorescence, atomic absorption spectrometry (AAS), and optical emission spectrometry (ICP-OES), which encompass most of the nutrients (Ca, Mg, S, Co, Cu, Fe, Mn, Mo, Ni, and Zn) and contaminants (As, Cd, Cr, Hg, and Pb). For B and P (P_2O_5), digital spectrometry can be used, for K (K_2O), flame photometry, and for N, the Kjeldahl method. Boron, P, and K can be determined by ICP-OES so long as adjustments are made to the methodologies.

Tip The methods mentioned here are the most common to fertilizers, but they are not the only ones and can vary from country to country. The idea is not to discuss them here. Many countries publish a manual of official methods for these analyses.

Most companies allow the product to be packed at that point if the above-mentioned sample analyses show conformation with the specifications.

Zeta (ζ) Potential

Zeta (ζ) potential is a measure that can revolutionize fertilizer stability testing. Current equipment is fast and accurate and can work with or without pH variation.

According to Hunter (1981), the zeta (ζ) potential is the measure of the average electrostatic potentials that occur on the shear surface, as can be seen in Fig. 28.

The analysis is able to revolutionize stability testing. Today, many companies use only the aging test, which works very well in determining which formulation is best or whether a formulation produced will show poor stability. However, aging tests can take up to 90 days, which, when finding a production or process issue and taking a decision, or waiting to check whether the formula is stable during the development period, is a long time.

The zeta (ζ) potential test takes a few minutes to carry out, and analysis allows you to know whether the formulation is initially unstable.

The analysis of the zeta (ζ) potential does not exclude the aging test; they are complementary analyses (Larsson et al., 2012). Therefore, even if a formulation was stable by the zeta (ζ) potential test, it is important to perform the aging test to make sure that it is stable.

Two gains are instantaneous with the adoption of zeta (ζ) potential analysis: gain of space by reducing the quantity of sample required (mainly in the development) and gain of time for decision-making.

Samples with zeta (ζ) potential of less than −30 mV and greater than +30 mV are considered stable. Values between −30 mV and +30 mV are considered to indicate instability, and the formulations tend to agglomerate, flocculate, or coagulate (Lin et al., 2014).

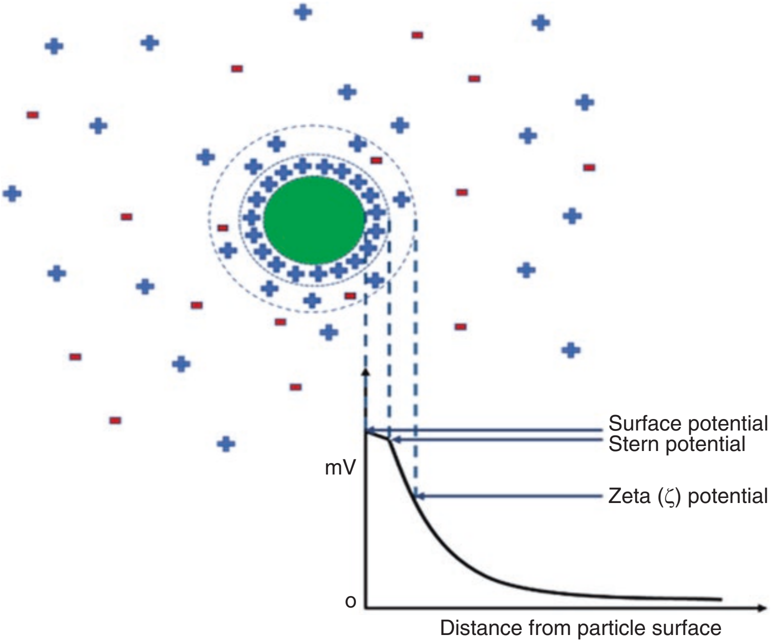


Fig. 28 Schematic of zeta (ζ) potential showing the surface charge, surface potential, and Stern potential

Aging Test

The most common methods used for aging tests are to subject the samples to cold and/or heat (FAO and WHO, 2016).

For cold, a refrigerator with temperatures of 4–8 °C is normally used.

For high temperatures, laboratory ovens are usually used at 42–44 °C, where 30 days are equivalent to 1 year, or 54 °C, where 15 days are equivalent to 1 year.

Tip At the beginning of product development, one should perform tests at both temperatures and room temperature. The test at 54 °C is faster and saves the company and the team a great deal of time. But, depending on the components of the formulation, it may not be a true indication of what will happen with the product over a year.

Figure 29 shows an oven running aging tests on several trials of various fertilizers. It is possible to see some phase separation.

Micro- and nanosuspensions in general behave very well at low temperatures and do not present any problems. On the other hand, they are more sensitive to heat because the higher temperatures cause an increase in the average kinetic energy of the

Fig. 29 Oven with products during an aging test

particles and the number of shocks between them. The increasing number of shocks and, consequently, of effective shocks will multiply the probability of aggregation as predicted by the DLVO theory. Hence, it causes a rise in the PSD and destabilizes the suspension if the formulation is not stable.

The elevated temperature can also destabilize or denature the surfactant or destroy the networks formed by the thickener, generating destabilization of the formulation.

Tip At the beginning of a factory operation, a process, or a new product, it is suggested to perform an aging test of all batches in order to verify possible unforeseen variations due to differences in scale or between batches of raw material or process variations.

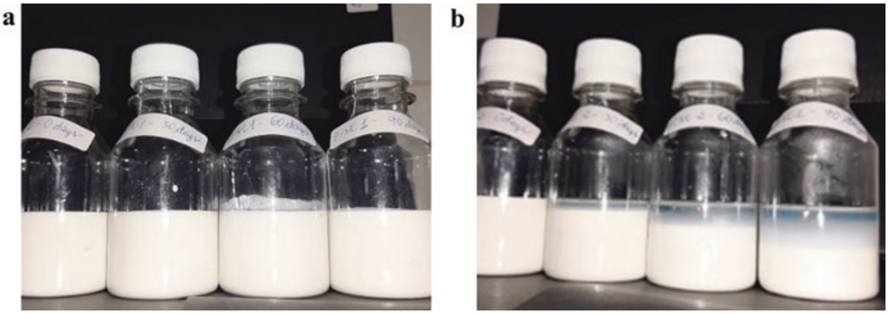


Fig. 30 (**a**) Stable zinc-based product at 0, 30, 60, and 90 days at 42–44 °C; (**b**) unstable zinc-based product at 0, 30, 60, and 90 days at 42–44 °C. Photo by Daiane Aparecida Marino

Figure 30 shows a stable and an unstable nanosuspension fertilizer. While the stable product remains homogeneous during the 90 days of the test, the unstable product settles over time. It is not possible to see in the image, but generally, together with this decantation, the agglomeration becomes so strong that it is impossible to resuspend the product again, even under strong agitation.

It is also possible to observe changes in the product color, crystallization, viscosity increase, changes in pH, changes in packaging (stuffing, wilting, incompatibility), formation or release of gases, oxidation, reduction, and a range of other problems intrinsic to the formulation.

The results of these tests will be important in collecting information for the areas of production and R&D for possible future changes in the formulation of a product or even for eventual reprocessing or recall decisions.

The aging test is part of this phase of the production because it must be applied to the final samples following the procedures described in the manuals of the quality control area (all batches, one batch a day, two batches per week, one batch per month). It is obviously neither possible nor necessary to keep the products in quarantine for 90 days waiting for the end of the aging test.

If a sample of one or more batches shows a nonconformity, the areas of production, quality control, and commercial and R&D should jointly define the actions to be taken to mitigate the problem and initiate the procedures to determine the cause and prevent its re-occurrence.

3.4 Filling

After all quality control approvals, the nanosuspension is ready to be packed. Suspensions are usually packaged in volumes of 1, 5, and 20 L. In some countries, however, there are weight restrictions in regulations and/or laws. The most common packages are of HDPE, as shown in Fig. 31.

Fig. 31 The 20-, 5-, and 1-L HDPE packing. Photo by Daiane Aparecida Marino

Filling can take place manually or on several types of machines ranging from semi-automatic to fully automated. Fig. 32 shows a 5-L semi-automatic machine (it can also fill 20 L by performing a setup).

Of course, the machines and the level of automation will depend largely on the volume and level of investment desired for the industrial plant.

Figure 33 shows a 1-L automatic rotating machine.

It is of utmost importance that the packages are of sufficient weight to support the products, considering the densities mentioned in this chapter. Packaging suppliers can not only support manufacturers but also perform packaging performance tests with each of the developed nanosuspensions.

Packaging tests must also be performed to determine the maximum stacking height.

Compatibility tests between the nanosuspensions and the packaging must be carried out in order to avoid dryness, leakage, or collapse of the packaging during the validity of the product (in the case of virgin HDPE packaging, problems of this type are very rare).

Another area that requires testing is the caps. Some nanosuspensions, depending on their formulation (those containing a significant amount of urea, for example), can release gases during the period of validity, even without affecting nutrient concentrations or product stability. In this case, a vented cap should be used, as shown in Fig. 34.

If there are no problems with gas release, it may be a good idea to seal the package, as shown in Fig. 35.

3.4.1 Nanosuspo-Emulsions and Nanoemulsions

Nanosuspo-emulsions and nanoemulsions must ultimately follow the same development steps and have, for the most part, the same components (surfactants, nutrients, other additives, and, eventually, thickener) as the concentrated suspension with specific characteristics.

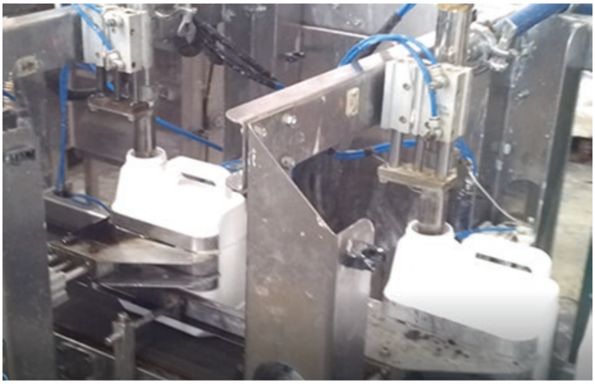


Fig. 32 Filling machine for 5-L packages during the process

Fig. 33 Rotative filling machine for 1-L packages. Photo by Clelio Verissimo de Almeida Veras

These formulas can be prepared from water-in-oil (w/o) or oil-in-water (o/w) emulsions, the choice of which completely changes the characteristics of the formulation, especially with regard to surfactants. It also drastically changes the method of use, depending on the organic phase and the additives used. This phase can be both beneficial and harmful for the mixture and for the plant that will receive the application.

Fig. 34 Two different vented caps

Fig. 35 Magnetic induction-sealed packaging

The production processes for nanosuspo-emulsions and emulsions are very similar. High shear is required during agitation in the reactor to ensure that the surfactant is able to reach the particles (suspo-emulsions) and drops (emulsions) to form a stable colloid.

In the case of nanosuspo-emulsions, the particles will already be of nanometric size, but for nanoemulsions a high shear will be vital for reducing the size of the drops of the insoluble liquid in the medium (Fig. 36).

Today, the focus of these fertilizers is still the slow release of nutrients and substances of interest (Mala et al., 2017). However, this technology may be increasingly widespread, making the absorption and delivery of nutrients more efficient.

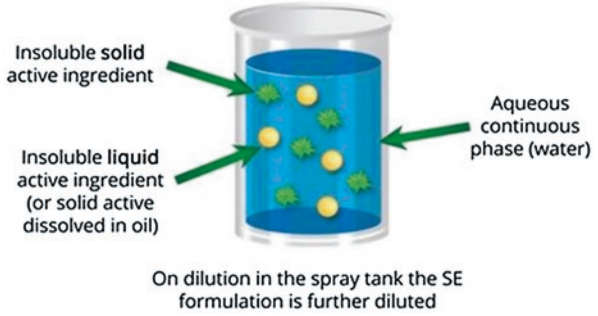


Fig. 36 Illustration of an oil-in-water suspo-emulsion. Image reproduced by permission of Croda

4 Final Discussion

The path toward nanofertilizers is still long. There is much to be researched and discussed. Better and cheaper processes are necessary, as well as formulations that are more stable and safer for the environment and consumers. Additionally, extensive compatibility tests must be carried out.

According to the statistics of the UN World Population Prospects 2019, the world's population will be approximately 9.7 billion people in 2050 (UN, 2019). There will be 2 billion (26%) more people in 30 years—people who will consume natural resources, energy, and, mainly, food and water. On the other hand, agricultural land covers 4.8 billion ha in the world. About 32.6% of the total (1.56 billion ha) is productive agricultural land (land under permanent crops and arable land) (FAO, 2018; IFA, 2021). However, this area is not evenly distributed around the world, with almost 90% of the remaining area in sub-Saharan Africa and South America (FAO, 2003).

As in other areas of knowledge, such as technology, nanoparticles have been revolutionized and have brought many benefits to the consumer. It is necessary that academies and companies join forces in these revolutions to reach agriculture, bring greater productivity, and make food richer in relation to nutrients, vitamins, and other compounds of market and consumer interest.

But not only that, new and intelligent ways of applying these products will be necessary so that all the technology incorporated in the product does not literally fall to the ground (with the exception of soil fertilizer). Will dosages reduce? How will one nutrient influence the absorption of others? Will they follow the same standards found today (Aref, 2011; de Oliveira Araújo et al., 2018)? How to align new technologies (and how they will behave) with climate change? What about the sustainability challenge and the safety of the environment?

Last but not least, it is necessary to give quality information to farmers. They receive and seek information through different media, but this is often of dubious quality or without any support from science.

The most expensive product may not be the best, just as the cheapest is usually not. But more important than the price is knowing how to use each product to get the most out of it, whether cheap or expensive. Which technology is involved in each product? What is the final efficiency of each one? Which will affect productivity and food quality? Information is the word.

In short, the route to feeding and nourishing the world is being followed, but it is necessary to stay focused on new technologies to increase the unit of food produced per unit of land to support population growth, health, nutrition, and environmental security (FAO, 2003).

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Nanoparticles on Seed Performance

Francisco Guilhien Gomes-Junior, Lívia Araújo Rohr, and Fernando Augusto Henning

Abstract Nanotechnology has significant potential to improve seed performance. In recent years, several studies have been published on the application of nanoparticles in seeds. The effects of nanomaterials on seed germination and seedling vigor have been assessed in different plant species. The modulation of reactive oxygen species, enhancement of α-amylase activity and starch metabolism, effect on drought resistance, effects on photosynthetic pigments and photosynthesis of seedlings, and inhibitory activity against microorganisms have been investigated. This chapter highlights basic aspects related to the physiology of seed germination, which is very important to understand the effects of nanomaterials on seed performance. The types of treatments used for the application of nanoparticles in seeds and the factors related to the efficiency of treatments are also covered. Approaches of the positive and negative effects of nanoparticle application in seeds are exposed herein, in addition to thoughts about future research and the need for additional investigation on the use of nanoparticles in seeds.

Keywords Nanomaterials · Seed germination · Seed vigor · Seed treatment · Seed priming

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1 Introduction

The establishment of production fields for most cultivated species is usually carried out using seeds, corresponding to about 80% of the economically exploited species. The successful implantation of crops in the field is conditioned to the use of high-quality seeds. Seed quality is conceptualized as a set of characteristics that determine its value for sowing, bringing together the genetic, physical, physiological, and health attributes. However, seedling emergence in the field after sowing is not always satisfactory and may vary depending on environmental conditions (biotic and abiotic factors) and aspects related to the physiological potential of the seeds used. The high performance in the establishment of an agricultural field is determined by the rapid and uniform seed germination and seedling emergence, which is directly related to the ability to mobilize and assimilate the reserves stored in the seeds to the growing points of the embryo; this process, which is coordinated by the action of specific enzymes, varies with the level of seed deterioration. In this sense, procedures that can improve the germinative performance of seeds are often recommended. Currently, agricultural usage of nanoparticles is an attractive area of interest. The use of nanotechnology in agriculture has been identified as a promising solution and capable of guiding a new era of agricultural production. In seed technology, nanotechnology can be exploited to improve the performance of seeds after harvest. Several research studies have been conducted using different types of nanoparticles and showing their effects (positive or negative) on the germinative performance of seeds. This chapter addresses aspects related to the application of nanoparticles in seeds and their effects on germination and seedling growth, also considering some factors associated with the efficiency of this treatment.

2 Seed Germination Process: Three-Phase Pattern of Water Uptake

Many of the effects of nanoparticles applied to seeds have been associated with the physiology of seed germination. For example, in tomato seeds carbon nanotubes can penetrate the seed coat and support water uptake (Khodakovskaya et al., 2009). Among other effects are those associated with the modulation of reactive oxygen species (ROS), enhancement of α-amylase activity and starch metabolism, and inhibitory activity against microorganisms. In this sense, for a better understanding of the effects of nanomaterials on seed performance, it is considered very important to know how the germination process occurs, which is characterized based on the water uptake by the seeds. The process of water uptake by seeds (with permeable seed coats) has a three-phase pattern, as proposed by Bewley and Black (1983) and shown in Fig. 1. Initially, rapid imbibition occurs because of the water potential gradient between the dry seed and external environment (Phase I). The initial rate of imbibition is determined primarily by seed coat permeability, seed/substrate contact

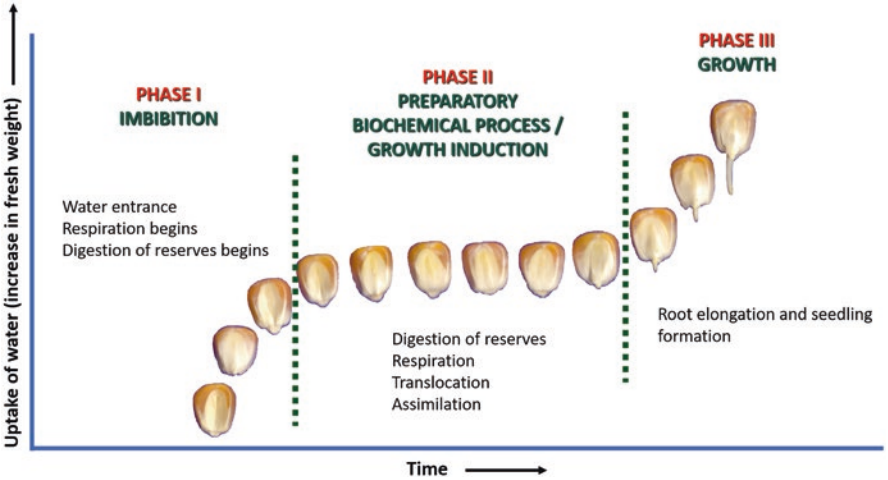

Fig. 1 Three-phase pattern of water uptake by seeds during germination (adapted from Bewley & Black, 1983). Hydration of seeds during germination shows three distinct phases, namely rapid hydration (imbibition; Phase I), a lag phase (Phase II), and a steady hydration phase (embryo elongation; Phase III), in accordance with the kinetics of water uptake

area, the hydraulic conductivity of the soil or substrate medium, and chemical composition of the seed (Copeland & McDonald, 2001; Marcos-Filho, 2016). At first, after the beginning of water entry, the mechanisms for repairing damage accumulated during maturation, drying, and storage of the seeds are activated, including the restructuring of the membrane system, disorganized with drying at the end of maturation (Marcos-Filho, 2016). In Phase I also begin the respiration and digestion of the reserves stored in the seed. Simultaneously, the metabolic activity of the seed is restored, which characterizes the beginning of the germination process. This stage is followed by a period of limited water absorption (Phase II) and is the final stage for dead seeds. Phase II is characterized by activities that are part of the preparatory biochemical process (or growth induction) and is necessary for the synthesis of enzymes, DNA, and pre-existing mRNA, consumed during Phase I (Marcos-Filho, 2016). During Phase II (also considered plateau phase), there is an increase in respiratory activity (anaerobiosis), enzyme activity (in response to hormonal activity), organelle activity, and protein synthesis. The reserve substances (proteins, carbohydrates, and lipids) present in the tissues of the seeds (endosperm or cotyledons) are decomposed, and the soluble products of this process are translocated to the growing points of the embryo (Copeland & McDonald, 2001; Marcos-Filho, 2016). Generally, enzymes that break down carbohydrates, lipids, proteins, and phosphorus-containing compounds are the first to be activated during Phase II (Copeland & McDonald, 2001). The plateau phase of the imbibition can be considered the period of germination sensu *strictu*, which is terminated by the initial growth (Bewley & Black, 1983). Thus, the assimilation of the digested and translocated products, marking the transition between Phases II and III of the imbibition, creates conditions for the resumption of embryo growth, constituting the visible sign of germination that, in reality, represents its end with the protrusion of the primary root, characterizing the beginning of Phase III (Marcos-Filho, 2016). The protrusion of the primary root through the seed coat is initiated by cell elongation, followed by cell division in most seeds. The root becomes functional during this phase and is responsible for the increased water uptake noted in Phase III (Copeland & McDonald, 2001).

3 Strategies for Application of Nanoparticles in Seeds

One of the relevant aspects to be considered in evaluating the effects of nanoparticles on the germinative performance of seeds is related to the procedure for applying these products to seeds. Nanoparticles are materials that have dimensions between 1 and 100 nm (Astm E2456 – 06, 2012). Nanoparticles can be synthesized by physical, chemical, or biological processes and have different types of classification. Based on physical and chemical characteristics, nanoparticles can be divided into carbon, metal, polymers, semiconductor, ceramics, and lipids (Khan et al., 2017). Nanomaterials can also be grouped into the following categories: carbon-based (single-walled (SWCNTs), double-walled (DWCNTs) or multi-walled carbon nanotubes (MWCNTs)), metallic (gold, silver, aluminum), metal oxides (ZnO, CuO, TiO_2, Fe_2O_3, SiO_2, etc.), quantum dots (QDs), dendrimers and liposomes, and nanogels (Sanzari et al., 2019).

Depending on the type of treatment used, nanoparticles can be more or less absorbed by the tissues of the seeds and require specific care after treatment, such as drying and appropriated storage conditions. In this sense, based on the reviewed literature, three types of treatments have been frequently used for the application of nanoparticles in seeds: seed priming, seed soaking, and seed coating (Fig. 2). Seed

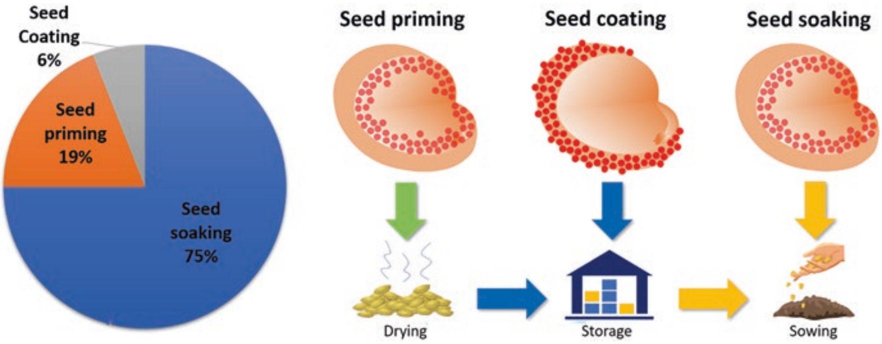

Fig. 2 Percentage of the research papers using soaking, priming, and coating for application of nanomaterials in seeds based on 46 works in the reviewed literature (on the left) and representative scheme of the procedure for each treatment (on the right)

priming treatments involve the germination synchronization by activating the metabolism of individual seeds, which usually present different physiological potentials, seeking to reach a uniform level and as close as possible to the protrusion stage of the primary root via controlled hydration (Marcos-Filho, 2016). Sowing in the field normally is carried out after drying the treated seeds, followed by storage until the appropriate time for sowing. Seed soaking treatments involve the direct immersion of the seeds in the water or solution, but without any control of the seed hydration. However, in this type of treatment, the very fast hydration may favor the occurrence of injuries during the imbibition of the seeds (cellular damage). In addition, the lack of hydration control, the uneven distribution of water in the seeds, and restriction to aeration can affect the reliability of the results. Seed coating includes the technique of applying materials to coat the seed surface. This type of treatment is more commonly used in the seed industry, with the application of different products such as fungicides, insecticides, micronutrients, germination promoters, growth regulators, and symbiotic microorganisms. For both seed priming and seed soaking, the nanomaterials can penetrate into seeds' tissues, whereas in seed coating this does not normally occur (Fig. 2). Seed priming and seed coating have the advantage of allowing seed storage after treatment, unlike seed soaking that requires immediate sowing (De La Torre-Roche et al., 2020).

Most of the treatments applied to investigate the effects of nanomaterials on seed performance have been based on seed soaking (Fig. 2), in concentrations of nanoparticle dispersions or suspensions and seed imbibition on moistened germination paper with nanoparticle solution. However, some researchers have also evaluated the effects of nanoparticles applied via seed coating (Siddaiah et al., 2018; Montanha et al., 2020) or as polymers (Chookhongkha et al., 2012). For example, Janmohammadi and Sabaghnia (2015) evaluated sunflower (*Helianthus annuus* L.) seeds after soaking in solutions containing different concentrations of nano-silicon (0.2, 0.4, 0.6, 0.8, 1, and 1.2 mM) for 8 h. Likewise, wheat (*Triticum aestivum* L.) seeds were soaked in different concentrations (1, 5, 10, 50, and 100 μg mL^{-1}) of chitosan nanoparticles (Li et al., 2019). Regarding the seed imbibition on moistened germination paper, Azimi et al. (2014) investigated the effect of SiO_2 nanoparticles on tall wheatgrass (*Agropyron elongatum* L.) seeds. In addition, nanoparticles of chitosan polymer solution dissolved with 0.5% v/v acetic acid were applied as a coating substance on chilli seeds at 20 and 100 ppm (Chookhongkha et al., 2012). Chitosan nanoparticles were also applied as seed coating treatment in pearl millet (*Pennisetum glaucum* L.) using concentrations of 50, 100, 250, and 500 mg of low-molecular-weight chitosan per 100 mL of solution, and this solution was treated at the rate of 100 mL kg^{-1} of seed (Siddaiah et al., 2018). In soybean seeds, Montanha et al. (2020) emulated the procedures carried out by farmers and seed treatment industry (seed coating) in a study of the application of zinc oxide nanoparticles (ZnO NPs).

4 Purposes of Seed Treatments with Nanoparticles

Research studies conducted using nanoparticles in seeds have been developed with different objectives such as efficacy on pathogen control, effect on drought resistance, and effects on photosynthetic pigments and photosynthesis of seedlings. However, most of the research works have been carried out to evaluate the direct effects of nanomaterials on germination and vigor (Fig. 3). For example, Azimi et al. (2014) investigated the effects of SiO_2 nanosized concentrations (0, 5, 20, 40, 60, and 80 mg L^{-1}) and three seed prechilling treatments (control, seed prechilling before nano SiO_2 treatments, treatments of seed with nano SiO_2 before prechilling) on germination and seedling growth of tall wheatgrass (*Agropyron elongatum* L.). Similarly, Almutairi and Alharbi (2015) examined the effect of silver nanoparticles (AgNPs) dosage on seed germination and seedling growth of three plant species: maize (*Zea mays* L.), watermelon [*Citrullus lanatus* (Thunb.) Matsum. & Nakai], and zucchini (*Cucurbita pepo* L.). Likewise, Duran et al. (2018) evaluated the effect of bare and poly(ethylene glycol)-coated Fe_3O_4 nanoparticles on the germination and seedling development of common bean (*Phaseolus vulgaris* L.). On the other hand, Dehkourdi and Mosavi (2013), besides evaluating the effect of different concentrations of anatase nanoparticles (nano-TiO_2) on germination and vigor parameters of parsley [*Petroselinum crispum* (Mill.) Nym.] seeds (percentage of germination, germination rate index, root and shoot length, fresh weight of seedlings and vigor index), investigated the influence of the nano-TiO_2 treatment on chlorophyll content of seedlings. However, other applications have been given to

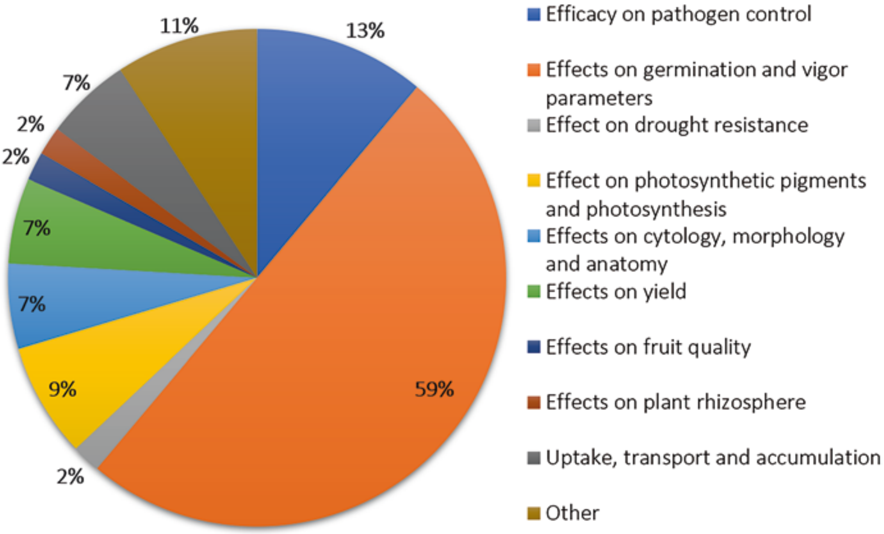

Fig. 3 Percentage of the research studies using nanomaterials in seeds according to the objective of the study, based on 46 works in the reviewed literature

the seed treatment using nanoparticles. Taran et al. (2014), as an example, investigated the effects of colloidal solution of molybdenum nanoparticles on the microbial composition in rhizosphere of chickpea seeds (*Cicer arietinum* L.). Some researchers also focused on the application of nanoparticles for seed disinfection and microorganism control. Thus, silver nanoparticles (AgNPs) were evaluated as an alternative agent for seed treatment in managing *Gibberella fujikuroi* on rice seedlings (Jo et al., 2015). In the same way, other researchers evaluated the effects of chitosan nanoparticles, due to their great potential for a wide range of uses in controlling plant pathogens. For instance, Chookhongkha et al. (2012) evaluated the effect of chitosan nanoparticles on fungal growth and the quality of chilli (*Capsicum annuum* L.) seeds, and Choudhary et al. (2019) evaluated the antifungal activity of zinc-encapsulated chitosan nanoparticles in maize.

5 Factors Considered in Assessing the Effect of Nanoparticles in Seed Treatment

In assessing the effects of nanoparticles on seeds, some factors can influence the efficiency of treatments, such as the concentration (dosage), nanoparticle types, the size of the particles, and the plant species. In this sense, Lin and Xing (2007) investigated the effects of five types of nanoparticles (multi-walled carbon nanotube, aluminum, alumina, zinc, and zinc oxide) on seed germination and root growth of six higher plant species (radish, rape, ryegrass, lettuce, corn, and cucumber). In addition, the use of the correct concentration is essential to obtain positive results from treatments with nanoparticles. Most research works aim to study distinct concentrations of different nanoproducts. Some examples are the works carried out with parsley [*Petroselinum crispum* (Mill.) Nym.] using nano-anatase in varied concentrations (10, 20, 30, and 40 mg mL^{-1}) (Dehkourdi & Mosavi, 2013), sunflower (*Helianthus annuus* L.) using the nano-silicon concentrations of 0.2, 0.4, 0.6, 0.8, 1, and 1.2 mM (Janmohammadi & Sabaghnia, 2015), chilli (*Capsicum annuum* L.) using concentrations of 0.0, 0.25, 0.50, and 0.75 g of zinc oxide nanoparticles (Afrayeem & Chaurasia, 2017), and wheat with different concentrations of zinc oxide nanoparticles (0, 25, 50, 75, and 100 mg L^{-1}) and iron oxide nanoparticles (0, 5, 10, 15, and 20 mg L^{-1}) (Rizwan et al., 2019). Regarding the particle size, Thuesombat et al. (2014) evaluated the effects of different sized silver nanoparticles (20, 30–60, 70–120, and 150 nm diameter) on jasmine rice, *Oryza sativa* L. cv. KDML 105 associated with different concentrations (0.1, 1, 10, 100, and 1000 mg L^{-1}). Regarding the response of nanoparticles depending on the species, Pokhrel and Dubey (2013), for example, observed that maize seed exposure to a wider range of zinc oxide nanoparticle concentrations (0.01–1000 μg mL^{-1}) did not inhibit seed germination, unlike what occurred with cabbage seeds when the increasing of zinc oxide nanoparticles dosage inhibited the germination.

Related to seed size, Jain et al. (2017) evaluated the phytotoxicity of nanoparticle, bulk and ionic forms of zinc at different concentrations on tomato, pear millet, and wheat, with varying seed size and surface anatomy. Due to the presence of thick cuticle on testa and root, pearl millet (xerophytic plant) was found to be relatively less sensitive to ZnO nanoparticles as compared to wheat and tomato (mesophytic plants) with normal cuticle layer. No correlation was observed between nanoparticle toxicity and seed size. The results indicated that variations in surface anatomy of seeds play a crucial role in determining the phytotoxicity of nanoparticles. The present findings significantly contribute to assessing potential consequences of nanoparticle release in the environment, particularly with a major emphasis on plant systems.

6 Effects of Nanoparticles on Seed Performance in Different Species

Many studies have shown the physiological responses of seedlings to nanoparticles during germination, but the influence of seed germination and root growth varied significantly among the plants and nanoparticles (Hao et al., 2016), and as previously emphasized, some types of nanoparticles have also been used to control pathogens. Based on the reviewed literature, the effects of nanoparticles have been evaluated in more than 20 plant species (Fig. 4) and almost 50% of the research studies are concentrated in only three species (rice, wheat, and maize). In spite of this evidence, research results have revealed both positive and negative effects when applying nanoparticles to seeds of several species, which will be covered below.

6.1 Positive Effects

Several nanoparticles applied to seeds have shown positive effects on germination and seedling performance of various species. In spinach seeds, the higher germination and vigor were observed with the application of nano-TiO_2 (rutile) in concentrations of 0.25% to 4% (Zheng et al., 2005). In tomato, Khodakovskaya et al. (2009) observed that the exposure of the seeds to carbon nanotubes (CNTs) can increase the germination percentage and enhance the growth of seedlings; these benefits were associated with the ability of the CNTs to penetrate the thick seed coat and support water uptake inside the seeds. Likewise, the application of SiO_2 nanoparticles significantly increased seed germination of tall wheatgrass from 58% in the control treatment to 86.3% and 85.7% in concentrations of 40 and 60 mg L^{-1}, respectively (Azimi et al., 2014). The authors also observed that the application of SiO_2 nanoparticles increased the dry weight of shoot, root, and seedling of tall wheatgrass. Similarly, research carried out by Janmohammadi and Sabaghnia (2015) revealed that controlled imbibition of sunflower achene in nano-silicon

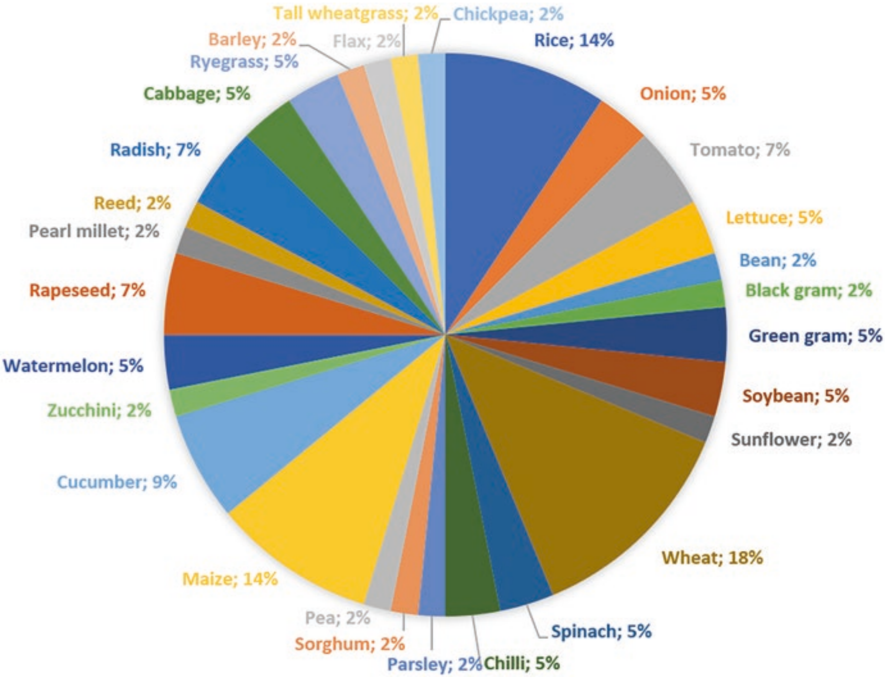

Fig. 4 Percentage of the research works related to the application of nanomaterials in seeds, per species, based on 46 works in the reviewed literature

solution followed by dehydration significantly enhanced seed germination. The authors observed that when achenes were primed in low concentrations of nano-silicon solution, it enhanced the percentage of germination, seed germination index, seedling vigor index, and seedling fresh weight and dry weight, as well as decreased mean germination time and T_{50}. They attributed these positive effects of nano-silicon on germination performance to a possible increase in cell division within the apical meristem of seedlings. The application of silica nanoparticles was also investigated in maize seeds by Suriyaprabha et al. (2012). The positive effects of this treatment were evidenced by increasing the germination rate when nano-SiO_2 was used as a source of Si supplement compared with other bulk sources (micro-SiO_2 and Na_2SiO_3). The effects of silica nanoparticles on seed germination and growth of the bean (*Vicia faba* L.) investigated by Roohizadeh et al. (2015) were confirmed by increases in the germination percentage.

The advantageous effects of chitosan nanoparticles on seed infection control and germinative performance have been observed by several researchers. In chilli seeds, Chookhongkha et al. (2012) observed lower seed infection when coating the seeds with chitosan nanoparticles at 20 and 100 ppm compared with the treatments with chitosan and fungicide (captan), without affecting germination and seed vigor. In pearl millet, seed treatment with 250 mg kg^{-1} of chitosan nanoparticles enhanced seed germination (percentage) and seedling vigor (Siddaiah et al., 2018). The authors also observed that the seed treatment with chitosan nanoparticles induced systemic and durable resistance and showed significant protection against downy mildew (*Sclerospora graminicola*) under greenhouse conditions in comparison to the untreated control. Likewise, research carried out by Li et al. (2019) with wheat seed demonstrated that the application of 5 μg mL^{-1} of chitosan nanoparticles induced the auxin-related gene expression, accelerated indole-3-acetic acid (IAA) biosynthesis and transport, and reduced IAA oxidase activity resulting in the increase of IAA concentration in wheat shoots and roots. The authors compared the effects of chitosan nanoparticles and chitosan and affirmed that these results suggested that chitosan nanoparticles have a more positive effect on seed germination and seedling growth of wheat at a lower concentration than chitosan due to higher adsorption on the surface of wheat seeds. In maize seeds, Choudhary et al. (2019) observed that treatment with zinc encapsulated chitosan nanoparticle exhibited significant disease control (antifungal action against *Curvularia lunata*) through the strengthening of plant innate immunity by elevating antioxidant and defense enzymes activities, balancing reactive oxygen species (ROS), and enhancing lignin accumulation.

The effects of silver nanoparticles on seed germination of corn, watermelon, and zucchini were evaluated by Almutairi and Alharbi (2015). The authors applied seven concentrations (0.05, 0.1, 0.5, 1, 1.5, 2, and 2.5 mg L^{-1}) of AgNPs and observed that the three species revealed different dosage responses on germination percentage and the measured growth parameters. The best dose of AgNPs for watermelon was 2 mg L^{-1}, which enhanced germination percentage and germination rate for the highest values. Exposure to 0.5 and 2.5 mg L^{-1} of AgNPs appeared to be proper to enhance zucchini seed germination, and seedling fresh weight increased with AgNP treatments for the three species. Research carried out by Jo et al. (2015) that focused on seed surface decontamination on rice using silver nanoparticles revealed that the AgNP reduced viability of *Gibberella fujikuroi* from the seed surface and subsequently prevented the seeds from developing disease symptoms, including low germination and stunted growth of seedlings caused by the pathogen. Furthermore, AgNPs did not affect seed germination or seedling growth of noninfested seeds. Belava et al. (2017) evaluated the effects of silver and copper nanoparticles on wheat–*Pseudocercosporella herpotrichoides* pathosystem and observed that both silver and copper nanoparticles did not affect the growth and development of *P. herpotrichoides*. The authors suggested that the effect of nanoparticles was determined by the plant's responses to the pathogen rather than the phytotoxic action of the copper or silver nanoparticles, at least during the initial stages of the pathological process. Research conducted by Mahakham et al. (2017) demonstrated that AgNPs can be applied as a nanopriming agent for enhancing water uptake, seed germination, and starch metabolism of rice aged seeds. The authors observed that AgNPs can surpass seed coat and support water uptake inside seeds, leading to promote seed germination and starch metabolism, enhancing the α-amylase activity and resulting in higher soluble sugar content for supporting seedlings growth. Other research evaluating the effects of silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) on onion seeds (Acharya et al., 2019) revealed that both nanopriming treatments exhibited positive effects compared to the unprimed onion seeds. The authors observed that applying AuNPs as a priming agent at low concentrations (5.4 ppm) resulted in enhancement of germination, plant height, leaf length, leaf diameter, neck diameter, and leaf surface area at both early and later plant development stages without toxicity symptoms. According to Acharya et al. (2019), nanopriming modulated antioxidant enzyme activity in onion seeds. They observed significantly higher activity of peroxidase (POD) in the nanoprimed seeds as compared to the dry and hydroprimed seeds. Similarly, in rice, Mahakham et al. (2017) observed reactive oxygen species (ROS) production in germinating seeds of nanopriming treatment with AgNPs compared to unprimed control and other priming treatments. They affirmed that nanopriming stimulated the upregulation of aquaporin genes in germinating seeds, suggesting that both ROS and aquaporins play important roles in enhancing seed germination.

The uptake and translocation of superparamagnetic iron oxide nanoparticles (SPIONs), with various surface charges, were evaluated on soybean [*Glycine max* (L.) Merrill] by Ghafariyan et al. (2013). They observed that various concentrations of SPIONs, with different charges, do not have significant effects on the germination index. Furthermore, positive and negative SPIONs showed positive influence on root elongation, whereas plain SPIONs have no significant effect. Similarly, Duran et al. (2018) investigated the effect of bare and polyethylene glycol-coated Fe_3O_4 nanoparticles on the germination and seedling development of *Phaseolus vulgaris* L. The authors observed that seed soaking in Fe_3O_4-PEG at 1000 mg Fe L^{-1} increased radicle elongation (8.1 ± 1.1 cm vs 5.9 ± 1.0 cm for the control) and attributed the higher root length promoted by the Fe_3O_4-PEG in comparison to Fe_3O_4 and soluble-Fe to water uptake enhancement induced by the PEG coating. The effects of seed priming with different concentrations of Fe-NPs (20, 40, 80, and 160 mg L^{-1}) were investigated in diploid and triploid watermelon by Kasote et al. (2019). The results revealed that Fe-NP priming treatments significantly improved germination compared to unprimed treatment. Furthermore, different Fe-NP priming treatments modulated antioxidant potential and defense-linked hormones in watermelon seedlings.

In onion seeds, Raskar and Laware (2014) investigated the effect of zinc oxide nanoparticles (ZnO NPs) on cytology and seed germination and observed a significant enhancement in shoot and root lengths only in lower concentrations of ZnO NPs (10 and 20 μg mL^{-1}) in comparison to higher concentrations (10 and 20 μg mL^{-1}). Still in onion seeds, the application of different dosages (0, 20, 40, 60, 80, and 100 mg L^{-1}) of hematite nanoparticles (HNPs) revealed that HNPs in lower concentrations led to increasing mitotic activity in onion roots, while in higher dosages (80–100 mg L^{-1}) minor inhibitory effects occurred (Rath et al., 2020). On the other hand, a study carried out with chilli seeds using different concentrations (0.0, 0.25, 0.50, and 0.75 g) of ZnO NPs revealed that seed germination and root, shoot, and seedling length increased at the highest concentration and decreased at lower concentrations (Afrayeem & Chaurasia, 2017). The effects of ZnO NPs (750, 1000, and 1250 mg kg^{-1}) were also evaluated in chilli seeds by Kumari et al. (2019). They observed higher germination and vigor (shoot and root length, and vigor index) in seeds treated with zinc oxide nanoparticles at 1000 mg kg^{-1}, and attributed these results to the increased activity of antioxidant enzymes and membrane stability. Montanha et al. (2020) investigated the effect of zinc oxide nanoparticles (ZnO NPs) on soybean seed germination and observed an increase in germination ratio, seedling root, and shoot development when comparing with the control (untreated seeds). Other research carried out by Raja et al. (2019) with blackgram (*Vigna mungo*) using different concentrations (400, 500, 600, 700, 800, 900, 1000, 1100, 1200, and 1300 mg kg^{-1}) of ZnO and Cu nanoparticles revealed that ZnO nanoparticles at 600 mg L^{-1} and Cu nanoparticles at 400 mg L^{-1} promoted maximum germination, root length, shoot length, and seedling vigor when compared to untreated seeds. The effect of Zn and Cu nanoparticles was also investigated on drought resistance of two ecotypes of wheat seedlings by Taran et al. (2017). The authors concluded that in drought conditions, the colloidal solution of Cu, Zn nanoparticles have a more positive effect on pro-oxidative/antioxidative balance and morphometric indexes of leaves more in seedlings of the steppe ecotype (Acveduc) than in seedlings of the forest-steppe ecotype (Stolichna). They observed a decrease in TBARS (thiobarbituric acid reactive substances) accumulation and an increase of antioxidative enzyme (SOD and catalase) activity, which characterize the increase of plant antioxidative status under the influence of nanoparticles in drought conditions. Furthermore, the influence of the colloidal Cu and Zn nanoparticle solution was manifested in changing the ratio of chlorophyll in the leaves (Chl a to Chl b), along with a high content of carotenoids in the leaves. Research carried out by Panyuta et al. (2016) evaluating the accumulation dynamics of lipid peroxidation products in winter wheat plants at pre-sowing seed treatment with biogenic metal nanoparticle solutions (Zn, Ag, Fe Mn, Cu) also revealed the reduction of TBARS in seedling tissues as compared to the untreated seeds. However, in this case, the authors investigated the effect of the nonionic colloidal solutions of nanoparticles on the formation of defensive reactions of winter wheat seedlings on pathogen infection of *Pseudocercosporella herpotrichoides* (Fron) Deighton. They concluded that metal nanoparticles may increase antioxidant properties of cells under phytopathogen stress conditions and improve physiological conditions of plants. The effects of silver sulfide nanoparticles (Ag_2S NPs), zinc sulfide nanoparticles (ZnS NPs), and their composite (Ag_2S–ZnS NCs) were investigated on the germination performance of soybean and wheat by Afsheen et al. (2020). The authors observed that the application of metal sulfide NPs and NCs can help enhance the germination, root and shoot length, and mean germination time (MGT) as compared to control treatment.

Evaluating the effects of zinc-functionalized thymol nanoemulsion (Zn-TNE) in soybean seeds, Kumari et al. (2019) observed that the treated seeds showed better seedling vigor index and higher activities of seed stored food mobilizing enzymes (α-amylase and protease). Similarly, the seed treatment of spinach with iron pyrite (FeS_2) nanoparticles promoted an enhanced breakdown of stored starch resulting in an increase of seedling emergence (Srivastava et al., 2014).

In corn seeds, polymeric nanoparticles were applied to improve seed germination and plant growth under copper stress (Xin et al., 2020). Extensive use of copper (Cu)-based agrochemicals such as fertilizers, pesticides, and nematicides has resulted in

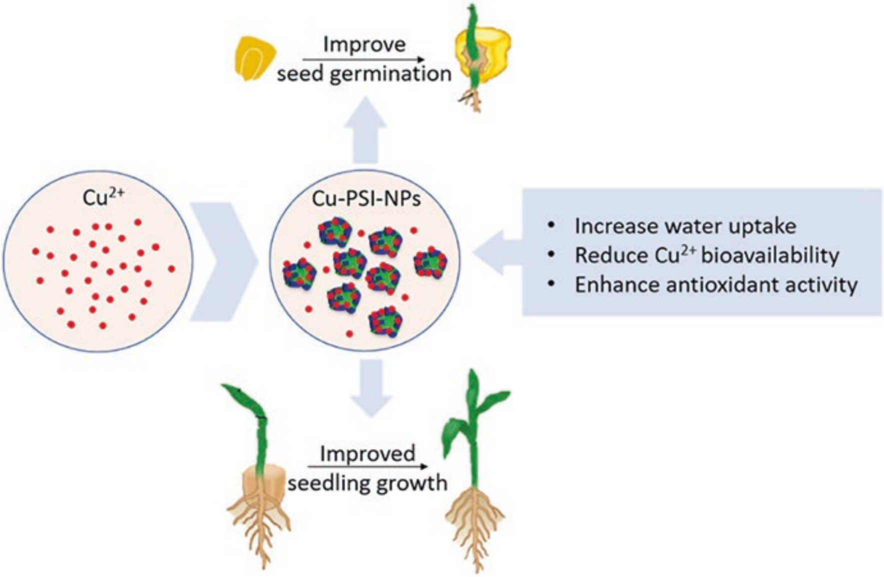

Fig. 5 The use of PSI-NPs to improve seed germination and seedling growth. Source: Xin et al. (2020)

the widespread Cu-contamination of soils in agriculture. In this pioneering study, the authors investigated the effects of newly synthesized polysuccinimide NPs (PSI-NPs) on corn seed germination and seedling growth under different levels of Cu stress. The results showed that PSI-NPs influenced seed germination in a dose-dependent manner with an optimal rate of 200 mg L^{-1}. In addition, the positive effects of PSI-NPs on seed germination indexes were found to be positively correlated with enhanced seed imbibition. The addition of PSI-NPs significantly mitigated Cu stress as indicated by improved growth of shoots and roots, and higher antioxidant enzyme activity observed with co-exposure to PSI-NPs as compared to Cu stress treatment only (Fig. 5). Copper concentrations in seedling root and shoot significantly increased with increasing Cu treatment rate. Higher uptake of Cu by the plant was observed in the Cu-PSI-NP co-treatment than single Cu treatment. The alleviation effect of PSI-NPs could be explained by the enhanced antioxidant enzyme activities and storage of Cu as Cu-PSI complexes in plants with reduced phytotoxicity.

6.2 *Negative Effects*

The negative effects of the application of nanoparticles in seeds have also been frequently reported, although in a smaller number of studies when compared to positive effects. The effects of different sized AgNPs (20, 30–60, 70–120, and 150 nm diameter) at different concentrations (0.1, 1, 10, 100, and 1000 mg L^{-1}) on rice seedlings were evaluated in terms of the level of seed germination and the subsequent growth and leaf morphology of the seedlings (Thuesombat et al., 2014). The results revealed that the level of seed germination and subsequent growth of those seedlings that germinated have both decreased with the increment in sizes and concentrations of AgNPs. The negative effects of AgNPs were supported by leaf cell deformation when rice seeds were treated with 150-nm-diameter AgNPs at the concentration of 10 or 100 mg L^{-1} during seed germination. The impacts of different concentrations of bulk (1, 2, 10, 100, and 500 ppm) and nanosized (1, 2, 10, 100, and 500 ppm) TiO_2 on seed germination and seedling growth of wheat were studied by Feizi et al. (2012). It was demonstrated that the use of nanosized TiO_2 in high concentrations (100 and 500 ppm) had an inhibitory or no effect on wheat seeds. Azimi et al. (2014) studied the effect of six SiO_2 nanosized concentrations (0, 5, 20, 40, 60, and 80 mg L^{-1}) and three seed prechilling treatments (control, seed prechilling before nano SiO_2 treatments, treatments of seed with nano SiO_2 before prechilling) on germination and seedling growth of tall wheatgrass and observed that under the 60 and 80 mg L^{-1} treatments, seedling weight decreased.

The application of Fe_3O_4-PEG and bare Fe_3O_4 nanoparticles on the germination and seedling development of beans and their effects were investigated by Duran et al. (2018). The results showed negative effects on seedlings' radicle elongation, indicating that Fe^{2+}/Fe^{3+} (aq) and bare Fe_3O_4 at 1000 mg Fe L^{-1} prevented its growth and was toxic for the seedling development. The authors hypothesize that these results are regarded to the hydrophilic nature of the PEG and that the polymeric coating might have reduced the water potential, which caused greater water absorption by the tissues when compared to the negative response of Fe^{2+}/Fe^{3+} (aq) and bare Fe_3O_4. Similar effects were found by Zhang et al. (2015) while studying the impacts of ZnO nanoparticles on seed germination and root elongation of corn and cucumber. The results showed that ZnO NPs (1000 mg L^{-1}) reduced the root length of corn and cucumber by 17% and 51%, respectively. Nair and Chung (2015) evaluated the toxic effect of different concentrations of silver nanoparticles (0, 5, 10, 20, and 50 mg L^{-1}) in seedlings of mung bean (*Vigna radiata* L.). In this study, the shoot length and weight were significantly reduced upon exposure to 50 mg L^{-1} of silver nanoparticles, and significant reduction in root elongation and weight was observed upon exposure to 20 and 50 mg L^{-1} of silver nanoparticles. When investigating the effects of different nanomaterial morphologies (multi-walled carbon nanotube, aluminum, alumina, zinc, and zinc oxide) on seed germination and root growth of six higher plant species (radish, rape, ryegrass, lettuce, corn, and cucumber), Lin and Xing (2007) observed that seed germination was not affected except for the inhibition of nanoscale zinc (nano-Zn) on ryegrass and zinc oxide (nano-ZnO) on corn at 2000 mg L^{-1}, and that inhibition on root growth varied greatly among nanoparticles and plants. Suspensions of 2000 mg L^{-1} nano-Zn or nano-ZnO practically terminated root elongation of the tested plant species. Similarly, Hao et al. (2016) evaluated the effects of different nanomaterial morphologies on rice germination and concluded that all nanoparticles studied (Fe_2O_3 nanocubes (5 mg L^{-1}), Fe_2O_3 short nanorods (10 mg L^{-1}), Fe_2O_3 long nanorods (30 mg L^{-1}), MWCNTs (100 mg L^{-1}), and TiO_2 NPs (150 mg L^{-1})) inhibited germination. Furthermore, Boonyanitipong et al. (2011) investigated the effects of zinc oxide nanoparticles (nano-ZnO) and titanium dioxide nanoparticles (nano-TiO_2) on rice roots. The results showed that nano-ZnO had detrimental effects on rice roots at the early seedling stage and is found to stunt root length and reduce the number of roots.

In the same work that presented positive effects on the use of silver nanoparticles on three crop plants (corn, zucchini, and watermelon), Almutairi and Alharbi (2015) also found negative effects. All AgNP concentrations tested (0.05, 0.1, 0.5, 1, 1.5, 2, and 2.5 mg L^{-1}) presented toxic effect on corn, causing inhibition in root length. Raskar and Laware (2014) investigated the effect on cell division, seed germination, and early seedling growth of different concentrations (0.0, 10, 20, 30, and 40 g mL^{-1}) of ZnO NPs in onion seeds. The results presented that seed germination decreased in values in the concentration of 40 g mL^{-1} and germination indices decreased in the concentrations of 30 and 40 g mL^{-1}. Zhang et al. (2020) evaluated the effects of biochar nanoparticles (BNPs) on seed germination and seedling growth of three different plant species (rice, tomato, and reed plants). The BNPs were collected from biochars derived from two feedstocks (rice straw and wood sawdust) under 300 °C (low temperature), 500 °C (mid-temperature), and 700 °C (high temperature). The BNPs collected from high-temperature biochar inhibited seed germination of rice and had an inhibiting effect on the reed that dramatically decreased shoot length and biomass. The authors explain that the inhibitory effects of BNPs were caused not only by phenolic compounds on its surface, but also by the blocking effect on epidermal openings resulting in a reduced transfer of nutrients and water. Another approach studied not only different types of nanoparticles (zero-valent iron—nZVI—and silver nanoparticles), but also their difference in average particle size from 1 to 20 nm (Ag cool, Ag 5, and Ag 20) and was evaluated using seed germination tests with ryegrass, barley, and flax exposed to 0–5000 mg L^{-1} nZVI or 0–100 mg L^{-1} Ag. For nZVI, germination tests were conducted both in water and in two contrasting soils to test the impact of assumed differences in bioavailability of nanoparticles. The results showed complete inhibition of germination at 1000–2000 mg L^{-1} for nZVI. The presence of soil had a modest influence on toxicity, and inhibitory effects were observed at 300 mg nZVI L^{-1} water in soil. Complete inhibition was observed at 750 and 1500 mg L^{-1} in sandy soil for flax and ryegrass, respectively. The three types of silver nanoparticles affected seed germination differently for the three plant species tested. The smallest particle type (Ag cool) had an inhibitory effect at a concentration as low as 10 mg L^{-1} in ryegrass, while the intermediately sized particle type (Ag 5) also had a weak inhibitory effect at 10 mg L^{-1} in barley, which increased at higher concentrations. No effect on germination percentage of flax was observed for any types of silver nanoparticles, even at the highest concentrations (El-Temsah & Joner, 2012).

Undoubtedly, the use of nanoparticles on seed can bring negative effects on its performance, and based on the studies presented above, the main negative effects of its use were pinpointed in the decrease of seed germination, seedling weight, root elongation, root number, and seedling's radicle elongation, and in some cases, even the inhibition of germination was noted. The harmful effects of the use of nanoparticles on seeds are mainly due to high concentrations, the element's composition, and its forms. According to Brunner et al. (2006), toxicity of nanoparticles may be attributed to two different actions: first, a chemical toxicity based on the chemical composition, e.g., release of (toxic) ions, and second, stress or stimuli caused by the surface, size, and/or shape of the particles. It is noteworthy that the toxicity of nanoparticles varies greatly among nanoparticles and plant species; therefore, as Murashov (2006) highlights, an appropriate experimental design and interpretation are a key fact to provide a defensible scientific understanding of the biological effects of nanoparticles.

7 Final Remarks

Although the use of nanoparticles in agriculture is relatively recent, several studies demonstrated the applicability of nanomaterials in seeds of different species. Based on the reviewed literature, it was observed that nanoparticles can play positive and/or negative effects on seed performance and these effects are mainly variable according to the type of nanomaterial, dose/concentration of the product, type of seed, and size of the nanoparticles. Furthermore, the objectives of the studies have been diverse, and most of them had focused on assessing the direct effects of different types of nanoparticles on germination and characteristics related to seedling vigor. It was also observed that the nanoparticle application in seeds has been mainly via seed soaking, highlighting the need for studies closer to commercial practices. Thus, there is a need for more research focused on the application of nanoparticles via seed coating and seed priming. In the same way, there is a great demand for more in-depth studies to investigate the effects of nanoparticles on seeds, considering that toxic effects are also verified after their application and to evaluate other plant species, since about 50% of the reviewed works were carried out with only three species of Poaceae. Further research is also needed to assess the effects of nanoparticles before and after seed storage since there is still no information on storability associated with the effects of nanomaterials on seed performance. In addition, there is a gap to be filled about the application of nanomaterials in plants (via soil and/or leaf) and the possible effects on the quality of the seeds produced; this could be a path for the production of enriched seeds that may express a better physiological and storage potential. Finally, there is still a long way to go in relation to the application of nanoparticles in seeds; however, considering the beneficial potential of these products, we believe that scientific progress will be significant in the near future.

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Biological Barriers, Processes, and Transformations at the Soil–Plant–Atmosphere Interfaces Driving the Uptake, Translocation, and Bioavailability of Inorganic Nanoparticles to Plants

Astrid Avellan, Sónia M. Rodrigues, Bruno P. Morais, Benjamin Therrien, Yilin Zhang, Sandra Rodrigues, and Gregory V. Lowry

Abstract The development of nanotechnologies for more sustainable agriculture is an innovative strategy proposed to increase food production while decreasing material inputs and reducing environmental impacts. Nanoparticles (NPs) applied to seeds, soil, or leaves interact with plants at two major interfaces: the rhizoplane (root–rhizosphere interface) or the phylloplane (atmosphere–leaf interface). NP transformations occurring at these interfaces control their bioavailability, while plant structures are barriers to NP absorption and bottlenecks for their translocation. This chapter focuses on the complex interplays driving NP uptake, translocation, and accumulation into plant tissues. Foliar treatments appear to present advantages over soil application for the delivery of NPs to certain compartments. The adjustment for nanoparticle's shape and surface properties could allow specific targeting (e.g., apoplast, symplast, organelles) and designed mobility to freely reach the phloem or accumulate in the mesophyll. This chapter highlights the knowledge gaps that need to be overcome for the safe and efficient development of nano-enabled agriculture. The parameters influencing for NP movement across cuticle barriers,

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cell walls, and cell membranes are still to be identified. Consequently, NP mobility in the root cortex and through the endodermis before entering the xylem or in the mesophyll before loading the phloem is not predictable yet. The processes that drive NP movement from the mesophyll cells to the sinks and their capacity to load the phloem are also poorly characterized. In addition, plant physiological responses and in vivo transformations, such as dissolution rates, or protein corona formation around NPs, remain important knowledge gaps that need to be addressed to understand, predict, and regulate NP translocation in plants and their bioavailability, thus enabling safe and efficient, targeted delivery of NPs for agricultural purposes.

Keywords Target · Fate · Nanobiotechnology · Plant-nanoparticle interaction

1 Introduction: Nano-Formulations Targeting Specific Plant Compartments

Agriculture is one of the largest and most significant industries in the world. The agri-food production chain causes relevant environmental hazards (biodiversity loss, disruption of global nutrient cycles, soil, and water pollution) (Rodrigues et al., 2017). The current use of fertilizers and agrochemicals is highly inefficient and polluting, partly due to the poor design of the products and their application strategies. Fertilizers and pesticides are applied annually by the ton (187 million metric tons and four million tons, respectively) (Zhang, 2018). Only a small percentage of the applied pesticides or fertilizers reach their target (Hofmann et al., 2020), and a major part of the applied products is lost, either to the atmosphere (during spray application), is degraded (volatilization or UV degradation) or is lost to the environment as run-off (approx. 50–70%) (Rodrigues et al., 2017). More efficient technologies are needed for the design of agrochemical and fertilizer that would protect the crops, but also their agroecosystems.

These concerns have led the scientific community to propose alternatives to conventional products to decrease environmental impacts and input quantities through the development of new nano-based technologies for more efficient delivery and increased efficacy (Lowry et al., 2019). These novel delivery systems for increased efficacy and delivery efficiency of agronomic products have shown potential to protecting the crops, increasing crop yields and the nutritional value of foods, while reducing losses of active ingredients (AIs) (Rodrigues et al., 2017; Wang et al., 2016). Nano-enabled products are an important tool and a promising opportunity to develop materials for timed and targeted delivery of products for crop growth, nutrition, and protection. Nanoparticles (NPs) can be formulated so that the AI delivery becomes time- and stimuli-responsive (Rodrigues et al., 2017) (for biotic or abiotic triggers (Camara et al., 2019)), releasing the product only when those specific conditions are met.

Examples of nano-enabled strategies for agriculture are the following (Rodrigues et al., 2017; Hofmann et al., 2020; Lowry et al., 2019; Camara et al., 2019; Shang et al., 2019; do Espirito Santo Pereira et al., 2021; Kah et al., 2019a):

- Gene editing for protection against environmental stresses (temperature changes, droughts, floods, increasing salinity, etc.) by foliarly applying nanocarriers loaded with genetic material (e.g., DNA plasmids or dsRNA).
- Plant protection against pests and pathogens, by delivering nano-enabled AIs to plant leaves, to crop soil, or by treating seeds.
- Fertilization, to increase yields and crop nutrition by providing micronutrients to crops either by foliar or soil application, but also by coating seeds before sowing.
- Growth improvement by soil or foliar application of NPs containing AIs improving photosynthetic performance and regulating plant stress hormones.
- Soil properties and health restoration and protection by directly applying NPs to soils to promote optimal conditions for soil microbiome to be maintained and/or improved but also for soil amendment to prevent soil degradation.

Among all of these NPs, inorganic materials are of particular interest for the range of potential benefits they may provide, but also of concerns because of their persistent nature in the ecosystems. One major challenge for developing more sustainable phytoprotection and fertilization products through an efficient design of these NP structures is their delivery to the crops. Depending on the type of product applied and the goals aimed at, NPs will be provided to the plant either through (a) seed coating, (b) the soil for root applications, (c) direct application to the foliage, or (d) feeding/injecting into the plant stems or trunks. The NPs will thus interact with different plant interfaces: the phylloplane (atmosphere–leaf interface), the rhizosphere (soil–root interface), and the rhizoplane (root–rhizosphere interface). The fate, transformation, and behavior of NPs will vary depending on which of these interfaces they will be in contact with. This chapter focuses on detailing what cellular barriers and plant bottlenecks need to be overcome for these NPs to reach their target. It provides insight into their *in planta* transformation, transport, and bioavailability. The NP properties that would allow for optimized design of nano-enabled fertilizers and agrochemicals are also presented.

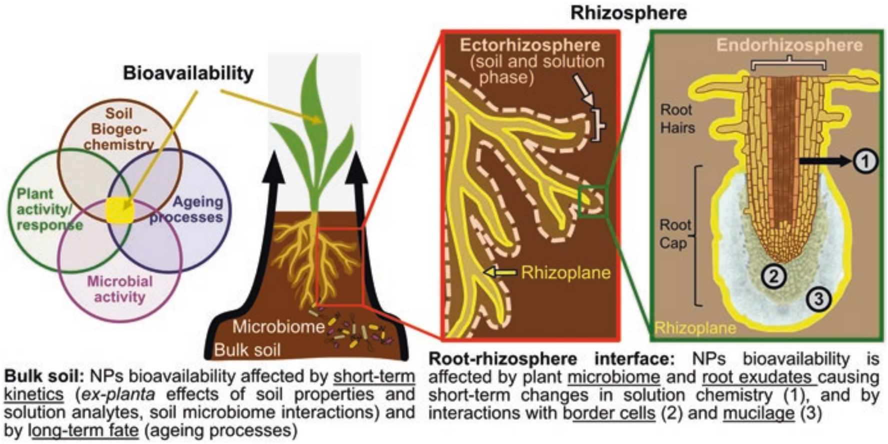
2 The Soil–Root Interface

2.1 The Rhizosphere, a Biologically Active Interface

The soil application of conventional fertilizers and micronutrients is currently inefficient (DeRosa et al., 2015; Bindraban et al., 2015; Raliya et al., 2018). This is mostly caused by run-off and rapid leaching of dissolved phases throughout the critical zone or by physical–chemical processes leading to the immobilization of inorganic elements in the solid phase. This hampers their diffusion toward the plant rhizosphere, where they must become available for root uptake. To reduce losses and collateral damages, materials must be tailored to target the plant root–soil interface (rhizoplane) and/or to enable biogeochemical transformations in the rhizosphere toward a steady-state release of inorganic elements to the soil solution, in physical–chemical forms (either ionic or nanoforms) that can be readily absorbed and/or taken up by plant roots. NPs can potentially enable the slow release of inorganic fertilizers and micronutrients applied to soil relevant to control their reaction at the rhizoplane, thus allowing to achieve effective concentrations in the rhizosphere with greater improvement in plant bioactivity (Rodrigues et al., 2017; Kah et al., 2019a; Dimkpa et al., 2017; Adisa et al., 2019; Dimkpa, 2018). Indeed, several studies have recently reported that NPs added to soils were more effective than conventional fertilizers in improving plant nutrition (Kah et al., 2019a; Kopittke et al., 2019). However, many of these observations were phenomenological rather than mechanistic in nature; appropriate controls were often not included in the experimental designs; and, in some cases, nano-specific effects were either unclear or disappeared when chemical speciation and elements' bioavailability in the root medium were considered (Kopittke et al., 2019; Qiu & Smolders, 2017). Thus, a better mechanistic understanding of the processes occurring in the rhizosphere is needed for investigating the bioavailability of NPs applied to soil so as to understand the conditions under which their application increases the efficiency of use.

The rhizoplane is a biologically active soil zone with complex plant–soil–microbial interactions, which have been largely overlooked in nanoparticle soil studies. In 1904, Hiltner clearly identified the key role of both microbial activity and of chemicals secreted by roots in controlling the conditions in the surroundings of the plant roots and first described the "rhizosphere." Operational definitions of the rhizosphere have often restricted it to the 2 mm of soil around the root surface (Dotaniya & Meena, 2015). However, it is now clear that the rhizosphere varies with plant species, plant type (monocot vs. dicot), and soil type, and that this is not a region of definable size or shape (McManus et al., 2018). Rather, it is a dynamic region where radial and longitudinal gradients of biogeochemical conditions occur driven by soil properties, by the root physical activity, and by root exudates, mediated by microorganisms in the soil and plant microbiomes. In turn, the biogeochemical processes occurring in the rhizosphere control a multitude of physical–chemical transformations regulating the fate of inorganic NPs and chemical element activities that control their bioactivity.

Three rhizosphere zones of relevance for the fate of NPs in soils have been identified (Fig. 1): the endorhizosphere refers to the apoplastic space between cells of the root cortex and endodermis, which can be occupied by microbes and dissolved ions (and eventually by NPs); the rhizoplane is the interface zone with the soil, directly adjacent to the root and including the root epidermis and mucilage, relevant for adsorption and eventual subsequent uptake of NPs; and the ectorhizosphere extends from the rhizoplane out into the bulk soil. The mucilage is formed by high-molecular-weight, insoluble polysaccharides secreted by root cells as the root grows through the soil (McManus et al., 2018). It can assist plants in nutrient acquisition,



Bulk soil: NPs bioavailability affected by short-term kinetics (*ex-planta* effects of soil properties and solution analytes, soil microbiome interactions) and by long-term fate (ageing processes)

Root-rhizosphere interface: NPs bioavailability is affected by plant microbiome and root exudates causing short-term changes in solution chemistry (1), and by interactions with border cells (2) and mucilage (3)

Fig. 1 Parameters influencing NP bioavailability in the bulk and rhizosphere soil

aeration, water filtration, and in the sequestration of toxic metals; as it binds soil particles, it may also play a relevant role in the binding of NPs and of their aggregates.

Plant roots can release up to 40% of their total photosynthetically fixed carbon in the rhizosphere (mostly in organic forms) as a response to nutrient deficiency, toxicity, or stress conditions (McManus et al., 2018). Root exudates are a complex mixture of low-molecular-weight organic acids (LMWOAs), phytosiderophores, phenolics, amino acids, proteins, sugars, vitamins, inorganic ions, volatile organic carbon compounds, enzymes, and root border cells (Dotaniya & Meena, 2015; Vives-Peris et al., 2020). These biomolecules enable plants to access nutrients by (a) changing the pH or redox conditions in the rhizosphere, causing dissolution of mineral phases or the desorption of nutrients from clays, oxides, or organic matter into the soil solution; (b) directly chelating with plant nutrients; or (c) rendering them available for absorption through enzymatic activity. Two root exudation strategies (Strategy I and Strategy II) enable plant acquisition of Fe and other micronutrients under nutrient deficiency stress. Dicotyledons and nongraminaceous monocotyledons release H^+ to increase free ionic Fe in the rhizosphere soil solution and increase Fe uptake (Strategy I). In Strategy II, graminaceous species (Gramineae) release Fe(III)-chelating, low-molecular-weight compounds, called phytosiderophores (e.g., mugineic acid) (McManus et al., 2018). Fe(III)–phytosiderophore complexes are formed at the mineral surfaces, transferred into the soil solution, and subsequently transported across the root plasma membrane (Ahmed & Holmström, 2014). Besides Fe, phytosiderophores also mobilize Zn, Mn, and Cu (Ahmed & Holmström, 2014). Root exudates have a major direct and indirect effect on the chemical reaction of metallic NPs and respective dissolved ions in the rhizosphere as well as on their absorption by plant roots.

2.2 Biogeochemical Processes in the Rhizosphere Influencing NP Transformation and Immobilization

Several recent reviews described the role of soil type and soil properties on the fate of NPs in soils and on their bioavailability for plants (Dimkpa, 2018; Cornelis et al., 2014; Rodrigues et al., 2016; Anderson et al., 2017; Layet et al., 2017). Soil pH, soil organic matter (SOM), clay, sesquioxides, ionic strength, cation exchange capacity, or redox potential governs aggregation and sorption/desorption, while redox processes of inorganic NPs in soil drive NP bioavailability either by adsorption onto the root epidermis or by absorption through the root apoplast or symplast (Layet et al., 2017). Over the last decade, a relevant effort was made to improve our analytical capacity to detect NPs in soil and solution phases. The physical–chemical processes that NPs will undergo as a response to soil conditions over time and how these will influence NP fate in soils are now better understood. Among them, we could cite homo- and hetero-aggregation, complexation, ion exchange, and electrostatic interactions, pH and redox reactions leading to precipitation or dissolution to ionic species and chemical speciation changes, changes in physical shape, surface coating by dissolved organic matter (DOM), or biomacromolecules (Dimkpa, 2018; Rodrigues et al., 2016; Rodrigues et al., 2020). Clearly, both the physical–chemical properties of the bulk soil and the localized biogeochemical conditions resulting from plant root exudates and microbial activity, such as those in the rhizosphere, determine the reaction of NPs in soil and their bioavailability for plants (McManus et al., 2018; Gao et al., 2017; Gao et al., 2018; Gao et al., 2019).

Current literature on the reaction of inorganic NPs in soil and their bioavailability to plants allows us to conclude the following (Dimkpa, 2018; Kopittke et al., 2019; Rodrigues et al., 2016; Anderson et al., 2017; Layet et al., 2017; Gao et al., 2019):

- The biogeochemistry and bioavailability mechanisms of NPs in soils are highly influenced by specific soil conditions/properties over time, including both short-term kinetics and long-term aging processes.
- In the bulk soil, and particularly in acidic soil, the pH will be the main driver of the short-term kinetic reactions and bioavailability of cationic elements, mainly through ion release resulting from oxidative dissolution; in this case, SOM can provide binding control of the solid-solution partition of dissolved ions and influence NP solubility in the bulk soil.
- Interactions of NPs and released ions with other cations in the solution phase of the rhizosphere zone will influence their root uptake due to both competitive binding and competitive absorption.
- Adsorption of inorganic anions can chemically alter the surface composition of NPs rendering them more available for plant uptake. For example, phosphate induces a change in the redox state of CeO_2 (from Ce(IV) to Ce(III)) causing the formation of more readily phytoavailable cerium phosphate (Singh et al., 2011).
- Soil salinity can increase NP retention in soil and reduce their bioavailability by increased aggregation and higher pore straining in soil (Cornelis et al., 2014).

- At alkaline pH conditions, such as calcareous soils (pH ≥ 8), aggregation processes will prevail, although plant uptake of both NPs and ionic phases may still occur; in this case, NP reactivity and bioavailability will be effective almost only at the rhizosphere, driven by i) protons released by roots and associated biogeochemical gradients at the root–soil interface as well as increase of the reducing capacity of the rhizodermal cells, as part of dicots Strategy I to take up Fe from soil; and ii) by complexation with LMWOAs and phytosiderophores released by plant roots as a response to nutrient deficiency; notably, elements such as Cu and Zn can compete with Fe at the Fe–phytosiderophore binding sites (as part of Fe uptake mechanism of Strategy II monocots).
- As NP doses in soil increase, complexation by chemical compounds released by plants and microbes at the rhizosphere (as a biological response to the presence of the NPs in the root soil interface) will be dominant, and will control their bioavailability in the rhizosphere (often increasing it); root exudation may be a response to the increase of the dose of NPs at the root rhizoplane and/or to an increase in metal cation uptake (McManus et al., 2018); for example, the release of Cu-complexing root exudates (LMWOAs such as citrate and malate) by wheat was reported as a response to CuO-NPs in the rhizosphere (McManus et al., 2018). Here, the exudates complexed with Cu, removing free Cu ions from solution driving the dissolution of the CuO-NPs forward.
- The plant microbiome, notably endophytic bacteria, or fungi at the endorhizosphere and microorganisms in the ectorhizosphere also secrete metabolites and ligands that further complex metal ions dissolved from NPs and further increase their solubility in the rhizosphere.

Nonetheless, the complexity and the dynamic nature of the reactions and interactions of NPs at the nanoparticle–root interface and of the underlying mechanisms at the plant physiological and molecular level still pose difficulties for a complete understanding of observed reactivities/bioactivities of NPs in the rhizosphere and for the characterization of nanospecific bioavailability effects on plants.

2.3 Reaching the Rhizoplane and Entering the Root

A fraction of the soil-applied NPs will reach the rhizoplane at the surface of plant roots. Plant roots are organs that allow uptake of water and (micro)nutrients from the soil. Environmental processes can prevent the NPs from reaching the root surface. Plants that undergo strong redox cycles along flooding seasons can, for instance, present an iron plaque formation at their surface. This iron plaque has been shown to strongly limit the uptake of CuO NP by rice (Peng et al., 2018). Other than chemistry changes due to water flooding, plant roots can release protons, amino acids, organic carbon, and CO_2, driving the rhizosphere biogeochemical conditions (as described above). These chemical changes at the root surface will be important drivers for the speciation of NPs, their association to the root surface, and the uptake of the metal species (McManus et al., 2018; Spielman-Sun et al., 2018). Viewing the importance of the chemical reaction and interactions taking place at the root surface, one could challenge the possible extrapolation between different matrix systems used to expose the plant to NPs through roots. For instance, a hydroponic system will prevent root anchoring. Their constant oxygenation through bubbling induces different redox and pH conditions, detaches the border cells from the root tips, and consequently modulates root exudation (Oburger et al., 2014). If system complexity needs to be decreased for experimental purposes, and if soil cannot be used for testing NP uptake and translocation in plants, it might be beneficial that scientific setups lean toward solid matrices more representative of a soil (e.g., sands or gels).

Once reaching the root surface, a fraction of the NPs can be absorbed in the roots. Morphological and physiological traits will be drivers for NP uptake. For instance, monocotyledons present fibrous root systems (higher surface area), while dicotyledons have a tap root system. This differential root architecture seems to influence NP uptake, and specific surface area is positively correlated with Ce uptake from CeO_2 NPs (Spielman-Sun et al., 2019). Furthermore, it is likely that NP uptake will follow the water flow driven by plant transpiration. Studies have shown a link between plant transpiration rate and NP root uptake (Spielman-Sun et al., 2019; Schwab et al., 2016), but this question remains overlooked. Furthermore, the correlation between root surface, water evapotranspiration, and NP uptake does not always hold for NP presenting a surface charge (either negative or positive) (Spielman-Sun et al., 2019). This is likely due to the electrostatic interactions between NP and the root surface and/or mucilage, which are strong enough to impair NP root uptake. Once reaching the rhizoplane, NP will interact with the root surface and the biomacromolecules exudated by the roots. The mucilage, described above, is exudated into the rhizosphere via the root cap (the border cells) and root hairs. It is rich in carboxyl groups, conferring an overall negative charge to the mucilage for rhizospherical pH. These NP–mucilage interactions have been shown to be an important driver regarding NP uptake limitation for NP presenting a positive surface charge (Avellan et al., 2017) across various plant species (Spielman-Sun et al., 2019).

The portion of NP that becomes mobile in the rhizosphere and that reaches the root cells' surface can either be adsorbed on the root surface or taken up in the root. The pathways of root uptake are highlighted in Fig. 2. There are several barriers NPs will have to cross before entering the plants through the roots: the cuticle made of waxes that covers young roots and emerging lateral roots (Berhin et al., 2019), and the cell walls of the hairs and/or the epidermis cells. Depending on the growth conditions, the root compartment, and the plant species, root cell walls can undergo suberization and/or lignification, making them—theoretically—highly impermeable (Schwab et al., 2016).

While hydrophilic NPs should not be able to directly cross the cuticle, recent work has described a higher root uptake of NP presenting a hydrophobic surface (Sharma et al., 2020). This suggests that the cuticle layers might not be as

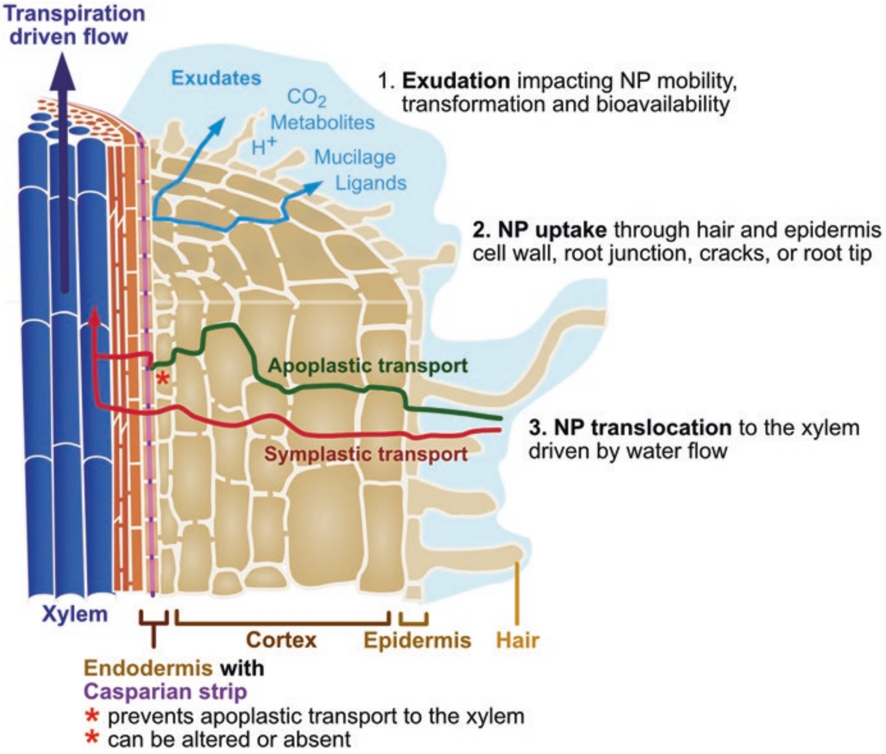


Fig. 2 Main barriers and bottlenecks for NP behavior at the root surface, their uptake and translocation to the plant vasculature. See Fig. 3 for more details regarding the cell compartments involved in apoplastic and symplastic translocation

impenetrable as what was previously hypothesized in the literature and that uptake depends on the NP coating, corona formation, and resulting surface properties. These processes are yet to be elucidated, and these routes of uptake deserve more attention. Several studies also observed NP accumulation where the mucilage is not too abundant, where the cuticle and the cell walls are thinner, or when cells are ripped. For instance, NPs have been shown to enter the roots through cracks at the root surface (“crack-entry” mode), at the primary root–lateral root junction areas (Lv et al., 2015), at the root tip where cell wall lignification is absent (Schwab et al., 2016; Avellan et al., 2017; Geisler-Lee et al., 2013), or through the cell wall of epidermis cells and root hair (Peng et al., 2018; Navarro et al., 2012).

Uptake of pristine NPs and/or their transformation products (i.e., ionic metal species) through the plant/root interface has thus been demonstrated multiple times. However, while research has highlighted some of the drivers for these mechanisms, the complex biological, environmental, and physical–chemical interplays that modulate NP uptakes are far from being predictable.

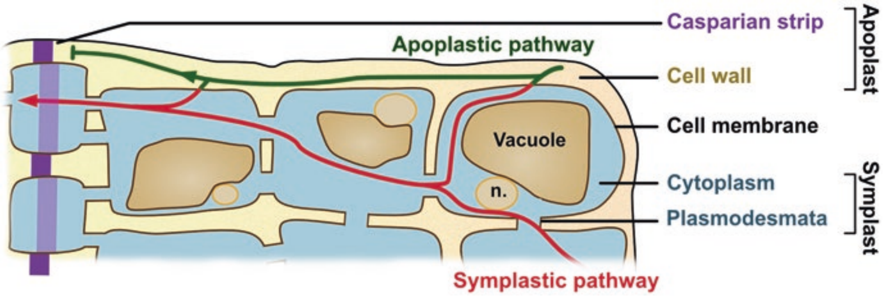


Fig. 3 Various pathways the NP can follow to translocate in roots, through the apoplast (extracellular continuum) or the symplast (intracellular continuum). The Casparian strip in the endodermis cell walls limits the translocation through the apoplast. (n. nucleus)

2.4 Moving to the Xylem and Translocating above Ground

After entering the roots, NP will be immobilized in the root tissues, or be mobile and enter the xylem. Before entering the xylem vessel and being transported to the above-ground tissues, NPs will cross several root barriers: the root surface (its cuticle and epidermis as described above), the cortex, the endodermis, and its Casparian strip (see Figs. 2 and 3). The Casparian strip of the endodermis is a layer of interstitial cell walls that are sealed by lipophilic lignin and suberin hydrocarbons between the cortex and the vasculature. This separation forces solutions to reach the xylem through symplastic routes. The endodermis and the Casparian strip should be the main bottleneck for NP transport to the shoots, as they present elongated and packed cells, with lignified cell walls.

Within the cortex, NPs will either follow an apoplastic or a symplastic pathway (Steudle & Peterson, 1998) (Fig. 3). As also described in more detail in the following section, the apoplast is the continuum of connected cell membranes and the symplast of cytosols connected through plasmodesmata. NPs and their aggregates have been observed in the root apoplastic space (Schwab et al., 2016) and symplastic space (Geisler-Lee et al., 2013; Sun et al., 2014; Li et al., 2019). The capacity of the NP to be mobile in the apoplast seems to be impacted by the NP surface charge. Cell walls present a negative charge, and NPs with positively charged groups at their surface have been shown to be less present in the apoplast than negatively charged NPs (Avellan et al., 2017; Li et al., 2019). Furthermore, endocytosis seems to be more efficient for negatively charged CeO_2 NPs (Li et al., 2019). This ease to reach the symplast could explain the higher translocation of negatively charged NPs in shoots observed in several studies (Spielman-Sun et al., 2019; Li et al., 2019; Spielman-Sun et al., 2017; Sun et al., 2020).

Numerous studies have shown translocation of NPs of various solubility, from the root to the above-ground tissue (leaves/fruits/grains) (Li et al., 2019; Spielman-Sun et al., 2017; Sun et al., 2020; Zhang et al., 2012; Ma et al., 2017; Zhao et al., 2015; Zhu et al., 2012; Wang et al., 2012; Raliya et al., 2015; Karas & McCully, 1973; Li et al., 2020). This translocation is size-dependent, as shown for Au in poplar trees (Zhai et al., 2014) or CeO_2 in cucumber plants (Zhang et al., 2011). Investigations have shown the enrichment of smaller TiO_2 NPs (<50 nm) in the roots and stem in comparison to the one present in the rhizosphere of wild plants growing in polluted soils (Belhaj Abdallah et al., 2020). It remains difficult to predict NP uptake based on their size. First, the lack of robust protocols makes it challenging to quantitatively measure the size distribution of NPs that had translocated *in planta,* even though tools are being developed (Laughton et al., 2020). Second, not only the NP size influences NP translocation, but, as discussed above, the NP surface properties will also play a major role. For instance, NPs of similar size but opposing charges exposed to plants roots with contrasting anatomy not only showed various translocation factors but also varying distribution in the leaf tissues they reached, accumulating in different compartments of the leaf veins and/or mesophyll (Spielman-Sun et al., 2019). Lastly, the size cutoff for NP uptake will likely vary depending on the plant internal morphology characteristics.

The endodermis and its Casparian strip (see Figs. 2 and 3) should strongly limit the translocation of micro-sized objects. However, recent work with microplastic has shown their uptake by wheat and lettuce roots and transportation to the shoots. The authors have shown a “crack-entry” mode, where the microplastic could enter the roots at sites of lateral root emergence and be transported through the apoplast (Li et al., 2020). Similarly, NPs could avoid the Casparian strip and the endodermis through the root apoplast on the root tip region, where it has not been formed yet, or at lateral root junction, where it can be disconnected. As the route of uptake and the pathways of translocation are still not fully elucidated, the size exclusion limit for NP uptake remains unclear.

Current research on NP uptake, translocation, and transport report the occurrence of events, often studied in regard to the NP physical–chemical properties. However, there is a lack of a mechanistic understanding on how these occur. While studies have demonstrated how NP properties can impact the mobility and interaction with plant structures, the influence of the plant morphology and physiology is largely unraveled. Furthermore, as discussed in more detail below, *in planta* transformations of NP have been reported, but the understanding of the underlying mechanisms remains limited. Multi-stressor, collaborative, and integrated studies are still needed to better comprehend NP fate *in planta.* Finally, this knowledge is critical to improving NP bioavailability when applied on soil to optimize and decrease the needed NP doses in order to guarantee their viability for agricultural purposes. Indeed, based on the current application rates, the economic and resource costs of most NPs applied through the soil remain very high for viable field applications in comparison to conventional practices (Hofmann et al., 2020). It remains unclear if root delivery will be widely adopted for high-cost NPs designed for targeted delivery to other plant compartments. Root application may still become an effective method for nano-sized fertilizer formulations that require delivery to the soil/root environment, but more research into fine tuning NP properties is needed to achieve a high bioavailability in the soil–rhizosphere–rhizoplane–plant continuum.

3 The Phylloplane

3.1 Above-Ground Application Strategies

Recent life-cycle analysis concluded that given the current embodied resources needed to synthesize practical NPs, targeted applications such as foliar treatments offer, to date, the best opportunity for crop over soil applications (Gilbertson et al., 2020). Indeed, foliar treatments present the advantage of being directly applied to the desired target and are not dependent on soil biogeochemistry. Foliar application and trunk injection are two methods for above-ground introduction compounds in plants. Trunk injection (including its multiple variations such as branch and root feeding) can be an effective way of delivering NPs to plants by directly introducing them into the vasculature, bypassing biological barriers, when compared with other methods (Su et al., 2020; Fischer et al., 2019). However, high particle count around the injecting point and high ionic strength in the sap can lead to NP aggregation to a certain extent, which can impact their transport, particularly of more reactive NPs. Furthermore, risks of damaging the plants through wounds are non-negligible. Injection/feeding methods also need relatively robust plant structures (e.g., thick trunk or sturdy branches), making them more suitable for perennial crops, such as trees and vines, or high-value crops such as berries. Leaf spraying (Prasad et al., 2012) and suspension dipping (Shen et al., 2020; Borgatta et al., 2018; Ma et al., 2020) seem more appropriate for crops planted as seedlings such as vegetables and herbaceous fruits crops.

Foliar application is an interesting delivery method when it comes to micronutrient-based metal NPs (Liu & Lal, 2015) and functional NPs (Wu et al., 2017). Also, it is relatively easy to apply on a large scale, making it an attractive method for field applications. It has been demonstrated that material attachment to the leaf surface and their uptake can be tuned through, for example, NP size and coating (Kah et al., 2019b; Avellan et al., 2019) or specific catechol-based modifications for improved adhesiveness (Liang et al., 2018; Jia et al., 2014). The main disadvantage in term of bioavailability/uptake are environmental factors such as rain or wind that can promote material run-off and the inherent biological barriers of the leaf as described below.

3.2 Leaf Barriers

The cuticle, epidermis, hydathodes, trichomes, and stomata are structures present on leaves that can influence nanoparticle foliar adhesion and uptake. The cuticle is a hydrophobic layer, covering the aerial epidermis of all terrestrial plants (Fig. 4). Functionally, the cuticle helps prevent moisture loss and generally serves as a barrier between the leaf’s internal structures and environmental stresses like temperature and ultraviolet radiation (Yeats & Rose, 2013). The epidermis is the outermost

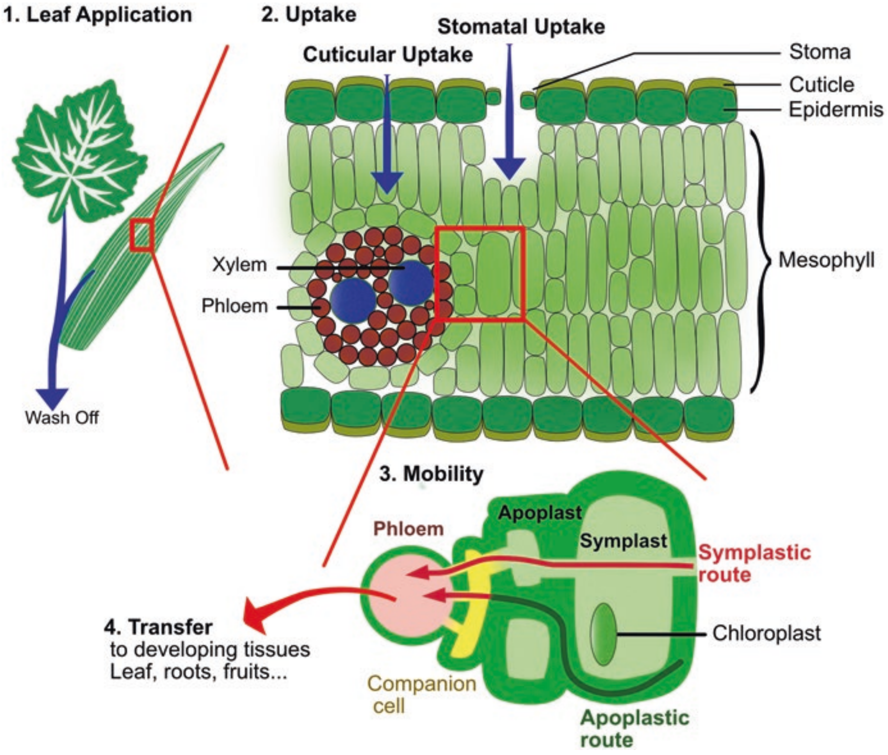


Fig. 4 Leaf cross section displaying key uptake and translocation pathways

layer of the leaf cell structure and serves as a protective barrier and interface for gas, water, and nutrient exchange (Javelle et al., 2011). In order to fulfill these two complex, and often competing, tasks, the epidermis can develop into more specialized cell types such as stomata and trichomes (Javelle et al., 2011). Stomata are pores on leaf and stem surfaces that regulate the exchange of gases, mainly water vapor and carbon dioxide, between the leaf and atmosphere (Hetherington & Woodward, 2003). Stomata have larger size exclusion limits than the cuticle, and their guard cells' cell walls have mechanisms that allow them to expand their pore sizes to larger than 20 nm, further facilitating hydrophilic nanoparticle uptake via the stomata (Eichert & Goldbach, 2008). Stomata density and aperture can vary in response to environmental factors like temperature, light intensity, and carbon dioxide concentrations (Hetherington & Woodward, 2003). Trichomes also play a role in leaf secretion, primarily serving to protect the plant from herbivorous insects, ultraviolet radiation, excessive transpiration, and freezing (Hülskamp, 2004; Mauricio & Rausher, 1997). Hydathodes allow for guttation or the release of apoplastic fluid from intercellular spaces to the outer leaf (Cerutti et al., 2019). Guttation occurs to prevent harmful water and xylem sap accumulation in the leaf during periods of low transpiration (Cerutti et al., 2019).

Drop deposition of nanoparticle solutions is mostly used to study nanoparticle–leaf interactions because this simulates nanoparticle spraying, which has the broadest agronomic potential. Before discussing nanoparticle uptake, adherence to the leaf surface must first be addressed. In general, smaller NPs have been found to adhere more to the leaf surface after the surface is washed (Avellan et al., 2019). Amphiphilic NPs have shown a higher adhesion to the leaf surface than hydrophilic NPs, likely due to the hydrophobic interactions between the amphiphilic particle and the lipophilic cuticle (Avellan et al., 2019). Furthermore, protein coatings have also been shown to target leaf stomata and trichomes, as demonstrated by Spielman-Sun et al. (2020) with the LM6-M protein antibody used to target gold NPs due to its affinity for α-1,5-arabinan, a chemical moiety found in stomata guard cells (Spielman-Sun et al., 2020).

3.3 Entering the Leaf and Interacting with Mesophyll Cells

Nano–bio interactions at the leaf surface will influence nanoparticle uptake, translocation, and potential for aggregation within plant tissues. The above-cited leaf structures all represent potential deposition surfaces following a foliar spray, and a possible path of entrance into the leaves. Although research repported the association of metals or NPs with trichomes' head and base after leaf deposition (Avellan et al., 2019; Spielman-Sun et al., 2020; Li et al., 2018), its role as a surface uptake pathway remains unclear. Studies that specifically looked at trichomes' density impact on ZnO NP uptake in soybean and tomato leaves found that trichomes did not impact NP absorption (Li et al., 2018). Regarding hydathodes, description has been done of NP accumulation in the hydathode apertures (Hong et al., 2016; Bombo et al., 2019), but the role of these structures on NP uptake is yet to be demonstrated.

There are two highlighted pathways for NPs to enter the leaf mesophyll: cuticle penetration and stomata infiltration (Fig. 4). Historically, and because it is the structure that can be observed the most easily, stomatal pathway is the route that has been investigated the most. Numerous studies have shown the colocalization of NPs with guard cells and/or the accumulation of NPs in the stomatal cavity (Avellan et al., 2019; Bombo et al., 2019; Eichert et al., 2008; Schreck et al., 2012; Larue et al., 2014a; Xiong et al., 2017; Kwak et al., 2017; Zhang et al., 2020). Demonstration of cuticle penetration has also been done, but mechanisms remain unclear. Studies have hypothesized cuticle penetration through (small, <2 nm) hydrophilic pores (Eichert et al., 2008), cuticle disruption and/or pore formation (Zhang et al., 2020), and direct crossing and/or crossing through the joints of the cuticular tissues (Avellan et al., 2019). The later mechanisms could explain the observed NP accumulation in the anticlinal wall of the epidermis cells on an area devoid of stomata (Avellan et al., 2019; Zhang et al., 2020; Nadiminti et al., 2013), and uptake might be possible through one or both routes, which can be dependent on factors such as plant leaf anatomy and the NP properties. For example, monocotyledon plants such as maize (*Zea mays* L.) have been shown to take up hydrophilic NPs mainly through the stomatal pathway, while dicotyledons plants like cotton (*Gossypium hirsutum L.*), that present less hydrophobic cuticles, could take them up through both stomatal and cuticular pathways (Zhang et al., 2020; Hu et al., 2020). ZnO NPs (15–40 nm) have been observed entering the leaf through the stomata, cuticle, and hydathode (Singh et al., 2018). Silica NPs (50 nm) in *A. thaliana* were found to only penetrate the leaf through the stomata and distribute within the large extracellular air spaces of the spongy mesophyll without penetrating the cell walls (El-shetehy et al., 2020). Slightly hydrophobic coating (PVP) was found to enhance NP penetration through wheat (*Triticum aestivum*) cuticle, compared to a more hydrophilic citrate coating (Avellan et al., 2019). Surfactants that can decrease water surface tension and/or dissolve the leaf cuticle also promote nanoparticle penetration through leaf surface (Zhang et al., 2020; Hu et al., 2020). The route uptake of NPs through the leaf seems to be influenced by morphological, physiological, environmental, and physical–chemical factors. The cuticle uptake pathway is still overlooked despite the cuticle being the major surface of the leaf compared to other structures. In order to improve nano-enabeled agrochemicals designed for foliar applications, more research is needed to further elucidate NP properties and cuticle surface parameters and structural organization affecting cuticular adhesion and uptake.

After getting through the leaf surface, NPs will enter the mesophyll. There, NPs can interact with mesophyll cells differently, depending on their size, charge, and coating chemistry (Lew et al., 2018). Some NP will be mobile in the mesophyll, where they will translocate through apoplastic and/or symplastic pathways. In apoplastic transport, NPs move through the apoplast, a highly flexible continuum of extracellular matrix consisting of a cellulose/hemicellulose network, pectin (polysaccharide) and proteins, filled with apoplast fluid and air (O'Leary et al., 2016). NP size is likely to impact their mobility potential within the apoplast due to the relatively reduced pore size of the cellulose/hemicellulose networks, which is estimated to be in the 5–20 nm range, although some flexibility is expected. Surface charge may play a crucial role in NP mobility as the cell walls are mainly negatively charged due to free carboxyl groups from the pectin, so the movement of positively charged NPs is expected to be limited. While studies on the effects of NP surface charge are scarce, a recent study found that positively charged NPs accumulate significantly more in the extracellular spaces of dicots compared to negatively charged NPs (Hu et al., 2020). Extensive studies involving ionic species, however, have shown that cations substantially accumulated in the apoplastic space, which supports the hypothesis that indeed positively charged NPs may have difficulties translocating through the apoplast.

For symplastic transport, NPs must first be internalized from the apoplast into the cell cytosol. Direct passive diffusion through the phospholipid bilayer and active transport through endocytosis are two mechanisms proposed for nanoparticle uptake through the cell membrane. Surface charge seems to be the main determinant on which type of active transport is induced (clathrin-dependent or -independent pathways) (Onelli et al., 2008), as protoplasts have been shown to internalize particles up to 1 μm in size, leading to distinct mechanisms of the NP management by the cell, e.g., internalization, degradation, or recycling pathways. Positively charged AuNPs were delivered to tubular vesicles and vacuoles, while negatively charged AuNPs were transported to inner vesicles (Onelli et al., 2008). Understanding the parameters influencing the movement of NPs through one or the other pathway is still needed to predict NP mobility in the mesophyll association with cell organelles, NP bioavailability, and phloem loading, allowing larger distance translocation to other sinks.

Nanoparticle physicochemical properties such as hydrophobicity, shape, size, and surface charge have been shown to influence passive diffusion. Models are attempting to describe the passive crossing of lipid membranes. This could help predict the ease for NPs to cross the protoplast membrane (mainly made of phospholipids) and enter the symplast and further the chloroplast membrane (mainly made of glycerolipids), thus potentially modifying photosynthesis processes (Wu et al., 2017). This passive lipid membrane crossing seems driven by the density of nanoparticle charges, as proposed by the lipid exchange envelope penetration (LEEP) model (Lew et al., 2018). When interacting with the membranes, NPs can induce a drop of the transmembrane potential across the lipid layers. This creates a driving force between the lipid bilayer and the NPs, softening the lipid bilayer and allowing the NP to cross it (Lew et al., 2018). This process has been experimentally investigated to quantify the charge and zeta potential leading to sufficient charge density for this phenomenon to take place. NPs with high net zeta potential and small sizes can thus enter into plant protoplasts and further chloroplasts if the zeta potential remains high enough after crossing the first lipid layer (Lew et al., 2018; Wong et al., 2016). More studies are needed to validate this model *in planta* and across a higher number of NP core composition, shape, and surface properties.

As NPs internalize into the cytosol, they can also be directed toward specific cell types or organelles. This targeted delivery can be mediated by modulating NPs' surface charge and size. NPs with a hydrodynamic size of 6–18 nm showed above-average colocalization to leaf guard cells in both monocots and dicots when compared to larger hydrodynamic sizes, while NPs smaller than 6 nm and 12 nm, in monocots and dicots, respectively, showed above-average delivery to chloroplasts in the mesophyll (Hu et al., 2020). A positive surface charge resulted in a significantly higher association with chloroplasts in both monocots and dicots (Hu et al., 2020), though high zeta potentials, either positive or negative, have shown to favor adsorption and uptake to the chloroplast (Wu et al., 2017; Spielman-Sun et al., 2020; Hu et al., 2020). This could be explained by the LEEP model described above, where higher net charge densities could allow for crossing several lipid bilayers, thus entering the protoplast and furthering the chloroplast. Finally, nanoparticle surface functionalization with targeting molecules also affects their affinity for cell organelles. The oligonucleotide of single-stranded DNA with the sequence $(AT)_{15}$ functionalized single-walled carbon nanotubes (SWNTs) and chitosan-SWNTs can assemble with the chloroplast lipid bilayer, while PVA or lipid functionalized SWNTs do not associate with plant chloroplast (Giraldo et al., 2014; Wu et al., 2020). Quantum dots (QDs) functionalized with Rubisco small subunit (RbcS) targeting peptide doubled QD colocalization with chloroplast compared to unfunctionalized QD (Santana et al., 2020). These studies underline the complexity of nanoparticle affinity to specific plant organelles, relying on an interplay between multiple factors (size, charge density, surface chemistry, and plant anatomy/species) and not an individual nanoparticle physicochemical property (Lew et al., 2018; Wong et al., 2016; Ma et al., 2010).

Once internalized into the symplast, the NPs that did not associate with the organelles can move intercellularly through the plasmodesmata (Zhai et al., 2014). Discussion on the size exclusion limit (SEL) of these channels is still ongoing, and the reader is directed to a recent review that details their structure and multiple studies reporting on factors affecting both SEL and NP mobility on plasmodesmata (Schwab et al., 2016). Current understanding thus leans toward a more fluid and dynamic model as opposed to a rigid one, underlining the flexibility of the SEL for NP mobility in these channels. For instance, 15-nm AuNP (Zhai et al., 2014), 20-nm AgNP (Ma et al., 2010), and TiO_2 (Larue et al., 2012) have been shown to transport between plant cells through plasmodesmata, which is larger than the basal SEL (5–10 nm) (Lucas & Lee, 2004). As metal-based NPs cannot undergo conformational changes, it is suggested that dilation by NPs or even NP-induced structural changes to the plasmodesmata (Larue et al., 2012) allow NPs to cross the plasmodesmata. Thus, tuning the NPs' size and surface properties should allow for specific targeting (apoplast, symplast, organelles) and mobility to freely reach the phloem or accumulate in the leaf mesophyll.

3.4 Reaching and Loading the Phloem

The pathway of nanoparticle phloem loading after foliar application remains unclear, in part, due to limited axial resolution of current imaging techniques that prevents imaging of the space between leaf surface and phloem vasculature. An imaging approach with better axial resolution and high sensitivity for nanoparticle elements is needed to resolve the nanoparticle phloem loading pathway, e.g., synchrotron-based nano-XRF. There is a general agreement that water, nutrients, and nonessential metal complexes preferentially translocate through the apoplast, particularly due to its nonselective nature, as opposed to the symplastic route, as described above (Fig. 3). Reduced size limitations (<36–50 nm) may favor symplastic transport (Raliya et al., 2016). However, to date, no definitive preference between apoplastic or symplastic transport for nanoparticle mobility is known. It is important to emphasize that several studies did show the translocation of metal from foliarly deposited NP into other developing plant tissues, indirectly demonstrating that phloem loading occurs (Avellan et al., 2019). Nevertheless, regardless of the mesophyll translocation pathway, in order to reach the phloem, NPs need to enter the phloem cells before systemic transport (Jensen et al., 2016). Plant phloem is responsible for delivering photosynthetic products, including sugar and amino acids from photosynthetic machineries (mature leaves) to sugar sinks like root, younger shoots, or fruits (Jensen et al., 2016). Since phloem sap generally flows out of leaves, systemic transport of foliar-applied NPs in plants is normally considered to be through phloem loading and transport (Avellan et al., 2019; Zhang et al., 2020). However, the possible nanoparticle phloem loading process is still not understood. No study so far has reported the interactions between NPs and phloem cells. The plant processes for sugar phloem loading have been well studied, and the transport mechanism of sugar generally involved three strategies that could potentially enable NPs loading (Jensen et al., 2016). Specifically, these three strategies for sugar phloem loading are apoplasmic loading (active apoplasmic), polymer trapping (active symplasmic), and diffusion (passive symplastic) (Jensen et al., 2016). In the apoplasmic loading, sugar is taken up into phloem by a sucrose transporter protein, which is fueled by the activity of the plant proton pump that hydrolyzes adenosine triphosphate (ATP) (Kühn et al., 1997). In plants that load their phloem through polymer trapping, small sugar molecules like sucrose flow into phloem companion cells through plasmodesmata and are subsequently converted into larger sugars such as raffinose, stachyose, and verbascose (Jensen et al., 2016). The larger sugar can then move into the phloem sieve element via the plasmodesmata-sieve pore contact. In passive symplasmic loading, sugar diffuses from mesophyll into the sieve elements through plasmodesmata in the companion cell wall (Turgeon & Gowan, 1990). Passive loading requires a sugar concentration gradient between phloem and mesophyll, with no sugar accumulation in phloem (Jensen et al., 2016). NPs loaded into phloem will thus first need to pass through plasmodesmata, which have a size cutoff that requires NPs to be smaller than a certain size, in the nanometer range (Zhai et al., 2014). This size cutoff is, however, in contradiction with studies that detected larger NP translocation from exposed leaves to downward compartments, as described below. Future studies are needed to better understand the nanoparticle phloem loading process and the major mechanism associated.

4 *In Planta* Translocation and Transport

Nanoparticle fate and transport within the plant is a key issue of concern, especially when considering the agronomic application of NPs on edible plants intended for animal or human consumption. Several studies looked at the species preferentially taken up, salt, chelated ions, or nanoparticles, and the transformation resulting from the uptake and the translocation. Doolette et al. (2020) studied zinc oxide NP translocation in comparison to traditional zinc formulation (ZnEDTA) in wheat after foliar application. It was found that zinc oxide NPs were translocated less to new plant tissues and grains than ZnEDTA in zinc-stressed growth conditions (Doolette et al., 2020). They also observed that a foliar application concentration of 75 mg Zn/L versus 7.5 and 750 mg Zn/L had the highest rate of translocation, likely due to zinc toxicity at high concentrations and insufficient application amount at small concentrations (Doolette et al., 2020). The differential uptake between salts, chelated species, and NPs will likely be influenced by the plant species (and its leaf surface properties) and the type of metal involved.

Publications have highlighted the transport of the metal taken up from NPs deposited on leaves to nonexposed plant compartments, as in the following:

- Flowers: from cucumbers leaves dosed with CeO_2 (Hong et al., 2014).
- Fruits: from cucumbers dosed with CeO_2 (Hong et al., 2016).
- Seeds: from rice leaves exposed to Se (Hussain et al., 2020).
- Nonexposed shoots: from rice leaves exposed to Fe_2O_3 (Hussain et al., 2020), different trees to Ag (Su et al., 2020; Cocozza et al., 2019), wheat to Au (Avellan et al., 2019), tomato to TiO_2 (Raliya et al., 2015) or ZnO (Raliya et al., 2015), basil to $Cu(OH)_2$ (Tan et al., 2018).
- Roots: from TiO_2 deposited on tomato (Raliya et al., 2015) or maize leaves (Lian et al., 2020), ZnO on tomato (Raliya et al., 2015), Au on wheat (Avellan et al., 2019) or watermelon (Raliya et al., 2016), and CeO_2 on cucumber (Hong et al., 2016; Hong et al., 2014), but also Ag injected into citrus trees (Su et al., 2020).
- Rhizosphere soil of lettuce foliarly exposed to $Cu(OH)_2$ (Zhao et al., 2016) and of wheat to Au (Avellan et al., 2019).

These publications tracking metal movement after foliar exposure remain scarce. The exudation in the rhizosphere is even more rarely investigated. However, this approach could represent a way of delivering nutrients or pesticides directly to plant roots and their surrounding soil, increasing efficiency over nontargeted methods like soil drenching.

Furthermore, investigation of whether the metal deposited on leaves and translocated in different plant compartments as the original NP or a transformed species (i.e., dissolved and/or re-precipitated metal species) is rarely reported. Biotransformation of engineered NPs such as SiO_2, TiO_2, Zn/ZnO, Fe/FeOx, Cu/CuO/$Cu(OH)_2$, CeO_2 in plants has been studied in the last decade (Spielman-Sun et al., 2017; Lv et al., 2019). The majority of these studies have focused on root uptake and subsequent transportation and transformation of NPs *in planta* (Spielman-Sun et al., 2018; Lv et al., 2019). The relatively labile metal/metal oxide NPs can undergo dissolution, uptake, and (re)precipitation in plants after being taken up. CeO_2 and ZnO NPs were reported to attach to plant root surface, dissolve by root exudates like organic acids, enter plant root in ion form, and re-precipitate in plants as metal phosphate or carboxylate (Lv et al., 2015; Zhang et al., 2012). Some metals also undergo changes in valence state after being taken up and transported through plant roots (Spielman-Sun et al., 2019; Spielman-Sun et al., 2017). Reports on NP transformation after leaf uptake remain scarce, but we can speculate about the potential transformations that may occur according to the chemical composition of plant micro-environments where NPs could go through after foliar uptake, including plant apoplast, cytosol, phloem, and xylem. Some articles have hypothesized the formation of a protein corona as a facilitation of NP transport from the leaves to the root through the phloem (Avellan et al., 2019). Some authors did measure an organic coating around internalized TiO_2 after foliar exposure (Larue et al., 2014b). The formation of a protein corona on NPs that enter plants remains a significant knowledge gap that must be addressed to be able to understand, predict, and tune the translocation of NPs in plants.

After getting through the plant root or leaves surface (cuticle and epidermis) and being taken up by plant leaves, NPs can be present in either apoplast or symplast continuums, depending on their size and charge (Hu et al., 2020; Lew et al., 2018). The plant apoplast and protoplast both contain sugar, cations (Mg^{2+}, Na^{+}, K^{+}, Ca^{2+}, etc.), anions (Cl^{-}, PO_4^{3-}, etc.), amino acids, and proteins. The pH in cytosols is normally neutral or slightly basic (pH ~ 7–7.5), while the pH in apoplast can be slightly acidic (pH ~ 5–6) (Zhang et al., 2020; O'Leary et al., 2016). Metal oxide NPs can dissolve under acidic pH (Dahle et al., 2015; Zhang et al., 2010); therefore, NPs that are present in apoplast are more likely to dissolve than particles in protoplast. After entering the plant's main vasculatures, NPs can be transported between phloem and xylem. The pH in plant xylem and phloem is also vastly different. pH in xylem is below 6.0 under normal conditions (Wilkinson et al., 1998; Gollan et al., 1992), while the pH in phloem is above 7.0 (Zhang et al., 2020; Jensen et al., 2016). Therefore, the pH condition in xylem could promote nanoparticle dissolution and transformation, while NPs could be relatively stable in phloem given the slightly basic pH conditions at the phloem sap. Other than pH, the major amino acids in phloem such as glutamine and glutamates could also act as ligands that potentially react with NPs (Turgeon & Gowan, 1990; Winter et al., 1992). Nanoparticle transformation post foliar applications has not been well studied, and in situ nanoparticle characterization is needed for the future studies to resolve nanoparticle transformation while being delivered in plants.

5 Conclusion and Future Perspectives

This chapter summarizes the current knowledge regarding the processes, chemical or bio-transformations, and biological barriers that affect the uptake, transport, and bioavailability of inorganic nanoparticles at the soil–plant–atmosphere interfaces. Uptake of nanoparticles at the soil–plant interface is heavily influenced by soil type and properties, encompassing not only the bulk soil environment, but also the biogeochemical conditions created by plant exudates and microbial activity in the rhizosphere. Studies looking into NP root uptake often utilize simpler matrix systems to study NP uptake (hydroponic systems, sand, gels), which partially disregard the complexity of NP transformation processes in soil. Although this provides valuable insight into how specific physical–chemical properties such as surface charge, size, or shape influence NP root uptake, it does not take into account the highly complex and dynamic nature of the reactions and interactions of NPs at the soil–root interface that can eventually alter their properties and result in NP entrapment or root adsorption. Studies have demonstrated the potential to target specific plant organs by tuning NP physical–chemical properties. However, the interplays between the ecto- and endo-rhizosphere microbiome, the plant responses, and the NPs' fate *in planta* remain overlooked. While translocation of NPs inside the plant seems to be modulated by plant morphology and physiology, future studies on the matter, as well as in planta transformations, are required to further understand the fate of NP upon root uptake. Finally, additional work is needed to either increase NPs' efficacy, reduce their cost, or improve strategies for them to reach the root target. As of now, the use of NPs for targeted plant delivery of fertilizers in soil seems to remain economically unviable for field applications when competing with current conventional fertilization methods (Gilbertson et al., 2020). By contrast, foliar application and seed coating with NPs seem viable strategies to deliver genetic material, micronutrients, or AIs for plant protection, which could be a significant improvement for more sustainable agricultural practices over conventional alternatives (Hofmann et al., 2020; Gilbertson et al., 2020).

Research regarding foliar-applied NPs is more recent. In this case, application is performed directly to the plant, and NPs are not under the effects of exogenous factors such as soil processes and conditions (root application). It thus presents a higher potential regarding improvement of NPs' bioavailability. Indeed, NP foliar application can achieve significantly improved results compared to their conventional analogs, at competitive resource consumption and costs. This makes foliar application a good candidate for targeted delivery of NPs to specific plant compartments or organelles in view of efficiently augmenting specific plant physiological processes. However, room for improvement is vast, and, similarly to NP root uptake, there are several key research questions that remain unanswered. Significant progress is being made on the establishing mechanisms underlying leaf NP uptake and translocation to the phloem. For example, it has been demonstrated that uptake can occur through the leaf cuticle as opposed to exclusively by stomata infiltration. NP affinity and adherence to leaf surfaces are beginning to be established in the literature with factors such as NP size, amphiphilicity, and charge that appear to be critical factors for NPs' leaf adhesion. However, the interplays between NP properties, environmental pressures, plant morphology, and physiology remain overlooked. Furthermore, most of the studies have been focusing on crop plants, while research on nano-enabled fertilization and protection on trees remains scarce.

The fate of NPs *in planta* after their leaf or root uptake remains poorly understood. Demonstration has been done that both apoplastic and symplastic transport could take place, yet the factors influencing one or the other routes are unknown. While active works start to unravel the NP properties allowing to cross lipid layers of various composition, our understanding of the capacity of NPs to cross cell walls or to move through (rather small) plasmodesmata is still poor. Further, *in planta* transformation has been demonstrated, but the mechanisms associated remain unknown. Finally, while organic coating (bio- and eco-corona) had been hypothesized to impact NP mobility and transport, this has been, to our knowledge, barely addressed.

Not only it is necessary to understand the multiple nano–bio interactions and mechanisms of NP uptake and *in planta* events, but there is also a need for quantifiable, comparable dataset to be built, considering NP properties, plant morphology, and physiological responses, so that accurate models can be drawn. As of now, it remains nonpossible to predict the fate of NPs in contact with various plant species and interfaces. There is also an urgent need for data and scaling-up experimentation in field conditions to assess the efficiency of not only different types of NPs but also of these methods (foliar vs. root) under a wide variety of scenarios. Integrated and comparative studies, across multiple plant species, will be required to better comprehend the effects of NP application in terms of bioavailability and impacts regarding crop yields, nutritious value, and soil biodiversity and health, while undergoing biotic and abiotic stresses. These will help determine which type of method and NP (or NP combinations) is better suited to deal with specific issues. Collaboration is an important aspect to integrate into these studies. Several levels of knowledge are required, from the soil geochemistry to the plant–microbiological relationships; the molecular and physiological plant processes and the environmental and climatic stresses, along with the associated risks, will be required for a complete analysis and corroboration of the efficiency, safety, and viability of NP usage in agriculture.

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Plant Biostimulation with Nanomaterials: A Physiological and Molecular Standpoint

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Abstract Due to the physicochemical characteristics derived from having at least one dimension <100 nm, nanomaterials are very reactive from a biological perspective. Concentration, surface free energy, charges, roughness, porosity, and functional groups of the coating or corona, among other properties, determine the nanomaterial's impact on organisms. The impact is variable, from biostimulation to toxicity, depending on the plant species and the route of application or entry of the nanomaterial into the plant. This chapter presents an overview of knowledge about the physiology and molecular biology of plants in response to synthetic nanomaterials. It begins with an introduction that indicates the framework and objectives and then continues by briefly presenting the pathways of entry of nanomaterials to ecosystems due to contamination or intentional application. Subsequently, the nanomaterial's interactions in the plant interfaces (root, leaves, stems, fruits in the epidermis, stomata, etc.) are reviewed. Next, the entry mechanisms to the apoplast and the cytoplasm, as well as cell compartmentalization and transport, are discussed. In each of the previous sections, the plant's physiological and molecular responses are described.

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1 Introduction

Food production represents a significant source of environmental impact. The growing human population, the greater life expectancy, and, in general, the higher standard of living of the population translates each year into growing needs for products obtained from agriculture, livestock, and forestry. The population projection of 9.6–12.3 × 10^9 people for the year 2100 (Gerland et al., 2014), in the complicated context of climate change that is expected to modify the distribution of precipitation, atmospheric humidity, and temperatures, represents a monumental multifaceted challenge (Mukherjee et al., 2018; Arora et al., 2018; Tong & Ebi, 2019). Until now, the growing need for food, fiber, and metabolites such as pigments and biofuels has been solved with the tools generated during the Green Revolution, which prevented potential famine in the second half of the twentieth century (Evans & Lawson, 2020). These tools, such as improved varieties, fertilizers, pesticides, and intense mechanization, seem to be reaching a limit of efficiency, in the sense that their extensive application for a larger world population represents an environmental impact that reaches unacceptable levels of contamination and degradation of soil, water, and natural ecosystems (Arora et al., 2018). The solution to the above issues requires social, cultural, ecological, economic, and technical considerations that must be applied integrally since none can function effectively on its own.

Solving the above challenge, in addition to the forced adjustments in the lifestyle and diet of the human population (Hurni et al., 2015), requires urgent advances and the application of techniques that, on the one hand, increase the efficiency in the use of inputs and energy used in agricultural, livestock, and forestry activities and that, on the other hand, substantially reduce the ecological impact of said activities (Evans & Lawson, 2020). An example of the above would be those techniques that increase agricultural or forestry productivity without changing the use of a larger surface area of land or applying fewer amounts of water, fertilizers, or pesticides.

Among the set of techniques that can be applied to improve the efficiency of inputs and energy use in agricultural, livestock, and forestry activities are those related to nanotechnology. Nanotechnology is the set of techniques to hold the advantage of the physicochemical characteristics of materials, called nanomaterials (NMs), which arise when they have dimensions in the range of 0.4–100 nm. This 0.4–100-nm range is simply an arbitrary formal agreement to delineate boundaries between materials since the characteristic properties of NMs can be observed as a continuum in dimensions (d) between NMs and micrometric materials $1 \text{ nm} < d < 1000 \text{ nm}$ (Miernicki et al., 2019).

The NMs useful for food production are multiple and varied; they are derived from metals and their oxides, from semimetals such as nanosilicon and nanoselenium, from inorganic materials such as nanoclays, from carbon materials such as graphene, and organic compounds such as nanochitosan, among others. The applications refer to their use as nanofertilizers, nanocarriers of fertilizers, nanopesticides, nanobiostimulants, nanocarriers of pesticides, regulators and other biomolecules, and nanosensors (Vázquez-Núñez et al., 2018; He et al., 2019; Medina-Pérez et al., 2019).

This chapter refers to the use of NMs as biostimulant compounds. The ability of NMs to act as biostimulants is related to several physicochemical properties of the NM. Still, it depends significantly on the NM's concentration in the medium where the cells are found. The response to concentration is adjusted to a biphasic or hormesis response (Agathokleous et al., 2019).

The biostimulant capacity of NMs results from a large amount of surface free energy (and a consequential reactivity) as an outcome of their high surface:volume ratio (Juárez-Maldonado et al., 2019). But it is also the result of other properties such as shape, aspect ratio, hydrophobicity and hydrophilicity, and the composition of the core of the material itself and the composition of the corona (Nel et al., 2009; Chowdhury et al., 2020).

Biostimulation of plant cells is thought to be the result of a two-phase process. The first phase occurs through interfacial interactions between NMs and their corona with cell walls and membranes. These interactions depend on the surface free energy, the interactions between surface charges, and the hydrophobic and hydrophilic interactions between the surfaces. The second phase results from the chemical properties of the corona and the NM core and occurs both in the apoplast and inside the cell when the functional groups of the corona or the core of NM, or the ions released from the NM's core induce modifications in the behavior or functionality in the integral proteins of the cell wall and membrane, or the internal membrane systems or the organelles (Juárez-Maldonado et al., 2021).

2 Nanomaterials in Ecosystems

In natural systems, the existence of NMs is a common reality. NMs represent a form of matter in a certain dimensional range defined arbitrarily from 0.4 to 100 nm, which presents characteristic properties that differ from those observed in other dimensional ranges smaller or larger than that spectrum of magnitudes. The occurrence of nano-dimensional structures in abiotic and biotic systems has been well documented; examples are viruses, ferritins, exosomes, and magnetosomes (Stanley, 2014). In the same way, many natural phenomena such as volcanism, fires, weathering, and various mechanical and chemical interactions can transform materials of lower-dimensional magnitudes (such as ions) or larger (such as micrometric materials) into nanostructures (Akaighe et al., 2011; Tepe & Bau, 2014; Hochella et al., 2019). Therefore, the presence of NMs in nature is not a novelty. In fact, they are considered dynamic and important actors at various scales (from atomic to planetary) of terrestrial evolution. However, in addition to the complex series of transformations related to NMs in nature (aggregation, corona formation, chemical alteration, biological assimilation, dissolution, evaporation, shape change, migration between ecosystem's phases), human activities have significantly modified the presence of NMs both in the amount that is released year after year in nature and in the diversity of NMs that reach ecosystems (Hochella et al., 2019).

In recent decades, the scale of manufacturing NMs with industrial applications has grown substantially. To note some examples, although precise data are not available, it is estimated that each year about 5500 tons of SiO_2, 3000 tons of TiO_2, 550 tons of ZnO, 300 tons of carbon nanotubes, and 55 tons of NMs of Ag, FeO_x, AlO_x, and CeO_x are produced (Piccinno et al., 2012). Other sources indicate the production of 55 to 1,500,000 tons per year of SiO_2 NMs, 5.5 to 100,000 tons per year of CeO_2, and 5.5 to 550 tons per year of Ag NMs (Giese et al., 2018). These NMs, used in the biomedical, chemical, manufacturing, and food industries, among others, can be released into the atmosphere, water, or soil through emissions from industries; another alternative is through garbage or by-products that reach the soil or water directly, or are recycled, incinerated or used in biosolids for use in landfills or soil amending material once the useful life of the product containing the NMs ends (Lead et al., 2018). Until now, there is no precise information about the volume of NMs discharged to the atmosphere, water and soils, and sediments. Based on the results of their mathematical model (Giese et al., 2018), the discharge of about 17 tons per year of Ag NMs, 1090 tons per year of CeO_2, and 58,000 tons per year SiO_2 is estimated. TiO_2, ZnO, and Ag are probably the NMs most likely to enter soils in large quantities because of the application of biosolids (Lead et al., 2018).

Another type of NMs, those used in agricultural and livestock activities, can be incorporated as pollutants into ecosystems due to the degradation or disuse of the material that contains them or when used in the treatment of water or recovery of contaminated soils. This type of unintended contamination is analogous to that which occurs with the NMs for industrial use described above. One example of this type of contamination is that which occurs when agroplastics are degraded by abiotic weathering or by the activity of the soil or water microbiome, generating micro and nanoplastics that move between the different components of ecosystems, including through the trophic chain (Fig. 1) (Guo et al., 2020).

Another way NMs designed for agriculture or livestock can be incorporated into ecosystems or agroecosystems is by mobilization after they are intentionally used as nanofertilizers or nanopesticides applied to soils, substrates, irrigation water, and plants (González-Morales et al., 2020). Other NMs with potential agricultural and livestock use, such as nanosensors, molecular vehicles for the transport of DNA or RNA and other biomolecules, and materials with nanobionic application to increase the metabolic capacities of plants, do not seem to be an important source of contamination taking into account that its use involves very localized applications and in minimal quantities (Omar et al., 2019).

Whether the incorporation of NMs is intentional or not, the result is the contact and interaction of NMs with biotic and abiotic components of ecosystems, including natural toxins and synthetic pollutants such as pesticides and hydrocarbons with which they can interact synergistically. The interaction of NMs with the various

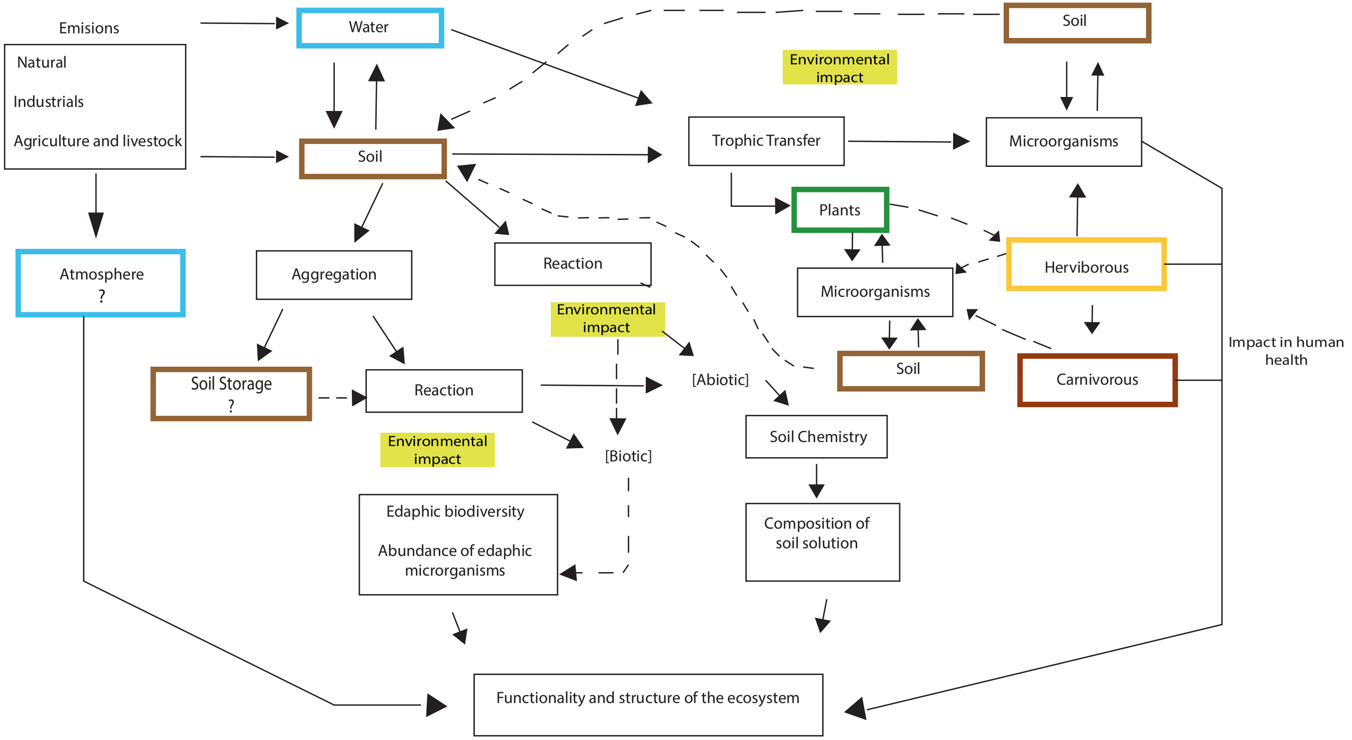

Fig. 1 Mobilization of NMs between different compartments of ecosystems from industrial, agricultural, livestock, and natural emissions. Figure from Morales-Díaz et al. (2017)

media in which they can move (water, soil, living organisms) causes changes in the composition and identity of NM's core and the NM's corona (Uddin et al., 2020). These NMs' corona changes have an unpredictable impact on their stability, mobilization capacity, and bioavailability. Depending on the environmental context and the type of NM in question, exposure to the environment may increase the NM's potential toxicity or decrease it (Nasser et al., 2020). Examples of the interaction of NMs with soil colloids and with dissolved organic matter illustrate this last point (Fig. 2) (González-Morales et al., 2020).

In addition to the corona changes, another situation that makes the prediction of the trajectory and environmental impact of NMs complicated is the interaction with environmental toxins or synthetic pollutants. The interactions between NMs and pollutants seem to be mainly physicochemical, with the adsorption process predominating, modifying both the original properties of NM and the pollutant molecule. Among the most studied types of interaction are those referring to heavy metals and metalloids such as Pb, Cd, Cu, and As, as well as organic molecules such as diuron, pyrene, atrazine, and polychlorinated biphenyls, among others, finding cases of toxicity increased or decreased by synergy, antagonism, or additive behavior (Liu et al., 2018).

One process that has received much attention is the trophic transfer of NMs. Trophic transfer causes the presence of NMs in organisms that, without being in direct contact with these materials, ingest them through the consumption of other

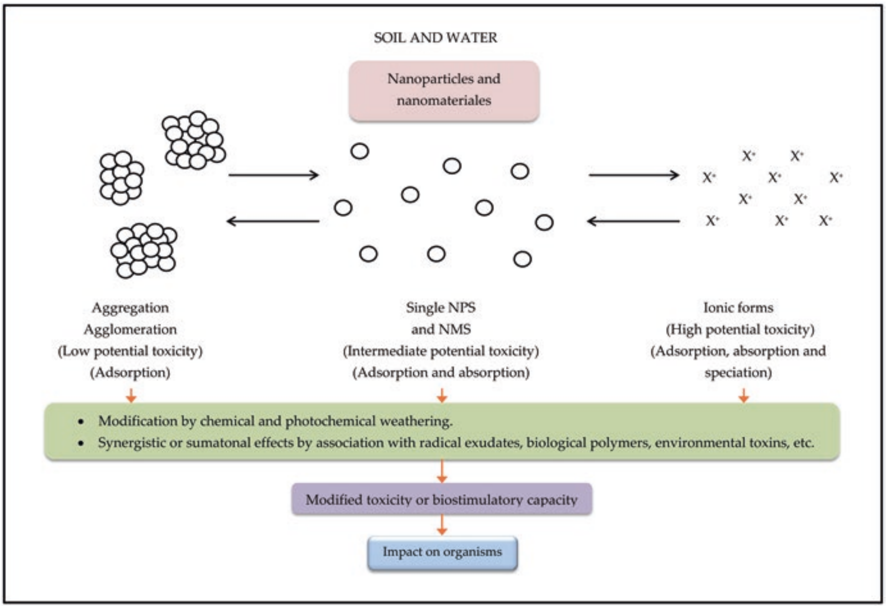

Fig. 2 Scheme of the modifications and interactions of NMs with different abiotic and biotic environmental components, with the consequent increase or decrease in toxicity. Figure from González-Morales et al. (2020)

organisms that have directly absorbed or ingested the NMs (Lead et al., 2018). During the trophic transfer, NMs can also carry other molecules such as toxins and contaminants, modifying the trophic transfer process and biomagnification of contaminants (Lu et al., 2021). Theoretically, the trophic transfer can span several trophic levels; however, it is not a proven fact at the ecosystem scale, and several studies indicate limited transfer rates to the superior trophic levels (Lammel et al., 2020; Shi et al., 2020). In human consumers, it has not been shown to occur, but it is not considered an impossibility (Parsai & Kumar, 2020). Historical examples of other contaminants such as heavy metals, pesticides, and radioactive material indicate that it is highly likely (Uddin et al., 2020). It is unknown the long-term consequences of the exposure of the human body to synthetic NMs to which it could potentially be exposed by trophic transfer (Morales-Díaz et al., 2017).

The previous data indicate that NMs will be present in ecosystems in increasing frequency and quantity. An example of this type of contamination is the case of microplastics and nanoplastics, which are present in the water and soils of practically all the planet, being found in the same way inside living organisms (Huang et al., 2020a). The preceding allows us to conclude that, although the use of NMs can result in great productive and economic advantages for agricultural and livestock activities (Medina-Pérez et al., 2019), their application must be based on the appropriate level of knowledge about the dynamics and impact on ecosystems. An adequate level of knowledge implies having information about the behavior of NMs in ecologically relevant times (years), in ecologically relevant concentrations (even in very low concentrations) to take into account the biomagnification phenomena (Uddin et al., 2020) and responses to the chronic exposure (González-Morales et al., 2020).

Another direct ecological impact of NMs on plants occurs through the soil microbiome and the rhizosphere microbiome. Under natural conditions, both the internal media, the epidermis, and the rhizosphere and soil volume near the plant's roots contain a complex community of microorganisms called the microbiome. The abiotic environmental variables and the microbiome's physiological and biochemical action on plant cells are key determinants to modeling plants' phenotype (Bahram et al., 2018). The microbiome is a dynamic soil–plant constituent that induces biostimulation and tolerance to stress. Therefore, any factor that modifies the biodiversity, profile of microorganism species, or their relative abundance will change the plant's biostimulation response to the microbiome (Berg et al., 2014).

The soil microbiome's exposition to NMs alters the species composition and relative abundance of microorganisms, mainly soil bacteria and protozoans. The above was demonstrated in several classes of NMs, including those contained in biosolids or subjected to environmental weathering (Asadishad et al., 2018). The concentrations of NMs capable of impacting the microbiome metabolism, enzymatic activities, abundance, or biodiversity were 5–50 mg kg^{-1} soil in the case of C60 fullerenes (Johansen et al., 2008), 1.2 kg TiO_2 NPs ha^{-1} (Simonin et al., 2016), and 1 mg Ag NPs kg^{-1} soil (Grün et al., 2018).

As with plants, the effect of NMs on the microbiome is dose-dependent, with positive effects on some variables when concentrations are low (e.g., <1 mg kg^{-1} soil) in the soil (Rahmatpour et al., 2017). Even though, in general, microorganisms are more tolerant than plants to abiotic stresses, in the case of NMs, the sensitivity of microorganisms seems to be much higher compared to those of plants (Juárez-Maldonado et al., 2021).

In the long-time range, the modifications in the soil microbiome could also modify the composition of the communities of protozoa and mesofauna and maybe plants, with a potential change in the structure of the ecological communities. Until now, there is not enough knowledge about how the distinct microbiomes can regulate and mold the properties of soil, groundwater, and plant and animal communities (González-Morales et al., 2020).

Considering the above, it can be affirmed that the use of NMs as biostimulants can be a form of application of NMs in agriculture with a potentially low environmental impact. The application of NMs as biostimulants, as seed priming (López-Vargas et al., 2020), seedling priming, or an inductor of tolerance or fertilizer or nanofertilizer vehicles in adult plants (Chhipa, 2017; Abdel-Aziz et al., 2019), involves the use of these compounds in low concentrations. The foregoing is the result of the ability of NMs to induce biostimulation and defense responses in plant cells even at low concentrations (Juárez-Maldonado et al., 2021).

3 Impact of Nanomaterials on Cellular Surfaces and Apoplast

As previously mentioned, biostimulation of plants occurs in two phases: the first one occurs through interfacial physicochemical processes, with an impact on the activity of proton pumps, receptors, channels, and transporters of cell walls and membranes; the above modifies the transmembrane potential and consequently the transport of ions and metabolites, cell signaling, energy metabolism, and gene expression. The second phase of biostimulation occurs through a mixture of physicochemical and biochemical processes in response to the internment of NMs, the contact of the corona and core components with cellular metabolites, and the subsequent release of chemical components (ions, functional groups, and low-molecular-weight metabolites) that compose the NMs and their corona (Juárez-Maldonado et al., 2019).

This section of the chapter deals with the first phase of biostimulation with NMs, which has been proposed to depend on the interaction between the NMs' surface charges and the cell surface charges.

3.1 The Cell Surface Charges

The surface charges of structural components, integral proteins, and functional groups of cell walls and membranes allow chemical interactions at the cell apoplast interface. Examples of these interactions are ionization of functional groups, acid/base dissociations, adsorption of ions and other chemical species, and the partial dissolution of some structural components of cell membranes (Wang et al., 2014). The density of surface charges (quantity by surface area) of the cell wall or membranes modifies the cellular interactions with the ions and other chemical species located in the apoplast. The surface charge density modifies the electrical potential of the surface of the membranes ($\psi 0$) as well as the transmembrane potential that sustains the ion channels and other integral proteins functional (Kinraide & Wang, 2010). Any change in $\psi 0$ and in the transmembrane potential implies an event of biostimulation and the consequent modification of cell metabolism. This is because the surface electrical potentials have an impact on the activity of channels, transporters, receptors, or in the importation via exosomes of ions (e.g., silicon and phosphorus), carbohydrates, lipids, lipoproteins, hormones, and other growth regulators (Haak et al., 2017).

The intensity and the final balance of the chemical interactions between the apoplast and the cell surfaces depend mainly on the ionic strength, pH, oxidation–reduction potential, and other extracellular medium properties. The cell surface maintains an equilibrium with the external fluids, where the interface acquires a net negative charge because the number of positive charges is less than the negative charges. The movement of ions in the apoplast, through attraction and repulsion, results in an electrical double layer (EDL) on the surface of the cell membrane (Fig. 3). The charge density, equivalent to the number of charges per unit area, determines the electrical potential of membrane surfaces and the transmembrane potential that supports the functionality and structure of integral proteins (Perry et al., 2016).

3.2 The Surface Charges of NMs

The characteristics of NMs, such as size, charge, roughness, shape, and hydrophobicity, among others (Barkataki & Singh, 2019), induce different cell responses when they meet with plant surfaces. However, it is believed that the surface charges of NMs produce the first metabolic changes and in cellular gene expression (Pérez-Labrada et al., 2020). NMs have a greater surface area vs volume compared to conventional materials, which results in a large amount of surface free energy and high reactivity (Pacheco & Buzea, 2018).

NMs do not appear in a pristine form in environments such as water, soil, biological fluids, or plant surfaces. Inorganic and organic compounds and biomolecules are joined by adsorption to the core of NM, forming a single layer or several layers

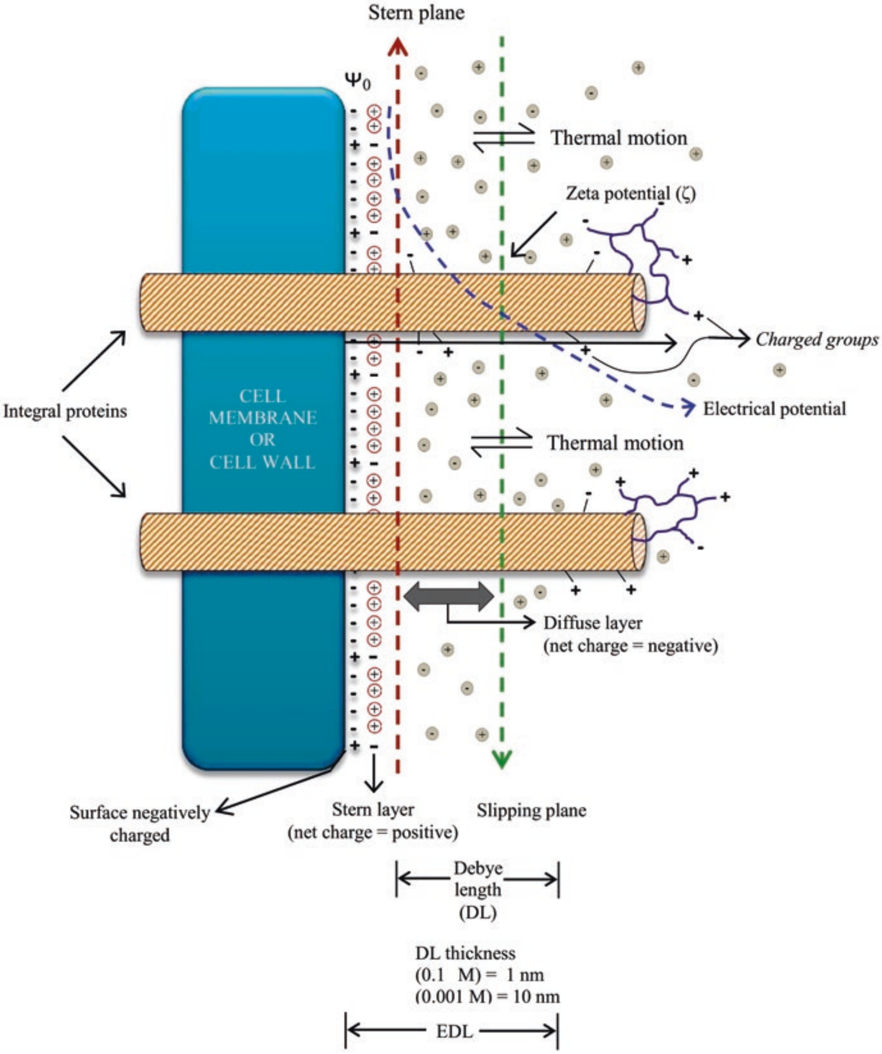

Fig. 3 Schematic illustration of a charged cell wall or membrane or nanomaterial (NM) forming an electric double layer (EDL) when exposed to the apoplast. EDL indicates two parallel layers of charges on the surface. The Stern layer includes ions adsorbed via chemical interactions and has a positive net charge. The diffuse layer includes ions associated with the Stern layer via the Coulomb force and has a negative net charge. The diffuse layer contains free ions under the influence of thermal motion and electric attraction. The Debye length is the thickness of EDL with mobile ions and denotes the distance under the influence of the surface's electric potential. The zeta potential is the electrical potential at the slipping plane. The volume included under the slipping plane shows tangential molecular motion about the surface. In plants, the Debye length is within 1–2 nm. As a consequence that the transmembrane domains of integral proteins can protrude from 2 to 7 nm, the receptors and the functional groups of proteins with positive and negative charges are located outside the EDL, which favor interfacial interactions with the EDL of NMs. Figure from Juárez-Maldonado et al. (2019)

of molecules, which constitute a structure called corona. The physicochemical characteristics and the biological reactivity of the corona depend on the profile of the adsorbed molecules. In biological fluids, it is common for the NM's corona to be constituted by proteins (Francia et al., 2019).

The formation of the NM's corona occurs spontaneously as a means of decreasing the free energy of the system containing the dispersed NMs. In a contaminant-free system, such as in a laboratory, pristine NMs have the same tendency to decrease free energy, but in this case, they do so through the agglomeration of the NM's particles. In both cases, the process is guided spontaneously toward a decrease in enthalpy (or an increase in entropy). The surface charge of the diffuse layer of the EDL of pristine NMs is commonly negative, while in biological fluids with pH <7 the diffuse layer of the EDL of the NM with corona has a net positive charge (Simon et al., 2018) (Fig. 4). This net positive charge on the corona surface facilitates interaction with the plant cell's EDL with a net negative charge.

The NMs' EDL acquires different characteristics depending on the coating used for their functionalization (Simon et al., 2018). For example, Li et al. (2019a) studied CeO_2 nanoparticles (NPs) with three different coatings (diethylaminoethyl dextran, dextran, and carboxymethyl dextran), observing that the three NMs showed different Zeta potential (+13, −3, and −15 mV, respectively). In another study, Li et al. (2016) observed that the tomato and rice's uptake of Au NPs of nearly identical size (8–12 nm) coated with cysteamine, cysteine, and thioglycolic acid was dependent on the surface charge of the functionalized NPs and related to the species of ligand used for the coating. The negatively charged Au NPs capped with cysteine were more efficiently absorbed in roots and transferred to stems and leaves than the NPs capped with cysteamine and thioglycolic acid.

As described, the surface free energy and the surface charges of NMs are key determinants in interfacial interactions. The final biological identity of the NM (that is, the impact it exerts on cell behavior) depends substantially on the asymmetric spatial distribution of surface charges, which in turn is the result of the aggregation/agglomeration of NMs, from the components and identity of the corona, and of the inorganic compounds present in the medium, such as Na^+, K^+, and Li^+. Therefore, the same NM placed in different environments or media will have a different impact on biological organisms (González-Morales et al., 2020).

3.3 Corona and Cell Surface Interactions

The positive net surface charge of the NM's corona can interact with the wall's or cell membranes' negatively charged surfaces. It can also interact with the negative or positive charges of the peripheral and integral proteins. The above activity can proceed without the intervention of specific cellular receptors (Fig. 5). The bonding process between the NM's and cell's surfaces also depend on the particles' hydrophobicity and particles' surface energy as aggregation factors to increase the entropy in NMs (Juárez-Maldonado et al., 2019).

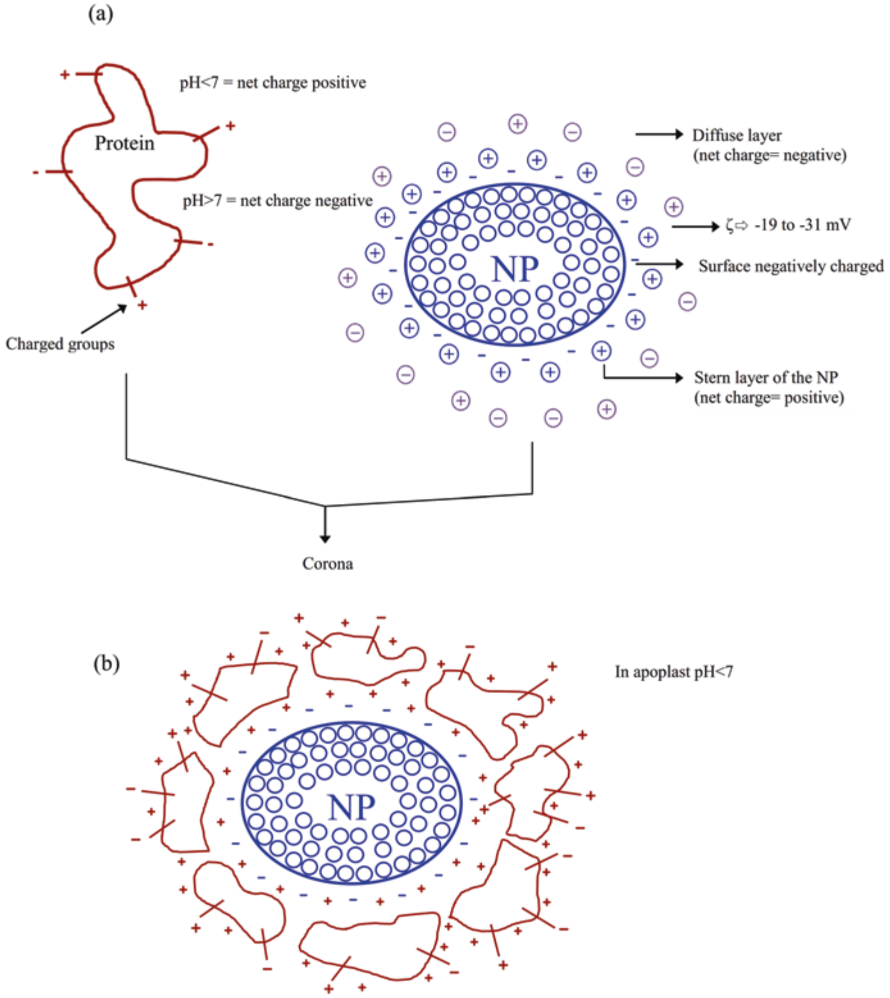

Fig. 4 Representation of formation of NM's corona in natural media. On the left side of (**a**), the net charge of the protein's surface is positive at pH < 7 (with a negatively charged Stern layer). On the right side of (**a**), the pristine nanoparticle (NP) shows a surface negative charge (with a positively charged Stern layer). In (**b**), due to the opposite charges of the protein's and NP's diffuse layers, the electrostatic interactions that give rise to the corona occur. Figure from Juárez-Maldonado et al. (2019)

The interaction between the surfaces of NMs and cells causes changes in the membrane potential and the activity of the cell walls and membranes' receptors and channels, causing metabolic adjustments (such as changes in ion fluxes) and energy metabolism and gene expression modifications (Hossain et al., 2016).

Interfacial interactions produce changes in the plant phenotype, from positive effects (biostimulation) to negative effects (toxicity), depending on the

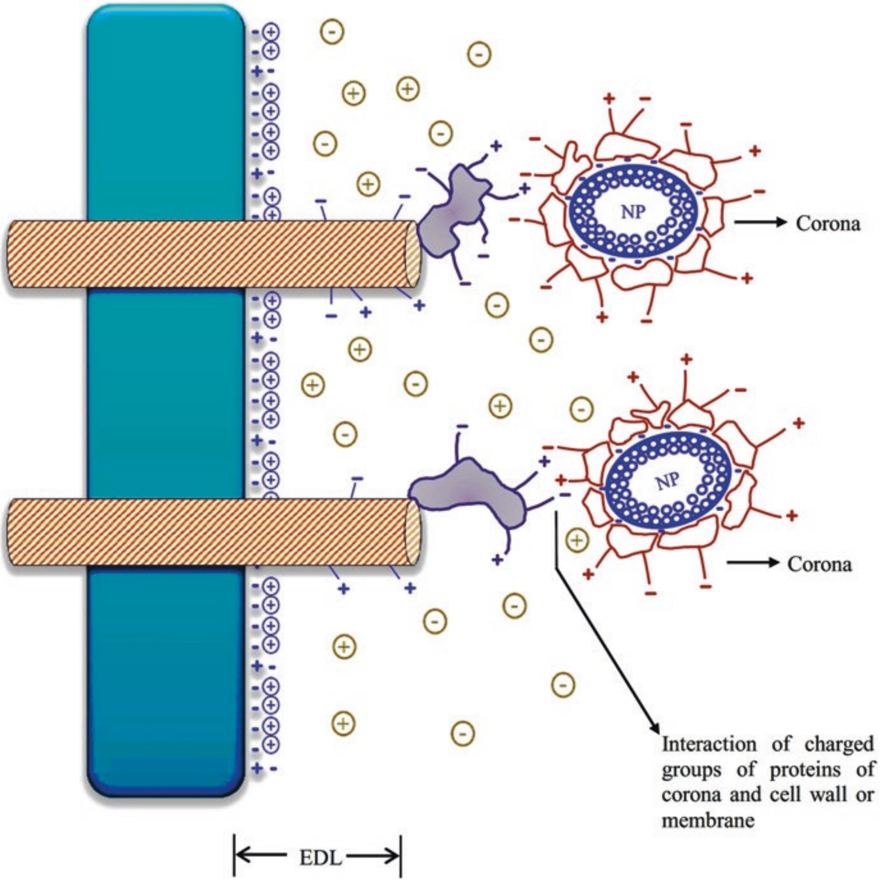

Fig. 5 Graphical representation of the interaction of charges on the surface of the proteins of corona, cell wall, or membrane. Figure from Juárez-Maldonado et al. (2019)

concentration and the physicochemical characteristics of the NMs, as well as the identity of the corona and the NM's core composition (Table 1).

The functionalization of NMs influences the surface charge, also changing the biological impact. Spielman-Sun et al. (2019) studied the interfacial interactions of CeO_2 NPs with different surface charges using corn, rice, tomato, and lettuce plants. The positively charged NPs showed greater adsorption in the root cells; meanwhile, the negatively charged and neutral particles showed greater translocation from the root to the stems. Translocation was more effective in tomato and lettuce plants compared to corn and rice plants. The functionalization of engineered NMs allows obtaining surfaces with specific characteristics and biological impact. Still, the characteristics and the biological impact can be modified once the materials are released in the environment or biological fluids and acquire a corona that modifies the surface functionalization (Goswami et al., 2017).

Table 1 Biostimulation effects of some NMs in plants

Nanomaterial	Plant species	Effect	Reference
nZnO	*Zea mays*	Improvement in the germination and related variables	Neto et al. (2020)
nZnO	*Latuca sativa* and *Daucus carota*	Increase in biomass and chlorophyll	Song & Kim (2020)
nZnO	*Glycine max*	Increased antioxidant activity and more yield	Yusefi-Tanha et al. (2020)
nSe	*Solanum lycopersicum*	Higher plant growth	Joshi et al. (2020)
TiO_2	*Solanum melongena, Capsicum annum*, and *solanum lycopersicum*	Increased vigor of seedlings	Younes et al. (2020)
nFe_3O_4	*Zea mays*	Increase in root length	Yan et al. (2020)
nCuO	*Allium fistulosum*	Increase in antioxidant enzymes and allicin	Wang et al. (2020)
nAg	*Eruca sativa*	Higher plant growth	Ahmed et al. (2020)
Carbon nanotubes and graphene	*Solanum lycopersicum*	Increase in antioxidant enzymes and decrease in some growth and vigor variables	López-Vargas et al. (2020)

Depending on the type and concentration of NM, and on the characteristics of the corona or the coating chemicals used for surface functionalization, the physiological, biochemical, and genetic impacts are different in organisms. The first interactions of NMs with the epidermis of the root or leaves can cause modifications in the cell structure. For example, NMs of CeO_2 caused lesions in tomato root hairs, necrosis, and malformations (Li et al., 2019a). A similar effect was reported in rice roots when exposed to Ag NPs, causing damage to the root cells (Huang et al., 2020b). Similarly, the first contact of some NMs with cell membranes can cause lipid peroxidation, evidenced by the increase in malondialdehyde (MDA) observed in maize plants using Y_2O_3 NPs (Gong et al., 2019). The same effect of increasing MDA was observed in rice seedlings when subjected toY_2O_3 NPs (Zhao et al., 2020). Even NMs made with essential elements for plants are toxic when they exceed adequate concentrations, as in the case of ZnO NPs applied at a concentration of 100 mg L^{-1} and which induced oxidative stress and alterations in the cell walls of the root epidermis of *Brassica napus* and *Brassica juncea* (Molnár et al., 2020).

Positive effects of NMs are also reported, manifested as modifications in cell surfaces. An example is the application of SiO_2 NPs in rice plants, which was associated with an increase in the cell wall thickness, restricting the flow of arsenic (As) to the cells (Cui et al., 2020). In this same study, the SiO_2 NPs induced changes in the cell wall's electrochemical potential (from −35 to −10 mV) in the presence of 40 µmol of As^{3+} in the medium. These adjustments did not occur in the absence of the SiO_2 NPs. As is known, changes in the surface potentials of the cell wall or membrane are the prelude to physiological adjustments and changes in gene expression (Juárez-Maldonado et al., 2019).

The above-mentioned interfacial interactions, upon the first contact of NMs with plant cells, produce biochemical signals (such as ABA, salicylates, or other hormones and metabolites) from root or leaf cells. These signals move through the vascular structures toward the rest of the plant, resulting in plant biostimulation in the form of adjustments in metabolism and gene expression and greater tolerance to biotic and abiotic stresses (Pérez-Labrada et al., 2020) (Fig. 6). An example is the impact of SiO_2 NPs in reducing the expression of the *PgSWEET* gene, responsible for regulating the flow of sugars in the apoplast, which favors the resistance to certain pathogens in *Panax ginseng* (Abbai et al., 2019).

The biological impact of NMs, either as biostimulation or toxicity, is also manifested in plant gene expression. In different studies, the physiological and biochemical response has been verified in parallel with gene expression changes. An example is that of multiwalled carbon nanotubes (MWCNTs) that enter protoplasts and can increase the expression of the aquaporin genes *PIP1s* and *PIP2s* in broccoli root. The result was a change in water permeability in the cells (Martinez-Ballesta et al., 2020). In maize plants exposed to different concentrations of La_2O_3 NPs, the content of abscisic acid increased, and water absorption was reduced by accelerating the development of apoplastic barriers in the roots, which caused growth inhibition in the plants. Also, the expression of some genes related to lignin biosynthesis was

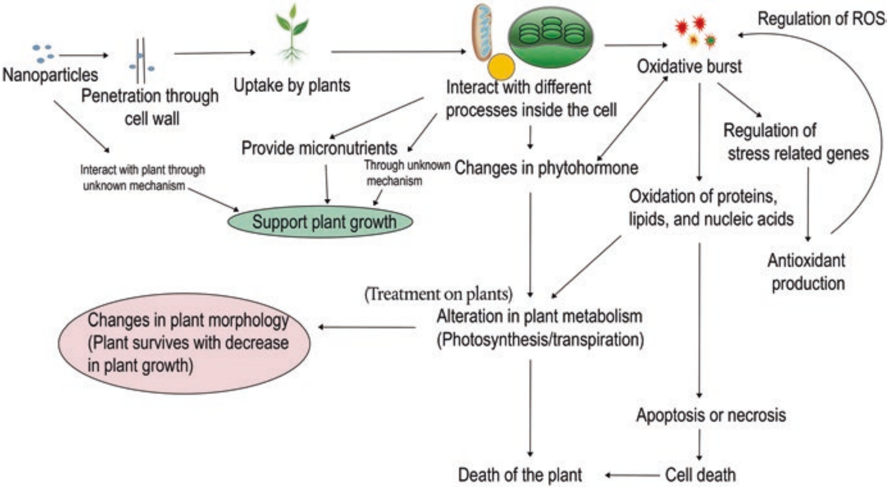

Fig. 6 A proposed general process of nanoparticles interaction with plants. The mechanism designated as an "unknown mechanism" is what this chapter calls the two-phase biostimulation process. Figure from Rastogi et al. (2017)

changed: some, such as *ZmPAL*, *ZmCCR2*, and *ZmCAD6*, were overexpressed, while the *ZmF5H* gene was repressed (Yue et al., 2019).

Hossain et al. (2016) studied the proteomic response associated with the phytotoxicity of the Al_2O_3, ZnO, and Ag NPs. A high oxidative burst was evidenced in the treatments with ZnO-NP and Ag-NP. The proteomic analysis of the roots revealed modifications in the amount of 104 proteins in the treatments with NPs; the proteins were associated with secondary metabolism, cell organization, and hormonal metabolism. Besides, Al_2O_3 NPs increased the expression of genes related to oxidation–reduction metabolism in roots, while the opposite occurred with the ZnO and Ag NPs. In the study of Xun et al. (2017), the maize plants with exposure to ZnO NPs modified the transcriptomic profile of the roots, showing an increase in the N metabolism pathways and synthesis of cellular components, while the processes related to metabolic rate were reduced.

Studies of transcriptomes have shown that the number of genes that modify their gene expression by exposition to NMs is significant, reporting that NMs of TiO_2 and ZnO induced the differential expression of 509 genes in leaves and 3666 genes in lettuce roots (Wang et al., 2017b); the genes were associated with different metabolic pathways such as photosynthesis, N metabolism, antioxidant metabolism, and carbohydrate metabolism. In another study, Zhang et al. (2019) found that Ag NPs modified the expression of 626 genes in *Arabidopsis*; in this case, the genes were associated with photosynthesis, antioxidant metabolism, response to ethylene, and responsivity to other metabolites and environmental challenge.

The changes that occur in transcriptomes and proteomes after exposure of plants to different NMs are extensive. Therefore, it is unlikely that the impact of NMs occurs through a single mechanism; rather, it is expected that a set of mechanisms involving multiple signaling pathways and their crosstalk participate. This situation explains the difficulty of predicting the global and long-term impact of NMs on plant organisms. Additionally, NMs can act synergistically or antagonistically depending on the environmental context, making the prediction and explanation of the mechanisms of action more difficult. An example of this is the synergism between the TiO_2 NPs and the high concentration of CO_2 in rice plants, while each factor separately did not influence the plants used in the experiment (Xu et al., 2019). However, as with other biostimulants whose mechanism of action is still not well understood (González-Morales et al., 2021), NMs used in low concentrations and by the most appropriate application routes (for example, as seed priming or by foliar spraying with preference over the application to the soil/substrate or the nutrient solution) can surely constitute a valuable alternative within the alternatives available to carry out biostimulation of crops (Juárez-Maldonado et al., 2021).

4 Cellular Internalization and Compartmentalization of Nanomaterials

During the second phase of the biostimulation process by NMs, the internalization and compartmentalization of NMs occur in plant cells. Like the first interactions of NMs with cells, internment depends on the material's characteristics, such as size, functional groups of the corona, or the compounds used for NM functionalization, shape, surface charge, hydrophobicity, and roughness, among others (Liu et al., 2020).

The following are the main pathways in which NMs can access plant cells (Fig. 7):

1. Through pores in cell walls and membranes. It can occur through pre-existing pores, or indeed the surface free energy of NM can enlarge the cell wall pores or create new pores in the membrane and allow access to the cellular environment (Yan & Chen, 2019; Barkataki & Singh, 2019; Singh & Kumar, 2020), maybe a main access route for NMs smaller than 100 nm.
2. Clathrin-mediated endocytosis is the main endocytic mechanism in plants, maybe a main access route for NMs 120–200 nm (Santiago et al., 2020).
3. Membrane microdomain-associated endocytosis. Membrane microdomains are nanodomains at the plasma membrane (PM) that are enriched in sterol and sphingolipids (Fan et al., 2015).

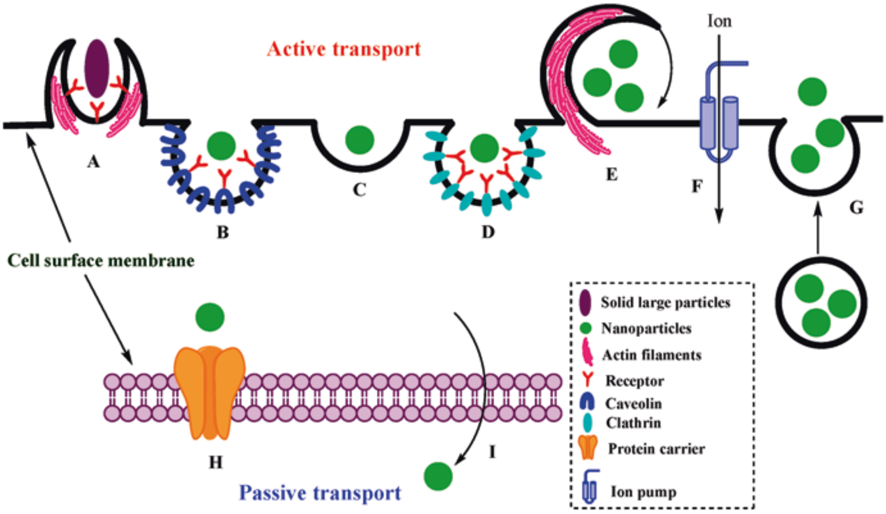

Fig. 7 Active and passive cell uptake of particles and NMs in animal and plant cells: (**a**) phagocytosis, (**b**) caveolin-mediated endocytosis, (**c**) clathrin–caveolin-independent endocytosis, (**d**) clathrin-mediated endocytosis, (**e**) macro-pinocytosis, (**f**) ion pumps, (**g**) exocytosis, (**h**) facilitated diffusion, and (**i**) simple diffusion. Figure from Sabourian et al. (2020)

There are not many studies regarding the cellular internment of NMs in plant cells. However, the forms of access appear to be similar in plant and animal cells. Table 2 shows the main cellular access pathways for NMs, depending on size, charge, and particle shape.

NMs constitute a point and reactive source that provides nutrients and other elements for cells. On the other hand, the ions of the different essential, beneficial, and toxic elements constitute a diffuse source with less reactivity whose cellular internment occurs through channels and transporter proteins that effectively regulate the entry and compartmentalization of these ions. In the case of NMs, as previously stated, there are several access pathways, several of them dependent on the surface free energy of the NM, which facilitates internment into the cytoplasm and organelles without showing the regulation that occurs for ions (Juárez-Maldonado et al., 2019).

The above possibly partially explain the differences observed in the impact of conventional fertilizers versus nanofertilizers on plants. Conventional fertilizer contributes ions that dissolve in the apoplast and from there are interned into the cell by mechanisms subject to strong regulation. In contrast, nanofertilizers provide NMs that initially induce biostimulation by the interaction of surfaces and later allow the entry of NMs through pores, membranes, and endocytosis. After entering the cells, the second phase of biostimulation occurs, followed by the release of the nanofertilizer ions that originate the well-known nutritional responses described for this category of elements. Together, the biostimulation and the nutrients provided by the nanofertilizers translate into a substantial improvement in the metabolism and growth of the crop, also increasing tolerance to environmental stress (Dimkpa & Bindraban, 2018; El-Desouky et al., 2021; Neto et al., 2021; Ahmadian et al., 2021). Additionally, the stability and bioavailability of nanofertilizers in the soil or substrate are greater than conventional fertilizers (Ojeda-Barrios et al., 2020).

Table 2 Main access routes in animal and plant cells of some NMs according to size, charge, and shape

NM	Main pathway to cells	Size (nm)	Charge (+/−)	Shape	Reference
Chitosan	CME	15–250	+	Ellipsoidal/ spherical	Lichtenberg et al. (2019)
Polystyrene	CME and PD	40–150	−	Not specified	Wang et al. (2017a)
Carbon nanotubes	MP	195–630	−	Cylindrical	Cui et al. (2017)
Carbon nanotubes	PD	50 nm	−	Cylindrical	Kang et al. (2010)
Quantum dots	CvME and CME	10–50 nm	−	Ellipsoidal	Saulite et al. (2017)
Au	CME	15–45	−	Spherical	Ding et al. (2018)
Si	CME	90–200	−	Spherical	Li et al. (2019b)

CME clathrin-mediated endocytosis, *PD* passive diffusion, *MP* macro-pinocytosis, *CvME* caveolin-mediated endocytosis

After entering the plant cells, the NMs, according to the identity of the corona, will accumulate in certain organelles, cell compartments, or the cell membrane, or they will react with the different metabolites of the cell environment, releasing the components of the corona or the components of the NM's core (Banerjee et al., 2019). An example is the release of Ag^+ and Cu^+ ions from Ag and Cu NPs. If the Cu^+ concentration is adequate, it will function as a nutrient (cofactor), and this positive effect will be added to the biostimulation created by the Cu NPs. But beyond a certain concentration threshold, the Cu^+ will cause toxicity. In the case of Ag^+, there is no known function as cofactors in living organisms, and rather they compete with Cu^+ as a cofactor of some proteins. Therefore, for Ag NPs, an impact is expected to occur as a biostimulant when it is in low concentration or as toxic when it exceeds a certain threshold. The toxicity threshold (20–100 mg L^{-1}) will depend on the plant species and the environmental context (Yan & Chen, 2019).

The second phase of biostimulation by NMs begins with the wide range of interactions that occur between NMs internalized to cells and the cell components: membranes, proteins, nucleic acids, regulation and signaling complexes, and diverse metabolites. The result is a series of modifications in metabolism, which originate biochemical and physiological changes and adjustments in gene expression that change cellular proteomes and metabolomes and the plant's phenotype (Zuverza-Mena et al., 2017; Anjum et al., 2019).

Seed priming is an example of the biostimulation process induced by NMs. NMs in contact with the seed coat can pass through this structure through the intercellular spaces in the parenchyma or through the creation of pores in the cell walls. In both cases, the presence of NMs causes the induction of enzymes that initiate germination events and the expression of genes associated with aquaporins. This effect of acceleration of germination and greater capacity of the seed to absorb water is explained as a response to eustress or biostimulation. It has been described for several NMs and is exemplified by the positive impact of carbon nanotubes on germination (Miralles et al., 2012). The biostimulant impact of carbon NMs is not limited to germination events but can modify plants' antioxidant status in later stages of development (López-Vargas et al., 2020).

The changes associated with the second phase of biostimulation were exemplified by Yan et al. (2020) in maize plants grown in soil with Fe_3O_4 NPs (0, 50, 500 mg kg^{-1}). The maize plants did not show impact on plant biomass or photosynthesis, but root length significantly increased, with decreased malondialdehyde (MDA) level, higher accumulation of Fe in root tissues, and a reprogramming of root metabolome with a decrease in pathways related to nitrogen metabolism, antioxidant metabolism, and defense. Another example of metabolic adjustments elicited by NMs was described by Anjum et al. (2019). It refers to the use of NMs (Ag, Cu, Au, Co, Zn) as biostimulants to induce the accumulation of specialized metabolites with pharmacological or nutraceutical applications in distinct plant species under different culture systems such as cell culture, organ culture, or growing seedlings. The concentration of NMs depended on the plant species and the cultivation system and was between 0.3 and 900 mg L^{-1} for metallic and metal oxide NMs and 2 and 500 mg L^{-1} for carbon NMs. In fact, this biostimulant potential of NMs can be widely applied in the agricultural practice for the nutraceutical improvement of harvested products (Juárez-Maldonado et al., 2018).

The compartmentalization of NMs can have positive or negative effects on plants, depending mainly on the NM concentration. If the levels of NMs are not high, those that are made up of essential elements for plants, such as Ca, Mg, Zn, and Fe, are expected to induce a dual effect of biostimulation and nutrition. Biostimulation occurs by the interaction of NMs with internal membrane systems and protein complexes or RNAs that regulate gene expression or post-translational modification of proteins; nutrition by the release of ions in the internal cell environment and their use as cofactors or by interaction with other ions present in the cell environment or the apoplast. On the other hand, the NMs of elements such as Ti, Ce, and Cd will cause biostimulation or toxicity depending mainly on the concentration and location of the NMs in the different cell compartments (Juárez-Maldonado et al., 2021).

In the case of NMs formed by essential elements and those formed by other elements, when a certain concentration threshold is exceeded, toxicity will occur. The threshold is highly variable, as it depends on the type of NM, the composition of the corona or capping material, the plant species and the stage of development of the plants, and the environmental context, e.g., temperature, the composition of the medium, and the presence of compounds that can antagonize or synergize with NMs (Juárez-Maldonado et al., 2021). Phytotoxicity can be manifested as inhibition in seed germination, root growth, biomass, and leaf area. At the physiological level is associated with oxidative stress and lipid peroxidation, alteration in fluidity and permeability of the cell's membranes, alteration of cell structure and cell division, hormonal balance changes, and a decline in chlorophyll, nutrient uptake, and transpiration rate (Yan & Chen, 2019).

When NMs reach high concentrations, vacuoles seem to play an important role in regulating the concentration of the released materials that result from the reaction of NMs with cellular metabolites such as organic acids, chelating agents, and redox metabolites (Ma et al., 2018). On the other hand, mobilization of NMs toward the vacuoles through endosomes also appears to occur, as reported for CeO_2 NPs (Li et al., 2019a) and CuO NPs (Dai et al., 2018). The compartmentalization also depends on the cellular structure of the plant species. Spielman-Sun et al. (2019) reported that CeO_2 NPs were accumulated in mesophyll cells to a greater extent in dicotyledonous plants (lettuce and tomato) than in monocotyledons (rice and maize), an effect attributed to the greater volume of intercellular spaces in the mesophyll of dicotyledons.

The two-phase biostimulation process, or the toxicity when NPs' concentration is high, occurs immediately (<24 h) in the cells adjacent to the NMs' entry sites or in cell cultures (Dai et al., 2018). In terrestrial plants, the entry sites can be the root epidermis, the epidermis of stems and leaves, the stomatal pores and lenticels, and the epidermis of flowers and fruits. In all cases, exposure to NMs induces changes in the cellular phenotypes of the different tissues (Zuverza-Mena et al., 2017). The phenotypic modification associated with biostimulation or toxicity is followed by metabolic, biochemical, and genetic adjustments followed by signaling toward other cells not directly exposed to NMs, which also modifies their phenotypes. The above mechanism is analogous to that proposed for other biostimulants and factors inducing biotic and abiotic stress (Fig. 8), mainly through induction of ROS synthesis, followed by an oxidative burst that unchains Ca^{2+} fluxes, and the subsequent action of ion channels (e.g., K^+ and Cl^-), hormones, and other regulatory metabolites, and non-coding RNAs. The regulator substances (e.g., salicylic acid and ABA) can be extruded to the apoplast or transported by plasmodesmata. Finally, the signaling spreads all the plant organs through the signaling agents' long-distance transport by the vasculature (Yan & Chen, 2019; Pérez-Labrada et al., 2020).

In addition to the signaling process of the second phase of biostimulation, dependent on hormones and other metabolites, the migration of NMs can also occur from the site where they entered toward other plant structures and organs. The process is described in the next section.

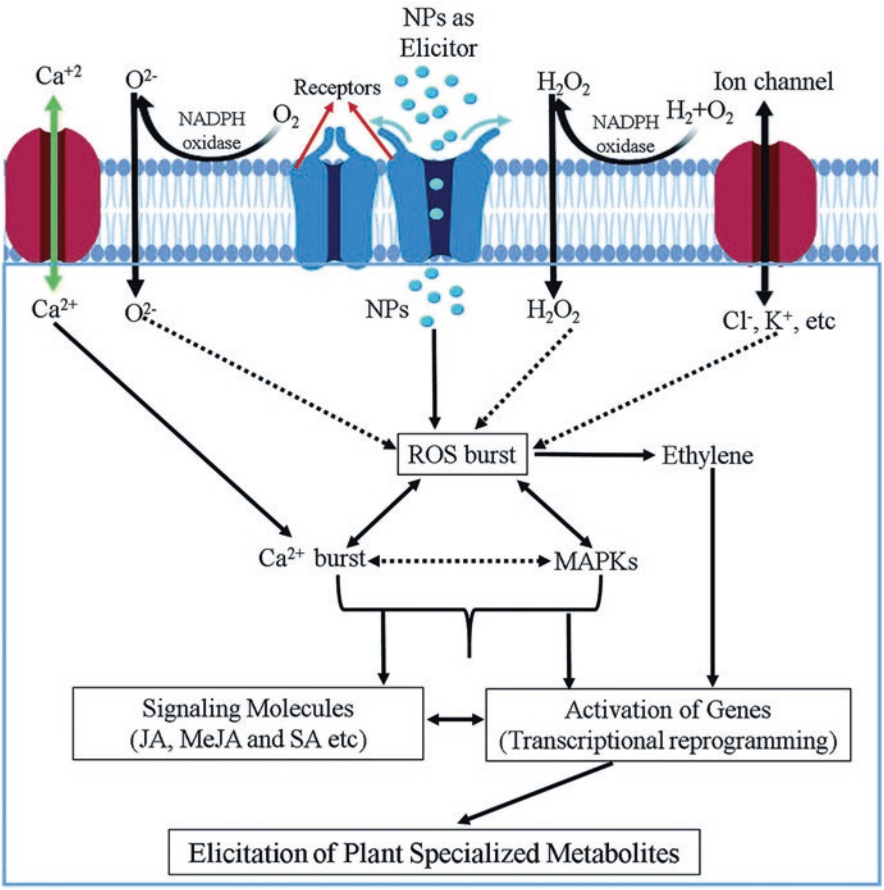

Fig. 8 The proposed mechanism to explain the biostimulation and elicitation capacity of NMs in plant cells. Figure from Anjum et al. (2019)

5 Transportation of Nanomaterials between the Organs of the Plant

The transport of NMs can be visualized as a phenomenon that in plants can occur in several dimensions: (1) from the initial point of entry to other plant organs; (2) from the different organs of the plant toward other organisms at different trophic levels (e.g., the direct transference of NMs to herbivores or impact through changes in the nutritional or nutraceutical quality); (3) from one generation to another through transgenerational modifications (e.g., epigenomic changes) or even by direct transfer. Topic (1) is the one that will be described in this section.

As already mentioned, NMs that come into contact with plants do so initially with the surfaces of the roots, stems, leaves, flowers, and fruits. NMs that enter the plant's internal volume move from the apoplast into the cytoplasm and cell organelles after interactions between the surfaces of the NMs and the walls and membranes occur. Subsequently, NMs can be subjected to chemical transformations or compartmentalization or migrate from one cell to another through symplastic transport. The above can be an important mechanism for the radial transport of NMs from the epidermis of the root or aerial structures toward the different organs' internal volume (Miralles et al., 2012).

Radial transport allows NMs to reach the cortex's internal tissues, the xylem and phloem tissues, and the pith. NMs enter the vascular structures and are mobilized by axial transport to the rest of the plant (Miralles et al., 2012). When the initial point of entry is via the root, the main transport route is believed to be via the xylem. On the other hand, when the entry of NMs occurs through the epidermis of leaves, stems, and fruits, the initial internment that seems to occur by simple diffusion is through the stomatal pores and lenticels, which can represent about 5% of the surface of the epidermis. Once the NMs reach the substomatal cavity or the intercellular spaces of the lenticels' complementary cells, it is believed that the phloem carries out the subsequent transport to the rest of the plant. It is not excluded that some NMs passively enter through the cuticle that covers the epidermis of leaves and stems, which presents pores <5 nm (Su et al., 2019). On the other hand, there is a possibility that the entry of NMs >5 nm through the cuticle could occur as a result of the lipophilicity of some NMs or the interaction of the surface free energy of NMs with the hydrocarbon molecules that build up the cuticle (Juárez-Maldonado et al., 2019).

Axial transport of NMs from the initial entry points to more distant organs triggers other biostimulation or toxicity events, depending on the concentrations, types of material, and the environmental context. These new events are different from those initially triggered since the target organs have different phenotypes and consequently respond differently to NMs. For example, if TiO_2 NPs are applied in the substrate of a plant in low concentration (e.g., 1–5 mg L^{-1}), these would enter through the epidermis of the root and promote biostimulation events in the root (with physiological impacts on the whole plant derived from the root's signaling with hormones and other metabolites). When the xylem transports the TiO_2 NPs to other plant organs, they will cause new biostimulation events, but now in the cells of the tissues of the stems or leaves, which would present different response profiles to those of the cells of the root tissues (Fig. 9).

The amount of the NM that moves radially or axially from the initial entry point to the rest of the plant is highly variable. It initially depends on the lifetime of the NM in the cell environment, in other words, on whether it is rapidly subject to chemical transformations that release elemental components, e.g., when Cu NPs are

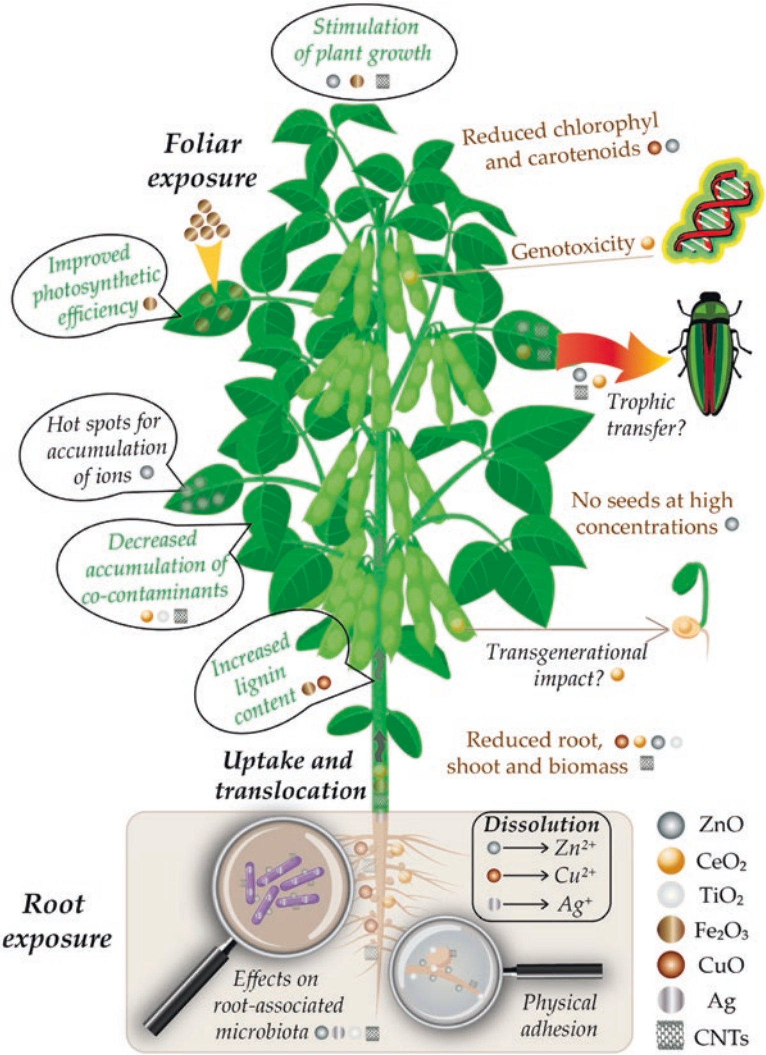

Fig. 9 Graphic representation of NMs' effects on plants. Positive impacts are depicted in green, negative ones in brown. More controversial topics as the trophic transfer and the transgenerational impacts are followed by question marks. Figure from Coman et al. (2019)

transformed into Cu^{2+}. The mobilization depends secondly on the characteristics of the NM and the plant species, the stage of development, growth rate, and its environmental context.

The different plant taxa present substantial anatomical and physiological differences; these intrinsic differences constitute another factor that significantly modifies the response, transport, and fate of NMs in the plant. As an example, there is a difference in the root structure between monocots (fibrous root) and dicots (taproot), which suggests that monocots may be more sensitive to NMs (Su et al., 2019). Analogous reasoning suggests that the differences in the root structure between crops in soil and crops in substrates different from the soil (e.g., peat moss, perlite) or in hydroponics would make the responses to NMs different in each environmental situation.

Photosynthesis appears to be a metabolic pathway sensitive to the presence of NMs in plant cells (Tighe-Neira et al., 2018); for that reason, like germination and increase in biomass, it is widely used in studies on toxicity and biostimulation. Whether the application of NMs in plants occurs via the roots or by foliar spraying, the impact of NMs on photosynthetic activity depends on the axial transport (presumably through the xylem) of NMs from the epidermis of the root, or radial and then axial transport (presumably through the phloem) from the stomatal pores toward the mesophyll of the leaves (Su et al., 2019).

Different variables associated with photosynthesis have been used to describe the impact of different NMs on plants. From Tighe-Neira et al. (2018), the following can be mentioned:

- CO_2 assimilation rate and stomatal conductance. With negative impacts of 1 mg L^{-1} CuO NPs, 0.2% w/v TiO_2 NPs, 200 mg L^{-1} CeO_2 NPs, 300 mg L^{-1} ZnO NPs, 800 mg kg^{-1} ZnO NPs.
- The concentration of photosynthetic pigments. With negative impacts of 1–400 mg L^{-1} CuO NPs, 5–10 mg L^{-1} Ag NPs, 25 mg kg^{-1} ZnS NPs, with a positive effect of 250 mg kg^{-1} CeO_2 NPs in tomato and negative effect of 250 mg kg^{-1} CeO_2 NPs in beans, and 400 mg kg^{-1} CeO_2 NPs in maize.
- Efficiency in the transport of electrons. With negative impacts of 32 mg L^{-1} CuO NPs, 5–300 mg L^{-1} Ag NPs, 200 mg L^{-1} CeO_2 NPs, 1–100 mg L^{-1} ZnO NPs, and with positive effects of 0.25% w/v TiO_2 NPs.

A significant amount of the above results pointed to negative impacts on photosynthesis variables. It is possible that these results, in many cases, were dependent on the use of high concentrations of NMs (e.g., >75 mg L^{-1}) (Juárez-Maldonado et al., 2021).

Many crop plant studies indicate positive impacts of NMs on antioxidant activity, biomass, and yield (Zuverza-Mena et al., 2017). It is not easy to think that these results are obtained without a positive effect on photosynthetic activity or other related activities such as respiration or photorespiration. However, as far as we know, there are no studies where the effect of NMs on plant metabolism is considered comprehensively (e.g., photosynthesis, photorespiration, respiration, biomass allocation; from physiological, biochemical, and molecular points of view). Considering that the biostimulant impact of NMs occurs through multiple signaling cascades and different metabolic pathways, studies aimed at understanding the impact of NMs should consider a more comprehensive view of plant responses.

6 Perspective of Crops Biostimulation with Nanomaterials

Biostimulation is a complex biological phenomenon that has been described for many physical processes, materials, substances, and organisms. NMs constitute a part of the universe of possibilities for the development of biostimulants. What is presented in this chapter indicates that there is a large amount of information about the positive impact of NMs in plants, not necessarily presented with the biostimulation label, but showing the characteristics of the phenomenon.

As with other biostimulants such as humic acids, chitosan, and growth-promoting fungi and bacteria, the responses of plants are not described by a simple model or limited to a few physiological, biochemical, transcriptomic, or proteomic responses. To reach a complete understanding of the biostimulation phenomenon of plants with NMs, great efforts will be necessary to integrate the existing information, e.g., in the form of meta-analysis or other kinds of models that integrate huge amounts of information, or comprehensive experiments that include a large number of response variables in plants, using series of response variables whose causal relationships are reasonably understood, located in different ambits of complexity, from the molecular level to the levels of populations and plant communities.

It is manifest that there are still many unresolved issues regarding the commercial-scale applications of NMs; the main topics still under discussion refer to ecological, economic, and innocuity issues. The possible assortment of interactions between NMs, plant species, soil types and substrates, climatic regimes, and agronomic management practices are numerous. It is quite a challenge to establish the first definition of a few selected NMs to be applied to certain crops under certain environmental conditions. This initial definition is possibly an important first step in advancing the commercial application of NMs as biostimulants in agriculture. The information obtained from the above-mentioned comprehensive studies would be useful for defining a selected group of NMs that could constitute the first wave of new materials for agriculture whose use would increase yield, mitigating the environmental impact of current agronomic practices, with the final objective of promoting the sustainable crop production.

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Copper-Based Nanoparticles for Pesticide Effects

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Abstract In recent years, engineered nanoparticles have been the focus of intensive scientific and technological development in different applications, including agriculture and food production/security. Copper-based nanoparticles have interesting features, such as low production cost and potent antimicrobial actions at concentrations considered safe to humans and to the environment, making them good candidates for agricultural applications. Moreover, copper-based nanomaterials can be prepared not only by traditional chemical and physical methods but also by green routes involving biogenic methods in a sustainable manner. Copper is involved in plant growth, metabolism, and defense, and it has been used in agriculture as a key player in fungicides in the combat of plant diseases. Recently, the design of copper-based nanoparticles has opened new avenues to protect and defend crops, with superior results and lower toxic effects compared with bulk copper (massive copper). In this scenario, the current chapter presents and discusses recent progress in the design and applications of copper-based nanoparticles with potent antimicrobial applications for agricultural pest management, green routes to synthesize the nanoparticles, and recent progress in the applications of copper-based nanoparticles as pesticides, as well as their phytotoxic activity. We hope that this chapter opens new avenues in this important topic involving nanotechnology and agriculture.

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1 Introduction: Importance of Copper in Agriculture

The biological role of copper (Cu) arose during the evolution of photosynthetic organisms, which changed the Earth's atmosphere from anaerobic to aerobic due to the progressive accumulation of oxygen (Burkhead et al., 2009). Under physiological conditions, Cu exists in two forms: the reduced state (Cu^+) and the oxidized state (Cu^{2+}), and it can bind to different substrates depending on its state. Cu has a significant influence on plant metabolism due to its presence in several biomolecules and its participation in numerous metabolic routes in the plant, as a metal cofactor in certain metalloproteins involved in electron transport and oxidative stress response. In chloroplasts, Cu is a constituent of plastocyanin (Pc), the most abundant Cu protein in plant chloroplasts, which acts as an electron carrier in primary photosynthetic reactions. Cu is also a constituent of stromal Cu/Zn superoxide dismutase (Cu/Zn-SOD), which protects against reactive oxygen species (ROS) generated during the oxygenic photosynthetic reactions (Yruela, 2013).

In addition to being essential for plant metabolism, Cu has been used in agricultural practice for years as an active ingredient of fungicides to enhance crop production by controlling plant diseases. The most common Cu-based fungicide formulations contain Cu sulfate, Cu hydroxide, Cu oxychloride, or Cu carbonate (Husak, 2015). The Bordeaux mixture (a complex of Cu sulfate pentahydrate and lime) has been used in viticulture as a plant protection product against the stated fungal diseases since the eighteenth century, being the first fungicide to be used on a worldwide scale. Nowadays, a Cu hydroxide- and Cu sulfate-based fungicide is the only product allowed under organic standards, which is effective against *Plasmopara viticola* (Vitanovic, 2012).

Since the Bordeaux mixture, there has been rapid growth in the development and use of Cu-based fungicides, revolutionizing plant protection in the twentieth century. Among the advantages conferred to the use of Cu in agriculture, we can highlight the low cost, relatively high toxicity to plant pathogens, chemical stability, and long residual periods (Lamichhane et al., 2018). Cu is used as an active ingredient strictly for its protective function, as it has no curative or systemic activity and, once applied, Cu particles may adhere to leaf surfaces to provide a protective film. This film is a reservoir that, when in contact with water and low pH, releases Cu ions, which act on the pathogen cells (Lamichhane et al., 2018). In other words, as Cu-based fungicides do not penetrate and translocate well in plants, coverage of the target is achieved through the application of large amounts of the product.

In this scenario, the frequent and extensive use of Cu-based fungicides, coupled with the limited Cu mobility in the soil, results in the accumulation of this metal in the upper soil layers as a consequence of direct application, drift, or dripping from leaf surfaces (Fan et al., 2011; Brunetto et al., 2016; Amlal et al., 2020). The long-term foliar application of Cu-based fungicides can easily increase the concentration of this metal to levels close to 200 mg kg^{-1}, contrasting with Cu concentration in noncontaminated agricultural soils that usually varies from 5 to 30 mg kg^{-1} (Adrees et al., 2015).

The heavy metals that act as micronutrients (e.g., Cu, iron, manganese, nickel, and zinc), when present in soils in concentrations above the optimum level, compromise plant growth and development due to changes in physicochemical properties of soil. In addition, they trigger adverse effects in various physiological processes of plants (Tiwari & Lata, 2018).

These metals cannot be degraded or destroyed, although their chemical forms can change. Once dispersed in water, soil, and air, they can accumulate in plant tissues (Cheng et al., 2017), posing a severe threat to human health through contamination of the food chain (Nuapia et al., 2018). Despite the environmental problems caused by the continuous use of heavy metal-based protective fungicides, there are additional problems related to synthetic pesticides in general.

The conventional application of synthetic pesticides coupled with a lack of proper rules and regulations causes serious environmental problems, releasing toxic compounds that contaminate the surrounding medium through leaching or rainfall runoff, reaching water bodies and even groundwater (Pradhan & Mailapalli, 2020). Moreover, only a minimal quantity of the applied pesticides (less than 1%) reaches the target species, while the remainder affects nontarget organisms, promoting resistance in weeds, insects, and pathogens, in addition to having an environmental impact (Usman et al., 2020).

In this context, nanotechnology has been studied in agriculture as a tool to increase the effectiveness of different agrochemicals as fertilizers and pesticides, helping to reduce the amount released into the environment (Kumaraswamy et al., 2018). Nanomaterials can be used to synthesize nanofertilizers (nano-sized nutrients, nano-coated fertilizers, or engineered metal-oxide/carbon-based nanomaterials) and nanopesticides (inorganic nanomaterials or nanoencapsulated active ingredients) to provide targeted/controlled release of nutrients and agrochemicals. Thus, they can deliver precisely the recommended dosage for plants, improving the biological efficacy and with less environmental damage (Iavicoli et al., 2017; Bhan et al., 2018).

Some studies have recently combined different nanotechnological approaches with Cu bioactivity, showing promising effects on plants. As examples, we can cite Cu nanoparticles (Cu NPs) (Hafeez et al., 2015), polymeric (chitosan) nanoparticles containing copper ions (Cu^{2+}) (Choudhary et al., 2017a, b), nanocomposites of chitosan/alginate loaded with Cu oxide (Leonardi et al., 2021), $Cu_3(PO_4)_2$ and CuO nanosheets, and copper oxide nanoparticles (CuO NPs) (Ma et al., 2020) developed as nanofertilizers to improve the efficiency of micronutrient use, aiming to enhance plant growth and development.

However, the association between nanotechnology and Cu bioactivity has been mainly used for the development of nanopesticides against plant pathogens

(Giannousi et al., 2013; Kanhed et al., 2014; Saharan et al., 2015; Vanathi et al., 2016; Choudhary et al., 2017b; Sathiyabama & Manikandan, 2018; Pariona et al., 2019; Ma et al., 2020). In addition, this combination has been applied for the control of storage pests (El-Saadony et al., 2020), for antibacterial composite food packaging (Longano et al., 2012), and to extend the shelf-life of stored tomatoes (*Solanum lycopersicum* L.) (Meena et al., 2020).

Here, we review recent progress in the design and use of Cu-based nanomaterials in agriculture, highlighting their potent actions as an antimicrobial agent in pest management.

2 Nanotechnology: Definition and Applications in Agriculture

Notably, the field that addresses nanotechnology (also known as "nanoscience") has received significant attention in recent years from scientific research (Arya et al., 2018; Camacho-Flores et al., 2015). As a form of technology and scientific study, nanotechnology addresses the study of materials developed at the nanoscale (Arya et al., 2018; Mohanpuria et al., 2008). Commonly, nanoparticles are classified as particles with a size on the scale of 1–100 nanometers (nm); however, some recent works address these same materials—also known as nanostructured materials—in a size range of 1–1000 nm, taking into account the composition and formation of these types of material, their properties, and applications in relation to their mass macrostructure (Arya et al., 2018; Camacho-Flores et al., 2015; Jeevanandam et al., 2018).

Several different kinds of nanoparticles (metallic, metal oxide, and hybrid nanoparticles) have attracted considerable attention due to their physical, biological, chemical, catalytic, optical, and, in some cases, magnetic characteristics, with promising applications in several fields, including, more recently, agriculture (Burdusel et al., 2018; Jeevanandam et al., 2018; Giannousi et al., 2017). Hybrid nanoparticles represent an example of versatile nanomaterials with superior advantages compared to monofunctional nanoparticles, allowing the design of nanostructures with different combinations in a unique stable nanostructure, which enables improvement in their application, including in agriculture and food storage (Burdusel et al., 2018; Kumar et al., 2018; Tavaf et al., 2017).

The considerable increase in agricultural production in recent years together with growing concern about environmental issues has accompanied innovation in the area of nanotechnology and nanobiotechnology, where science seeks the development and improvement of materials such as metallic nanoparticles, cationic polymers, and antimicrobial agents (Giannousi et al., 2017; Ahamed et al., 2014). Cu-based nanoparticles have been used as a priming agent post-harvest and in food storage, in addition to enabling some aspects of the harvest, such as an increase in productivity and a reduction in the impacts of abiotic and biotic stress factors, including pest control (Kasana et al., 2017; Ahamed et al., 2014).

2.1 Copper Nanoparticles (Cu NPs) and Copper Oxide Nanoparticles (CuO NPs)

Cu NPs particularly are a type of material with a low cost of production (Gawande et al., 2016; Shobha et al., 2014; Evano et al., 2008). Despite the extensive history of applications and large-scale uses of Cu in various fields, one must always consider the instability that Cu^0 presents under an ambient atmosphere, causing its oxidation (Gawande et al., 2016; Shobha et al., 2014; Hafeez et al., 2015). In this way, methods are being explored for the development of more stable Cu NPs to avoid or minimize the oxidation of this type of nanomaterial, aiming at the development of structurally more complex Cu-based materials, leading to the formation of "core–shell" nanomaterials (Gawande et al., 2016; Giannousi et al., 2017; Hafeez et al., 2015).

Nanotechnology can provide advantages for the agricultural sector to develop more sustainable activities (Hafeez et al., 2015; Gawande et al., 2016). Crop yield is controlled by different and complex characteristics that can be explained by biotic and abiotic factors linked to the genetic issues of each species (Hafeez et al., 2015). According to some studies, the contamination of soil or water caused by various microorganisms can cause disturbances to agricultural health as well as to human health (Ahamed et al., 2014). As such, Cu NPs or CuO NPs find their places in agriculture as part of mitigating actions in irrigation and management, breeding, protection, fertilization, pest control, and production of numerous crops of wheat (*Triticum aestivum* L.), cotton (*Gossypium hirsutum* L.), and lettuce (*Lactuca sativa* L.), among others (Hafeez et al., 2015; Kasana et al., 2017; Pelegrino et al., 2020; Pereira et al., 2021).

Cu itself is an important micronutrient, playing an essential role in plant nutrition and health. Cu NPs and CuO NPs can promote soil remediation, protection against pathogens, and plant growth (Seabra et al., 2014; Rajput et al., 2017; Pelegrino et al., 2020). Some desirable advantages in the application of these nanomaterials are demonstrated by their potential effects on the decrease in post-harvest plant sensitivity, reducing the potential adverse effects observed during the storage, transport, and exposure of the final product (Managa et al., 2018). In this way, Cu-based nanoparticles can improve not only crop production, but also health and food safety when applied in agriculture as fertilizers, herbicides, and antimicrobial agents (Pelegrino et al., 2020; Wang et al., 2019; Kumar et al., 2015).

2.2 Chemical and Biological Routes to Prepare cu NPs and CuO NPs

There are several routes to synthesize Cu-based nanoparticles (Gawande et al., 2016). Metallic and metal oxide nanoparticles can be prepared using physical, chemical, or biological methods (Pereira et al., 2021). Each synthetic route demonstrates advantages and disadvantages, including parameters to control nanoparticle features, such as particle size, degree of agglomeration, surface charge, and morphology (Gawande et al., 2016; Umer et al., 2012; Mijatovic et al., 2005).

Cu NPs and CuO NPs can be synthesized by chemical routes, such as condensation, chemical reduction, and oxidation (Gawande et al., 2016; Ahamed et al., 2014). Basically, the synthesis of Cu NPs is based on the reduction of Cu^{2+}. Commonly, the chemical routes for obtaining nanoparticles are performed under a controlled experimental setting, leading to nanomaterials with controllable size, aggregation state, stability, and morphology (Gawande et al., 2016). However, in some cases, chemical routes might involve high energy input and the presence of toxic chemicals.

In contrast, biological routes to synthesize nanoparticles are considered a low-cost, clean, nontoxic, and eco-friendly approach (Salvadori et al., 2013; Thakkar et al., 2010). Our group has reported the plant-mediated synthesis of CuO NPs for agricultural approaches (Pelegrino et al., 2020; Kohatsu et al., 2021). Green tea-synthesized CuO NPs were applied on lettuce seedlings, in the range of 0.2 and 300 $\mu g\ mL^{-1}$. As expected, low nanoparticle concentrations (up to 40 $\mu g\ mL^{-1}$) enhanced seed germination, whereas higher concentrations (higher than 40 $\mu g\ mL^{-1}$) inhibited seed germination. Moreover, CuO NPs increased the levels of nitrite and nitric oxide, molecules involved in plant growth and defense (Pelegrino et al., 2020). In a further study, green tea CuO NPs were applied (either by foliar application or soil irrigation) on lettuce under greenhouse conditions. Foliar administration of CuO NPs (20 mg per plant) improved lettuce dry weight, number of leaves, CO_2 assimilation, and macronutrient content, enhancing the nutritional value of the lettuce (Kohatsu et al., 2021).

Biogenic synthesis of nanoparticles is based on biological entities that act as reducing agents, leading to the formation of the nanoparticles while promoting their coating, which diminishes nanoparticle oxidation and degradation. Thus, nanoparticles can be biologically synthesized by plants, fungi, some yeasts, and bacteria (Krumov et al., 2009; Rahman et al., 2009; Honary et al., 2012). For instance, Cu NPs were biologically synthesized by various plant extracts, such as gotu kola (*Centella asiatica* L.), flowers (*Aloe vera*), latex (*Calotropis procera* (Aiton) W.T Aiton), brown algae (*Bifurcaria bifurcata* R. Ross), and coffee (*Coffea Arabica* L.) powder extract (Shobha et al., 2014). The Cu source employed can be copper nitrate, acetate, or sulfate, leading to Cu NPs with different sizes and antimicrobial activity (Kasana et al., 2017; Shobha et al., 2014; Lee et al., 2008; Mohanpuria et al., 2008). Overall, biological routes are cost-effective and eco-friendly methods to synthesize Cu-based nanoparticles, and these green routes demonstrate advantages over

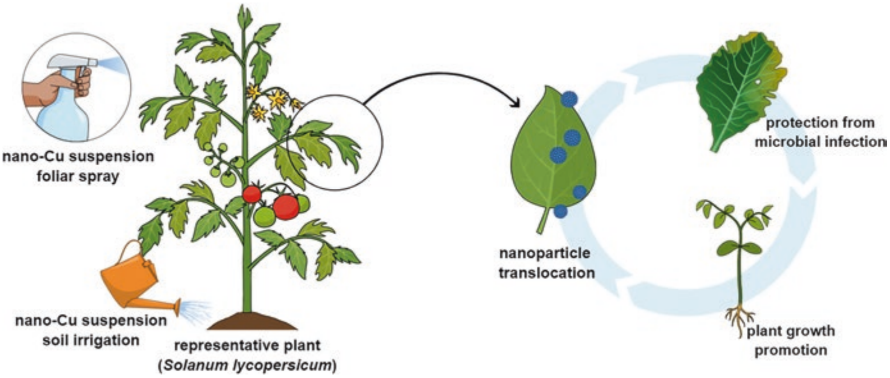

Fig. 1 Schematic representation of copper-based NP application in plants and expected effects

traditional chemical routes (Hafeez et al., 2015; Shobha et al., 2014; Salvadori et al., 2013).

2.3 *Copper-Based Nanocomposites in Agriculture*

In addition to the use of Cu NPs and CuO NPs in agriculture, other kinds of nanomaterials, such as silver (Ag NPs), selenium (Se NPs), silica (SiO NPs), zinc (Zn NPs), and gold (AuNPs) nanoparticles can be used as fertilizers, increasing seed germination and crop growth, in addition to acting as natural pesticides and antimicrobial agents (Pestovsky & Martínez-Antonio, 2017).

Nowadays, versatile nanomaterials can be prepared by using a combination of different kinds of nanoparticles, and thus the synthesis of hybrid nanoparticles consists of the combination of nanomaterials with specific properties to compose a single nanomaterial (Tung et al., 2016). Core–shell nanoparticles might present advantages over simple nanoparticles, enhancing the nanomaterial biocompatibility, stability, and dispersion in the environment in which they are inserted (Iravani, 2020). Some types of nanoparticles that additionally have a layer of another type of nanomaterial or a non-toxic agent end up not only improving the property of the hybrid nanomaterial but also protecting their core against oxidation, degradation, and incompatibility (Wakaskar, 2018; Iravani, 2020; Pestovsky & Martínez-Antonio, 2017).

In this direction, the antimicrobial actions of Cu NPs covered with silica were reported in tomato plants (Carvalho et al., 2019). In a similar approach, Cu silica gel coated with ZnO NPs was effective in bacterial control in plants, proving to be more effective than commercially available Cu-based bactericides (Iravani, 2020; Carvalho et al., 2019). Likewise, iron nanoparticles and Cu NPs increased the antioxidant activity in wheat seeds, inducing resistance against abiotic stress (Pereira et al., 2021). Although each of these nanoparticles, in isolated form, demonstrates a

Table 1 Representative examples of the effects of Cu-based nanopesticides on plants

Nanostructure	Condition and/or species	Pathogen	Dosage	Application	Phytotoxicity	Outcomes	Author
Cu-MoS_2 nanocomposite	*Oryza sativa* cv. Huanghuazhan	*Xanthomonas oryzae* pv. *oryzae* (Xoo)	5 mL (4, 8, 16, or 32 μg mL^{-1})	Foliar spray (detached leaf experiment)	Not reported	The disease severity decreased from 86.25% to 7.5%; increased content of Mo and chlorophyll; induction of the activities of antioxidant enzymes; improved growth of rice seedlings	Li et al. (2020)
CuO nanosheets/$Cu_3(PO_4)_2$ nanosheets/CuO NPs	*Glycine max* (L.) Merrill cv. Seedranch	*Fusarium virguliforme* (Isolate Mont-1)	50 and 250 mg L^{-1}	Foliar (shoot dipping procedure)	Not reported	Reduction in pathogenicity and increased soybean growth; Cu-based nanosheets exhibited greater disease suppression than CuO nanoparticles	Ma et al. (2020)
Cu-curcumin nanocomposite	*Cicer arietinum* L.	*Fusarium oxysporum* f. sp. *ciceri*	0.01% (w/v)	Seed coating	Not reported	Improved germination and seedling growth	Sathiyabama et al. (2020)
Cu NPs + silicon	*Solanum lycopersicum* vr. El Cid F1	*Clavibacter michiganensis* subsp. *michiganensis (Cmm)*	Cu-NPs (50 or 250 mg L^{-1}) + silicon (184 or 460 mg L^{-1})	Foliar spray	Not reported	Synergic effect in reducing the severity of disease and the loss of yield; increased activities of defensive enzymes, lycopene, and β-carotene; reduced glutathione and total phenol contents in the leaves	Cumplido-Nájera et al. (2019)
CuO-alginate nanocomposite	In vitro	*Aspergillus niger*	CuO (0.4%, w/v) + alginate (0.1%. w/v)	Petri dishes	N/A[a]	High inhibition rate on fungal growth (83.17%)	Safaei et al. (2019)

Cu NPs	*Prunus domestica*	*Botrytis cinerea*	100 and 1000 μg mL^{-1}	Fruit (sprayed until runoff)	Not reported	The lowest Cu-NPs dose resulted in more limited inhibition of disease (16%) than the highest dose	Malandrakis et al. (2019)
Cu NPs	In vitro	*Fusarium solani* (strain INECOL_BM-04)/*Neofusicoccum* sp. (strain INECOL_BM-03)/*Fusarium oxysporum* (strain INECOL_CBF-185)	0, 0.1, 0.25, 0.5, 0.75, and 1.0 mg mL^{-1}	Petri dishes	N/A[a]	Higher concentrations promote smaller colony areas; *F. solani* is the most affected fungus at low Cu-NP concentrations (0.1%); *Neofusicoccum* sp. exhibited high tolerance to Cu-NPs at low concentrations	Pariona et al. (2019)
Cu NPs + Se NPs	*Solanum lycopersicum* vr. El Cid F1	*Alternaria solani*	Cu-NPs (10 or 50 mg L^{-1}) + silicon (10 or 20 mg L^{-1})	Foliar spray	Not reported	Combined NMs decreased the disease severity; high doses induced the activity of the antioxidant enzymes and chlorophyll content in leaves; increased vitamin C, glutathione, phenol, and flavonoid contents in fruits	Quiterio-Gutiérrez et al. (2019)
$Cu(OH)_2$-bimetallic nanocomposite/Cu-chitosan nanocomposite	*Gossypium barbadense* cv. Giza 92	*Rhizoctonia solani* AG2-Cot9 and AG4-Cot2	100 μg mL^{-1}	Seed coating	Not reported	Suppression of disease caused by *R. solani* in cotton seedlings	Abd-Elsalam et al. (2018)
Cu-chitosan nanocomposite	*Phoenix dactylifera* cv. Sewi	*Fusarium oxysporum*	50 mL (0, 0.5, 1.0, 1.5, or 2.0 g L^{-1})	Soil	Not reported	Enhanced plant immune response and inhibition of the fungal growth at 2.0 g L^{-1}	Mohamed et al. (2018)

(continued)

Table 1 (continued)

Nanostructure	Condition and/or species	Pathogen	Dosage	Application	Phytotoxicity	Outcomes	Author
Cu-chitosan nanocomposite	*Eleusine coracana* Gaertn.	*Pyricularia grisea*	5 mL (0.1%, w/v)	Foliar spray or seed coating + foliar spray	Not reported	Disease suppression (75% protection in combined application); increased defense enzyme activities	Sathiyabama and Manikandan (2018)
CuO-chitosan nanocomposite	*Cicer arietinum* cv. JG-62	*Fusarium oxysporum* f. sp. *ciceri*	10 mL (100 μg mL^{-1})	Seed coating + soil	Not reported	Disease reduction (46.67%); promotion of plant growth	Kaur et al. (2018)
Cu NP/Cu-Zn-chitosan nanocomposite	In vitro	*Alternaria alternata*/*Botrytis cinerea*	0, 30, 60, or 90 μg mL^{-1}	Petri dishes	Not reported	Significant antifungal activity by both types of nanoparticles at the highest concentration	Al-Dhabaan et al. (2017)
Cu-chitosan nanocomposite	In vitro	*Sclerotium rolfsii*/*Rhizoctonia solani* AG-4	0, 30, 60, or 100 mg L^{-1}	Petri dishes	Not reported	Significant antifungal efficacy against both fungi; higher inhibition of the fungal growth at 100 mg L^{-1}	Rubina et al. (2017)
Cu-chitosan nanocomposite	In vitro/*Zea mays* L. cv. Surya local	*Curvularia lunata*	0.01, 0.04, 0.08, 0.12, and 0.16%, (w/v)	Seed coating + foliar spray	Not reported	Higher activities of antioxidant and defense enzymes; disease control (0.01 to 0.04% on pot experiment and 0.08 to 0.12% on field experiment); enhancement of plant growth	Choudhary et al. (2017b)
Cu-BTC MOF	In vitro	*Candida albicans*/*Aspergillus niger*/*Aspergillus oryzae*/*Fusarium oxysporum*	0, 100, 200, 300, 400, or 500 ppm	Petri dishes	N/A[a]	Effective inhibition of pathogen growth	Bouson et al. (2017)

Cu NPs	*Citrus sinensis* (L.) Osbeck vr. Valencia	*Penicillium digitatum*/ *Fusarium solani*	30 µL (20 µg mL^{-1} for *P. digitatum*, 40 µg mL^{-1} for *F. solani*)	Fruit	Not reported	Cu-NPs induced degradation of fungal DNA post-treatment even with concentrations of 20 and 40 µg mL^{-1} against both pathogens	Khamis et al. (2017)
Cu-graphene oxide sheets	*Lycopersicon esculentum* cv. Shi Hong 9	*Pseudomonas syringae* pv. tomato (Pst) strain	4 or 8 µg mL^{-1}	Foliar spray	Not reported	Reduction in the severity of bacterial speck (below 25%).	Li et al. (2017)
Cu NP	*Camellia sinensis* (L.) O. Kuntze clone UPASI-9	*Poria hypolateritia*	1.5 L $bush^{-1}$ (0, 1, 1.5, 2.0, 2.5 ppm)	Soil	Not reported	Commercial fungicide exhibited superior control followed by NPs at 2.5 ppm; maximum leaf yield was observed with the NP treatment; Cu-NPs impacted positively the soil and its nutrients	Ponmurugan et al. (2016)
Cu NP	In vitro	*Fusarium* sp.	0, 300, 380, or 450 ppm	Petri dishes	N/A[a]	High inhibition of fungal growth (93.98%)	Viet et al. (2016)
CuO NP	In vitro	*Aspergillus flavus*/*A. niger*/*A. fumigatus*/ *Fusarium oxysporium*/*F. culmorum*	0, 25, 50, 75, or 100 µg mL^{-1}	Petri dishes	N/A[a]	100 µg mL^{-1} induced the highest inhibition zone	Vanathi et al. (2016)
Cu-chitosan nanocomposite	*Solanum lycopersicum* Mill. cv. Navodhya	*Alternaria solani*/*Fusarium oxysporum*	10 mL (0, 0.08, 0.10, or 0.12%, w/v)	Foliar spray	0.12% induced a slight decrease in morphological variables during the in vitro assay	Promoted seedling growth and in vitro antifungal activity (with the highest values at 0.10%); the 0.12% concentration was the most effective treatment in disease control during the pot experiment	Saharan et al. (2015)

(continued)

Table 1 (continued)

Nanostructure	Condition and/or species	Pathogen	Dosage	Application	Phytotoxicity	Outcomes	Author
Cu-silica nanocomposite	*Vinca* sp./*Hamlin orange*	*Xanthomonas alfalfae* strain F1 ATCC 49120	90, 450, or 900 ppm of metallic Cu	Foliar spray	*Vinca* sp. exhibited plant tissue damage (moderate to serious damage at 900 ppm); phytotoxicity was absent in *Hamlin orange*	Enhanced antimicrobial efficacy over traditional Cu (II) compounds	Young and Santra (2014)
Cu NP	In vitro	*P. destructiva* (DBT-66)/*C. lunata* (MTCC no. 2030)/*A. alternata* (MTCC No. 6572)/*F. oxysporum* (MTCC no. 1755)	20 μg/disc	Petri dishes	N/A[a]	Significant antifungal activity against all phytopathogenic fungi; *C. lunata* and *A. alternata* showed resistance to the commercial product, but they were sensitive to Cu-NP	Kanhed et al. (2014)
Cu-chitosan nanogels	In vitro	*Fusarium graminearum*	150 μL (0.1%, w/v)	96-well polystyrene microtiter plates	N/A[a]	Strong synergistic effect between cu and chitosan in the inhibition of fungal growth	Brunel et al. (2013)
Cu-chitosan nanocomposite	In vitro	*Alternaria alternata*/*Macrophomina phaseolina*/*Rhizoctonia solani*	0.001, 0.005, 0.01, 0.02, 0.06, and 0.1% (w/v)	Petri dishes	N/A[a]	Cu-chitosan NPs were more effective at 0.1% (89.5, 63.0, and 60.1% growth inhibition of *A. alternata*, *M. phaseolina*, and *R. solani*)	Saharan et al. (2013)

CuO NP/Cu_2O NP/Cu/Cu_2O-nanocomposite	*Lycopersicon esculentum* vr. Belladona	*Phytophthora infestans*	CuO (15 g hL^{-1}), Cu/Cu_2O (30 g hL^{-1}), Cu_2O (34 g hL^{-1})	Foliar spray	Cu_2O-NP and Cu/Cu_2O promoted initial phytotoxicity (3–7 days after application), which disappeared 10 days later	All Cu-based NPs (applied at a reduced concentration of active ingredient) were more effective than the commercial agrochemicals	Giannousi et al. (2013)
Cu NP	*Punica granatum* cv. Bhagwa	*Xanthomonas axonopodis* pv. *punicae* (Xap) strain ITCC BD0003	0, 0.2, 0.4, 0.5, 2, 4, 8, 16, or 20 ppm	Foliar spray (detached leaf experiment)	Not reported	Cu-NP suppressed Xap growth at 0.2 ppm, which is a much lower dosage than that usually recommended for Cu-oxychloride	Mondal and Mani (2012)

[a] N/A: Phytotoxicity assessment does not apply

specific type of antimicrobial activity on crops, turning these nanomaterials into hybrid nanosystems might enhance their advantages for agricultural applications by increasing their antimicrobial activities. Thus, the use of Cu-hybrid NPs in pest control is a promising topic to be further explored.

3 Applications of Cu-Based Nanoparticles as Nanopesticides

Currently, more than 30% of crop production is lost due to various plant diseases caused by bacteria, fungi, viruses, and insects (Rai et al., 2018). Cu-based compounds have been used since early times for pest control, as they are able to damage biomolecules such as DNA, lipids, and proteins (Borkow & Gabbay, 2005). Among various forms of Cu, copper sulfate ($CuSO_4$), copper oxide (CuO/Cu_2O), and copper hydroxide ($Cu(OH)_2$) are the most commonly employed as pesticides, although they present potential risks such as soil damage and environmental hazard (Wilbois et al., 2009). In this field, nanoscaled pesticides demonstrate promising improvement compared to conventional bulk pesticides, promoting better penetration and higher efficiency of Cu (Parisi et al., 2014). Therefore, the evaluation of Cu-based NPs on crops, both as a micronutrient and pesticide, has increased in the last decade. Figure 1 illustrates possible applications of Cu-based nanoparticles in crops, enabling their translocation and action as a micronutrient and/or pesticide.

It should be noted that Cu might positively or negatively affect plants, mainly depending on its concentration. In this direction, the administration of Cu-based nanomaterials in crops might allow sustained and controlled Cu release, avoiding undesired effects. Among different Cu-based nanomaterials, nanostructured $Cu(OH)_2$ has been one of the most studied as a nanopesticide. The increasing number of scientific articles employing nanostructured $Cu(OH)_2$ mainly results from the commercialization of a formulation containing 20-nm needles of $Cu(OH)_2$, Kocide® 3000 (Li et al., 2019). In this sense, Kocide® 3000 has boosted the agricultural market regarding the use of nano-formulations and the research field regarding the evaluation of the benefits and impacts of Kocide® 3000, as well as comparisons with other Cu-based nanoparticles. For example, the beneficial effects of Kocide® 3000 on crops were compared with bulk copper chloride ($CuCl_2$) and CuO and with nanoparticulated CuO and Cu NPs in sugar cane (*Saccharum officinarum* L.) (Tamez et al., 2020). For nanoparticulated formulations, including Kocide® 3000, significant changes were observed in root Cu levels, while the translocation of Cu in the leaves was consistent with all forms of analyzed copper. Moreover, the accumulation of Cu in sugar juice and alteration in the activity of antioxidant enzymes were also observed in the highest evaluated concentration (60 mg kg^{-1}).

Regarding the application of Cu-based nanomaterials as nanopesticides, the long-term effects of $Cu(OH)_2$ NPs were monitored over one year in both soil microorganisms and plants (Simonin et al., 2018). Even after three sequential applications of Kocide® 3000 (6.68 mg L^{-1}), no negative side effects were observed in plants and in the microbiota. Positive effects were verified in plants treated with the $Cu(OH)_2$

product, evidenced by an increase of 27% in the biomass. In contrast, there were no significant modifications in nontarget soil microbiota, corroborating previous publications (Hong et al., 2015; Zhao et al., 2016; Zhao et al., 2017).

Although presenting promising potential, it has been revealed that $Cu(OH)_2$ treatment using Kocide® 3000 was not efficient for reducing bacterial disease (Qushim et al., 2018). Bacterial spot disease was favored by humid weather in tomato plants, which were treated with various commercial products, including Kocide® 3000. Results indicated that $Cu(OH)_2$ nano-needles present in the formulation did not reduce bacterial spot disease severity (Qushim et al., 2018). Furthermore, in a study with tobacco (*Nicotiana tabacum* L.) hornworm (*Manduca sexta*)-infected tomato leaves treated with either Kocide® 3000 or laboratory-synthesized $Cu(OH)_2$ nanowires, it was evidenced that the life-stage of the pest is a key point for the application of $Cu(OH)_2$ nanopesticides, as significant results were observed in the first-instar larvae, but not in the second-instar larvae for both treatments (Li et al., 2019). Interestingly, the growth retardation of tobacco hornworm was higher for Kocide® 3000 than for the laboratory-synthesized $Cu(OH)_2$ nanoparticles. This tendency was associated with the dissolution percentage of Cu ions (five times higher for Kocide® 3000), indicating that the release of the Cu ions is an important aspect for pest control.

Besides $Cu(OH)_2$ nanoparticles, other Cu-based nanoparticulated forms have been used as nanopesticides, such as Cu NPs (Cumplido-Nájera et al., 2019), CuO NPs (Giannousi et al., 2013; Ma et al., 2020; Vanathi et al., 2016), CuS NPs (Shang et al., 2020), Cu-chitosan NPs (Vanti et al., 2020), and Cu-SiO_2 NPs (Xu et al., 2020). Cumplido-Nájera et al. (2019) evaluated the combination of Cu NPs and potassium silicate in the control of *Clavibacter michiganensis* in tomato plants (Cumplido-Nájera et al., 2019). Cu NPs presented spherical morphology, with a size of 42 nm. At both evaluated concentrations (50 and 250 mg L^{-1}), Cu NPs were effective in reducing the plant contamination, inducing the activity of the enzymes superoxide dismutase (SOD), phenylalanine ammonia-lyase (PAL), glutathione peroxidase (GPX), and ascorbate peroxidase (APX). Besides changing levels of key defense compounds in tomato plants, Cu NPs promoted a reduction of 16.1% in yield loss (Cumplido-Nájera et al., 2019).

A similar pattern was observed using Cu NPs against *Alternaria solani* infesting tomato plants (Quiterio-Gutiérrez et al., 2019). The contamination was significantly reduced by Cu NPs, while the activity of antioxidant enzymes increased in the leaves, and GPX activity also increased in the fruit. Moreover, Cu NPs increased the content of nonenzymatic antioxidant compounds, such as vitamin C, chlorophyll, phenols, and flavonoids.

In vitro studies have also evidenced the potential of Cu NPs as nanopesticides (Banik & Pérez-de-Luque, 2017; El-Saadony et al., 2020). Biosynthesized Cu NPs presented a spherical shape and a diameter ranging from 10 to 70 nm, coated with characteristic biomolecules, such as phenols, amines, and alcohol (El-Saadony et al., 2020). When evaluated against *Tribolium castaneum* at six different concentrations (from 50 to 300 μg mL^{-1}), it was observed that Cu NPs were able to promote 100% mortality after 5 days. Moreover, better results were obtained for biosynthesized Cu NPs when compared to chemically synthesized Cu NPs, which might be attributed to the characteristic surface coating. A similar pattern was observed for commercial Cu NPs tested against various pathogenic microorganisms, employing concentrations from 100 to 400 mg L^{-1} (Banik & Pérez-de-Luque, 2017).

CuS NPs are less commonly employed in crops compared to $Cu(OH)_2$ NPs, Cu NPs, or CuO NPs, although CuS NPs have demonstrated promising potential and advantages depending on the targeted application (Shang et al., 2020). CuS NPs demonstrated the highest antimicrobial activity in vitro compared to both control and CuO NPs. In a greenhouse study, rice seedlings (*Oryza sativa* L.) were infected with *Gibberella fujikuroi* and treated with CuS NPs, CuO NPs, and Kocide® 3000. Both forms of Cu nanoparticles effectively inhibited the infection, highlighting the highest efficacy of CuS NPs. In contrast, Kocide® 3000 demonstrated no effect against *G. fujikuroi* infection in rice seedlings. In foliar application, CuS and CuO NPs (50 mg L^{-1}) reduced the infection by 30%, while Kocide® 3000 achieved only 15%.

Cu NPs may also be allied to other molecules and/or nanoparticles. For instance, a nanocomposite based on Cu NPs and chitosan demonstrated 98% inhibition of phytopathogens *Rhizoctonia solani* and *Pythium aphanidermatum*, allied with beneficial effects on chilli (*Capsicum annuum* L.), cowpea (*Vigna unguiculata* (L.) Walp), and tomato plants (Vanti et al., 2020).

4 Phytotoxic Effects of Cu-Based Nanopesticides

Nanopesticides have been developed as an efficient alternative to reduce the impacts of agricultural practices on the environment and on nontarget organisms, creating better crop protection management. However, the effects of these agrochemicals on plants have not been fully characterized, and more research is essential to distinguish the benefits and risks they confer to the agrosystem (Carley et al., 2020).

Different studies in the literature have discussed the dual effect of nanoparticles on crops, which can exhibit both negative and positive impacts. The effects triggered on the plant are dependent on factors such as plant species, size, structure, shape, concentration, stability, and other chemical properties of nanoparticles (Gabal et al., 2018). The toxicity of metal-based nanoparticles to plants may involve at least three different mechanisms: i) released ions from nanoparticles may be toxic to exposed plants, ii) nanoparticle interactions with environmental media may produce chemical radicals able to generate oxidative stress on plants, and iii) nanoparticles interact directly with plants, leading to toxic effects on metabolism (Chen, 2018). Although engineered nanomaterials can suppress crop diseases by directly acting on pathogens through ROS generation (Adisa et al., 2019), the same mechanism, when excessively induced, causes phytotoxicity, leading to plant oxidative damage (Ahmed et al., 2019).

Considering the diversity of studies over the years on Cu-based nanomaterials applied as nanopesticides, a summary of applications and potential phytotoxic effects on plants is presented in Table 1. Some of these are discussed in more detail in the text below.

The application of Cu-based NPs of different compositions and sizes against *Phytophthora infestans* was tested in tomato plants (*Lycopersicon esculentum* var. Belladona) in comparison to the performance of the registered commercially used Cu-based products (Giannousi et al., 2013). Cu_2O NP was the most efficient formulation against *P. infestans* (73.53%) in comparison to all products ten days after application. In general, all Cu-based NPs were found to be effective, while the applied dose of the products was reduced significantly without affecting their efficacy. In addition, phytotoxicity symptoms such as small necrotic spots and some chlorotic spots on the leaves were observed in plants treated with the Cu_2O NPs and Cu/Cu_2O composite nanoparticles, 3 and 7 days after application, which disappeared 10 days after application. However, no phytotoxicity symptoms were found in fruits and flowers. Cu/Cu_2O composite NPs exhibited the highest phytotoxicity (3.75%) compared to the other formulations. This behavior can be attributed to the presence of the metallic core in the NPs, which can be considered more bioreactive than the oxides. Although Cu/Cu_2O composite NPs demonstrate excellent efficiency in suppressing the pathogen growth, their application approaches the limit between plant protection and phytotoxicity.

Young and Santra (2014) reported that a composite material of sol–gel silica host matrix loaded with mixed-valence Cu could be an alternative to conventional biocides against *Xanthomonas alfalfa* strain F1 ATCC 49120. Phytotoxicity studies were performed using *Vinca* sp. and Hamlin orange (*Citrus sinensis* (L.) Osb) under greenhouse conditions to observe potential plant tissue damage. Formulations were sprayed at concentrations of 90, 450, and 900 ppm of metallic Cu, and observations were taken at 24, 48, and 72 h after spray application. Except for $CuCl_2$ and Kocide® 3000 (commercial product), all other treatments containing Cu at 900 ppm induced mild phytotoxic symptoms in *Vinca* sp. 24 h after application. In addition, *Vinca* sp. exhibited moderate to high levels of plant tissue damage 48 h after application of CuSiNG (water-soluble composite copper (II) loaded silica nanogels) and MV-CuSiNG (composite mixed-valence copper loaded silica nanogel), which remained after 72 h. On the other hand, Hamlin orange exhibited strong tolerance to Cu-induced phytotoxicity even at the highest Cu concentration (900 ppm), regardless of the formulation.

Saharan et al. (2015) synthesized chitosan NPs loaded with Cu ions and evaluated their growth promotion and antifungal efficacy in tomato seedlings (*Solanum lycopersicum* Mill cv. Navodhya) under laboratory conditions. Seeds treated with Cu–chitosan NPs (0.08% and 0.10%) showed improved seed germination and seedling growth compared to all other treatments. On the other hand, at the highest NP concentration (0.12%), slight decreases in seedling length, vigor index, and biomass were observed compared to 0.08% and 0.10%, but not when compared to the control (water), chitosan (dissolved in 0.1% acetic acid), and $CuSO_4$ 0.1% (dissolved in water) treatments. Furthermore, the 0.12% concentration was the most effective treatment in disease control during the experiment.

As can be observed in studies from the last eight years that used Cu-based nanoparticles as nanopesticides, there is a lack of information about the possible phytotoxicity conferred by the application of these nanoformulations. A few studies have performed specific analyses or more careful monitoring to detect possible phytotoxic symptoms. As previously described, some symptoms appear some hours after application and may disappear or intensify during the following days, depending on the plant species, nanoformulation type, and concentration (Li et al., 2020; Ma et al., 2020; Sathiyabama et al., 2020; Cumplido-Nájera et al., 2019; Quiterio-Gutiérrez et al., 2019). In addition to the complete characterization of antifungal activity in vitro and in vivo, careful monitoring of plants (visible symptoms, morphophysiological, and/or metabolic alterations) after nanopesticide application is of utmost importance for better characterization of the effects of Cu-based nanopesticides, highlighting the pros and cons of their use for plant protection.

Because the evaluations of effectiveness and potential uses are directly related to the effects on plant growth, some studies in which Cu-based nanomaterials were applied as nanofertilizers reported relevant information about phytotoxicity.

Lee et al. (2008) evaluated in vitro the growth of beans (*Phaseolus radiates* L.) and wheat seedlings, as well as the bioaccumulation of Cu NPs applied at concentrations of 0, 200, 400, 600, 800, and 1,000 mg L^{-1} with an exposure period of 48 h. A decrease in seedling length was observed for both species, reaching the lowest values at the highest concentration (1,000 mg L^{-1}). Beans were more sensitive than wheat to Cu NPs, with the induction of root necrosis. The no-observed-adverse-effect concentrations for wheat root and shoot exposed to Cu NPs were less than 200 and 800 mg L^{-1}, respectively. In addition, bioaccumulation increased with increasing concentrations of Cu NPs. The cupric ions released from Cu nanoparticles had negligible effects in the concentration ranges used in this study, which suggests that the apparent toxicity resulted from Cu NPs.

Hafeez et al. (2015) carried out a study to determine the potential of Cu NPs to enhance the growth and yield of wheat cultivar Millat-2011. Although germination was not affected by Cu NP concentrations up to 0.8 ppm, it decreased significantly with nanoparticle application in concentrations equal to or higher than 1 ppm, using a medium composed of three layers of sterilized filter paper in Petri dishes. Cu NP concentrations higher than 2 ppm were deleterious to wheat plants in solution culture, whereas lower concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 ppm) enhanced seedling growth. When applied to the soil, Cu NPs (10, 20, 30, 40, and 50 ppm) significantly increased the growth and yield of wheat compared with control. The results showed that Cu NPs can enhance the growth and yield of wheat, but their effects are dependent on the concentration and the growth medium.

Zuverza-Mena et al. (2015) evaluated the impact of Cu-based formulations on agronomic and physiological parameters of cilantro (*Coriandrum sativum* L.) plants. The treatments ($Cu(OH)_2$; Cu NPs; Cu µPs (micro-Cu); CuO NPs; CuO µPs (micro-Cu oxide) or $CuCl_2$) were applied at 20 or 80 mg Cu per kg of commercial substrate. Cu NPs, CuO NPs, CuO µPs, and $CuCl_2$ reduced seed germination at both concentrations, while only CuO µPs decreased shoot growth. All Cu-based treatments impaired nutrient accumulation in shoots, except Fe and Ni. The results showed that, even at a low concentration (20 mg kg^{-1}), the Cu-based nanoparticles or compounds might affect plant nutritional quality.

Yang et al. (2015) evaluated the roles of dissolved metal ions in the CuO NP phytotoxicity against maize (*Zea mays* L.) and rice. Root elongation was significantly inhibited by CuO NPs in both species in a concentration-dependent manner (25 to 2000 mg L^{-1}), which was not related to Cu^{2+} release.

The data discussed here show that there is a narrow concentration range between the protective and the phytotoxic effects induced by engineered Cu-based nanomaterials applied to plants as nanofertilizers and/or nanopesticides. Moreover, factors such as nanomaterial concentration, plant species, and exposure route are determinants for the intensity of each effect. Studies need to describe all the conditions involved in the application of nanomaterials and provide as much information as possible about their effects on plants to allow the continuous development of nanostructures aimed at improving agricultural practices.

5 Final Remarks

In recent years, nanotechnology and agriculture have been areas of intensive interest from the scientific, technological, and commercial fields. In general, engineered nanoparticles can be used to promote plant growth and defense against pathogens while increasing crop resistance under biotic stress. Cu is an important micronutrient in plants, participating in several endogenous activities, acting in the metabolism of carbohydrates and proteins as well as being directly involved in the role of chlorophyll synthesis in photosynthesis. However, it is known that the use of Cu at high concentrations can have negative effects on plants.

Cu-based nanoparticles are nanomaterials with potent antimicrobial effects that can be used as pesticides in agriculture. The use of nanomaterials has several advantages over massive (bulk) materials, including higher efficacy and less toxicity. Recently, greener routes to synthesize Cu-based nanoparticles have been widely investigated. These nanoparticles can be prepared using several approaches, their surface can be coated or functionalized with active polymers or other metallic nanoparticles, or they can be incorporated into inorganic or organic materials leading to the formation of hybrid nanoparticles. These strategies can minimize nanoparticle toxicity and maximize their biological effects and biocompatibility. Moreover, Cu-based nanoparticles might have superior effects to commercially used fertilizers, pesticides, and herbicides, which do not contain nanomaterials.

Considering the last few years, several signs of progress have been achieved in using Cu-based nanoparticles as pesticides in agriculture. However, further studies are still required to better understand the phytotoxicity of these nanoparticles. It is essential to highlight that the safe and conscious use of nanomaterials in different crops could minimize ecological impacts, such as pollution and ecotoxicity. Thus, recent efforts have been focused on understanding and improving nanomaterials to mitigate unwanted effects on plants and the environment. The use of Cu-based nanoparticles as active agents in pesticides is a promising and realistic approach in agriculture.

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Nanoparticles in Biosensor Design for the Agrifood Sector

Francesca Petronella, Amina Antonacci, and Viviana Scognamiglio

Abstract In the last years, there was an increasing demand for portable, affordable, and effective diagnostics for the agrifood sector. Advances in nanotechnology have led to the design of nanostructured (bio)sensors with excellent analytical features in terms of stability, sensitivity, specificity, and versatility. Nanoparticles play a crucial role in the design of smart nano(bio)sensors, demonstrating their ability to enhance the analytical performances of such diagnostics when exploited as transducers, signal amplifiers, biocomponent labels, support modifiers, as well as to design nanoelectronics, microfluidics, and lab-on-chip. This has allowed for the development of nano(bio)sensors custom-made for specific purposes according to the need of the whole agrifood system, from crop field monitoring to food processing, packaging, and storage, as well as for the assessment of food quality and safety. Herein, we report an overview on nanoparticle classification, synthesis, and characterization, as well as their exploitation in the design of nano(bio)sensors for the agrifood sector.

Keywords Nanoparticles · Green nanoparticles · Biosensors · Agrifood field

1 Introduction

As stated by Srivastava and co-workers "*Nanotechnology puts the impetus to revolutionize the area of diagnostics in health, medicine, food, environment, and agriculture sector, transitioning theoretical aspects into the practical output*" (Srivastava et al., 2018). Nanostructured (bio)sensors for the agrifood system are a crucial

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example of technology that take advantages from the smart use of nanoparticles to improve key analytical performances as sensitivity, stability, and selectivity (Antonacci et al., 2018).

Nanoparticles (NPs) are a wide class of materials that include particulate substances with dimension less than 100 nm. Thanks to their nanodimensions, nanoparticles show unique optical and electrical properties that make their incorporation into (bio)sensor configurations particularly attractive, as large reactive surface, small particle size, finely adjustable optical properties, and the ability to modify the surface. To this aim, nanoparticles play a significant part in the development of (bio) sensors as transducers, mediators, support modifiers, platforms for the immobilization of biocomponents (DNA, enzymes, antigens, or antibodies), biocomponent labels, as well as to design nanoelectronics, microfluidics, and lab-on-chip (Attaallah et al., 2020a).

Nanoparticles can be classified according to the size, morphology, physical, and chemical properties, and include a wide range of nanostructured materials such as carbon-based, ceramic, metal, semiconductor, polymeric, and lipid-based nanoparticles as well as quantum dots and dendrimers. Depending on the overall shape these materials can be 0D, 1D, 2D, or 3D. As described by Jeevanandam and colleagues, "*this classification is highly dependent on the electron movement along the dimensions*": in 0D nanoparticles electrons are entrapped in a dimensionless space; in 1D nanoparticles electrons can move along the *x*-axis; in 2D and 3D nanoparticles electron movement occurs along the *x*-*y*-axis, and *x*, *y*, *z*-axis respectively (Jeevanandam et al., 2018).

The use of nanoparticles dates back to more than 4.500 years ago when natural asbestos nanofibers have been exploited for the reinforcement of ceramic matrices (Box 1).

Since then, diverse sources have been available for the obtainment of different types of nanoparticles. Such sources can be classified into three main categories based on their origin:

1. Incidental nanoparticles: are incidentally produced as a byproduct of industrial processes from vehicle engine exhaust, welding fumes, combustion, and natural process as forest fires, photochemical reactions, volcanic eruptions, and dust storms.
2. Engineered nanoparticles: are purposely manufactured to have desired features for specific applications.
3. Naturally produced nanoparticles: can be found in living organisms ranging from microorganisms, such as bacteria, algae, and viruses, to complex organisms, as plants, insects, birds, animals, and humans.

Plants, for example, utilize nutrients available in soil and water leading to their accumulation in nanofibers with diverse purposes, e.g., nanocellulose as the main component of stems, leaves, and roots or leave's nanostructures to confer as insects sliding, mechanical stability, super-wettability, superhydrophobicity, as well as visible light, radiation, and harmful UV protection. Algae are also known to support the formation of nanoparticles. Both macroalgae as *Turbinaria ornate* (Ashokkumar

& Vijayaraghavan, 2016) and microalgae as *Chlorella vulgaris* (Hosea et al., 1986) have been described capable of forming gold nanoparticles, as well as diatoms as *Phaeodactylum tricornutum*, which, exposed to Cd, forms Cd-PC complexes in which sulfide ions can be incorporated to stabilize PC-coated CdS nanocrystallites (Scarano & Morelli, 2003). Furthermore, scientists are trying to exploit these organisms to synthesize more environmentally friendly nanomaterials by green ways with the aim to reduce risks to the environment and human health (Box 2).

Several (bio)sensors have been developed exploiting nanoparticles to be applied in the agrifood sectors, from the field to the fork. Nano(bio)sensor applications include the evaluation of the main physico-chemical parameters in the crop field (e.g., temperature, humidity, seed viability, soil quality, or the presence of residual pesticides, fertilizers, toxins, and plant pathogens) (Arduini et al., 2020; Scognamiglio et al., 2016a), food processing monitoring, food quality and safety assessment, food packaging and storage (Scognamiglio et al., 2016b; Arduini et al., 2016).

In the following sub-chapters, nanoparticle classification as well as synthesis and characterization are described, and their exploitation in the design of innovative nanostructured (bio)sensors for the agrifood sector reported according to the literature of the last few years.

2 Nanoparticle Classification

2.1 Carbon-Based Nanoparticles

Carbon-based nanoparticles can assembly into allotropic structures thus forming fullerenes and nanotubes (CNTs). The first are globular hollow cages constituted by carbon atoms arranged into pentagonal and hexagonal units, while each carbon is sp^2 hybridized. CNTs are tubular structures 1–2 nm in diameter made of rolled graphite sheets which can arrange into single-walled (SWNTs), double-walled (DWNTs), or multi-walled carbon nanotubes (MWNTs), respectively. Both fullerenes and CNTs have been used in pristine form and in nanocomposites in the design of many (bio)sensors for the agrifood field. CNTs have been coupled with molecularly imprinted polymers (MIPs) for the selective and sensitive detection of fisetin, a flavonoid with high antioxidant properties, and thus exploited for the production of dietary supplements (Ma et al., 2020). In detail, the authors realized a porous MXene/NH2-CNTs film by self-assembly of negatively charged Ti_3C_2Tx MXene flakes and positively charged NH_2-CNTs. These latter demonstrated their capability as interlayer spacers able to inhibit the aggregation of MXene flakes to form a well-defined porous structure (Fig. 1a). This resulted in an increased surface area for MIPs immobilization and thus to an enhancement of the electrical conductivity and electrocatalytic activity. This configuration allowed for the obtainment of a good linear relationship with fisetin concentration ranging from 0.003 to 20.0 μmol L^{-1} with a limit of detection of 1.0 nmol L^{-1}.

DWCNTs in combination with graphene have been employed to form a hybrid film synthesized on polycrystalline copper foil to modify the electrode surface of screen-printed electrodes with the aim to increase the electroactive surface area by 1.4 times and the electrochemical current by 2.4 times (Fig. 1b). This transparent and conductive hybrid film was used for the electrochemical detection of arsenic(V) by cholesterol oxidase in the range from 1 to 10 ppb, with a limit of detection of 0.287 ppb (Duoc et al., 2020). Such a sensitive sensor can be useful for the monitoring and the arsenic migration assessment in agricultural soils and crops.

Copper oxide-decorated MWCNT has been prepared to detect lactic acid (Hussain et al., 2020), which can find useful application for lactate online monitoring in fermentation processes. The CuO·MWCNT thin layer was exploited for the nanomodification of a flat glassy carbon electrode (GCE, surface area = 0.0316 cm^2) (Fig. 1c) and lactic acid was detected through a dependable current-voltage procedure within a linear range of concentrations between 100.0 pM and 100.0 mM, a sensitivity of 633.0 pA μM^{-1} cm^{-2}, and a detection limit of 88.5 pM.

Other carbon-based nanoparticles encompass carbon black nanoparticles (CBNPs), characterized by carbon nanoparticle aggregates with diameters from 17.95 to 32.5 nm (Arduini et al., 2010). This nanomaterial also showed its high potential for biosensor development, thanks to its large number of defect sites, high electroactive surface area, great number of edge plans, and oxygenate species (Cinti et al., 2015). Arduini's group developed many biosensors for pesticide monitoring exploiting CB for the nanomodification of screen-printed electrodes to enhance the sensitivity of cholinesterase enzymes (Arduini et al., 2015). CB has been used also in combination with whole cells of *C. reinhardtii* to monitor the algae evolution of oxygen for herbicides analysis (Attaallah et al., 2020b). In detail, an electrochemical algae-based biosensor was designed immobilizing algae cells on carbon black-modified screen-printed electrodes (Fig. 2), using carbon black to sensitively monitor variations in algae oxygen production during the photosynthetic process. Atrazine was detected in a concentration range from 0.1 to 50 µM, with a linear range from 0.1 to 5 µM and a detection limit of 1 nM.

2.2 Metal Nanoparticles

Metal nanoparticles are made of pure metals (e.g., gold, platinum, silver, titanium, zinc, cerium, iron, and thallium) or their compounds (e.g., oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides). Metal nanoparticles' opto-electrical

Fig. 1 (continued) Copyright (2021) Elsevier journals. (**b**) Principle of fabrication of the DWCNTs-Gr hybrid thin film and using it as electrochemical electrode structure for detection of As(V). Reprinted with permission from (Duoc et al., 2020), Journal of Hazardous Materials, Copyright (2021) Elsevier journals. (**c**) Preparation of CuO·MWCNT NCs by using a wet-chemical technique, electrode modification, and expected current-voltage (I-V) curve regarding detection of a bio-molecule. Reproduced from Ref. (Hussain et al., 2020) with permission from the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry

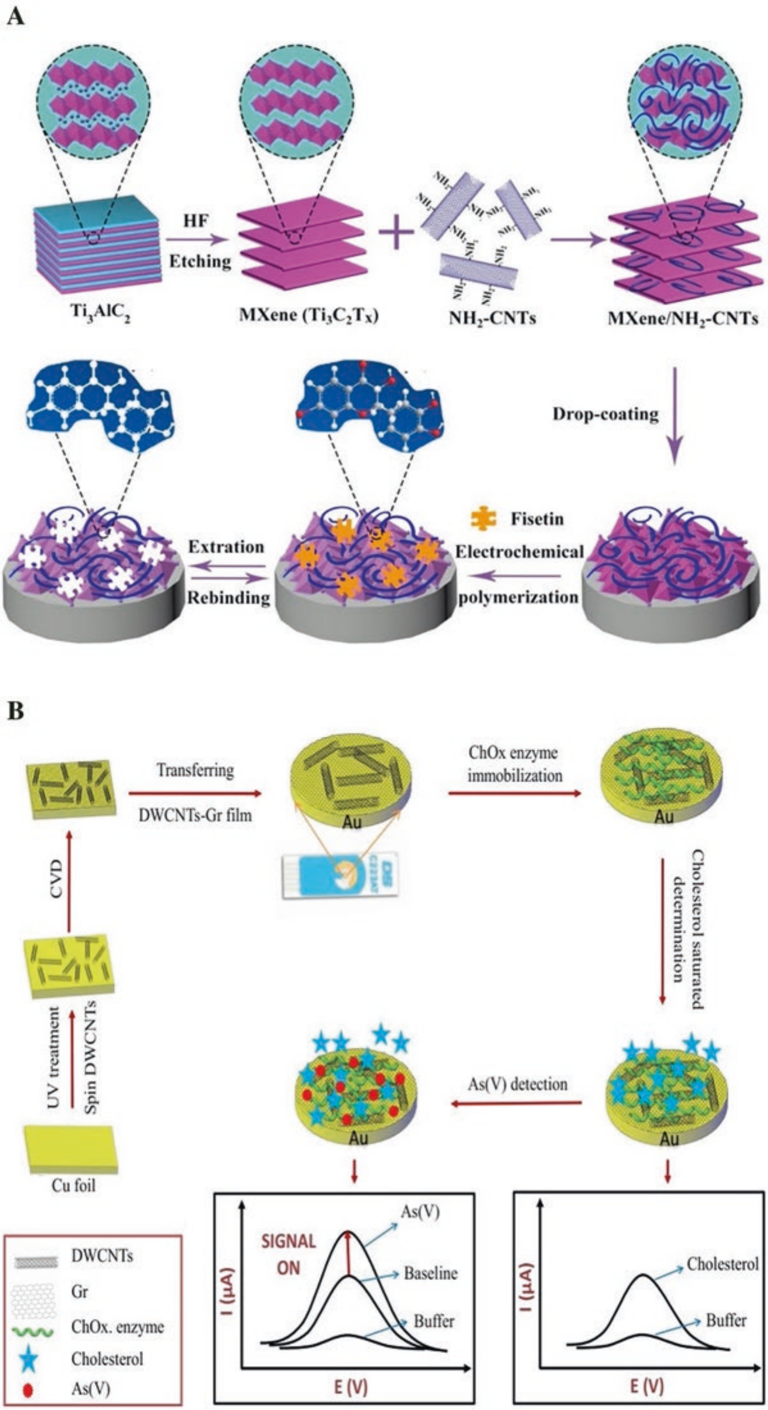

Fig. 1 (**a**) Fabrication scheme of the electrochemical sensor based on hierarchical porous MXene/Amino carbon nanotubes (MXene/NH_2-CNTs) composite and molecularly imprinted polymer (MIP). Reprinted with permission from (Ma et al., 2020), Sensors and Actuators B: Chemical,

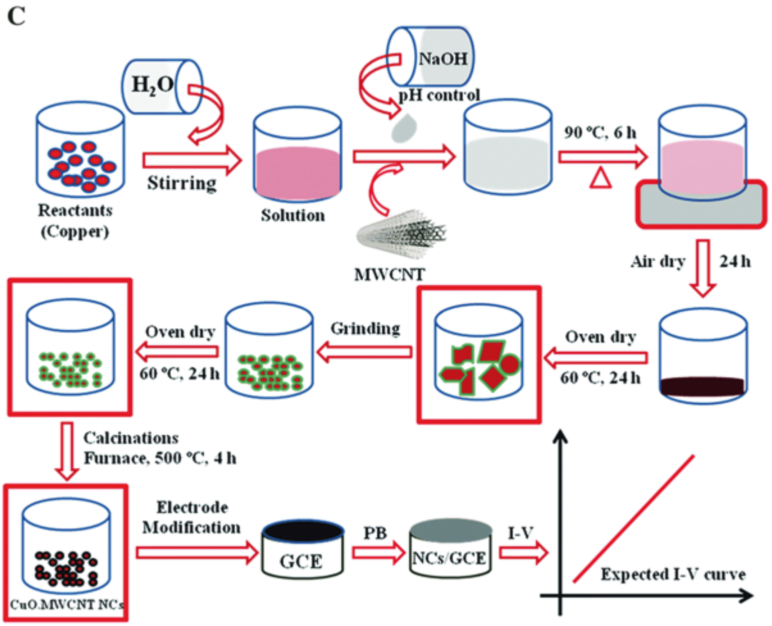

Fig. 7.1 (continued)

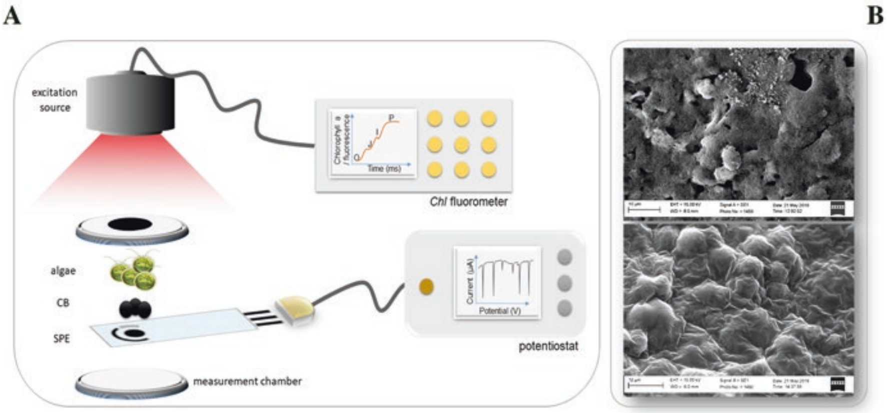

Fig. 2 (**a**) Scheme of the CC125/CB-SPE biosensor set up. (**b**) Scanning electron microscopy image of carbon black modified screen-printed electrode in the absence (top image) and in the presence (bottom image) of immobilized *C. reinhardtii* CC125. Reprinted with permission from (Attaallah et al., 2020b), Biosensors and Bioelectronics, Copyright (2021) Elsevier journals

properties and chemical reactivity is closely connected to their elementary composition, atomic arrangement, shape, and size.

Gold nanoparticles (AuNPs) have found noteworthy use in agrifood thanks to: (a) chemical stability, and thus less toxicity; (b) simple synthesis and manufacturing; and (c) biocompatibility with, e.g., antibodies, enzymes, and nuclei acids.

Figure 3 shows an example of AuNPs' different sizes and shapes, showing characteristic colors and properties. In particular, AuNPs' color changes according to size variation, aspect ratio, nanoshell thickness, and dimension of gold domains.

Several (bio)sensors have been realized thanks to the astonishing properties of AuNPs. A very recent example reported in literature describes the design of an electrochemical biosensor exploiting AuNPs decorated with MIPs for the electrochemical detection of ethephon, a plant hormone widely used in crop fields, using potassium ferricyanide as a probe. In this configuration, reported in Fig. 4a, AuNPs demonstrated their ability to act as carrier to load a high MIP amount, and increase the electron-transfer rate and thus the sensitivity by three orders of magnitude. Ethephon was quantified within the linear concentration range from 1.0×10^{-13} to 1.0×10^{-9} mol L^{-1} and a detection limit of 2.78×10^{-14} mol L^{-1}, also in apple with satisfactory data (Li et al., 2020).

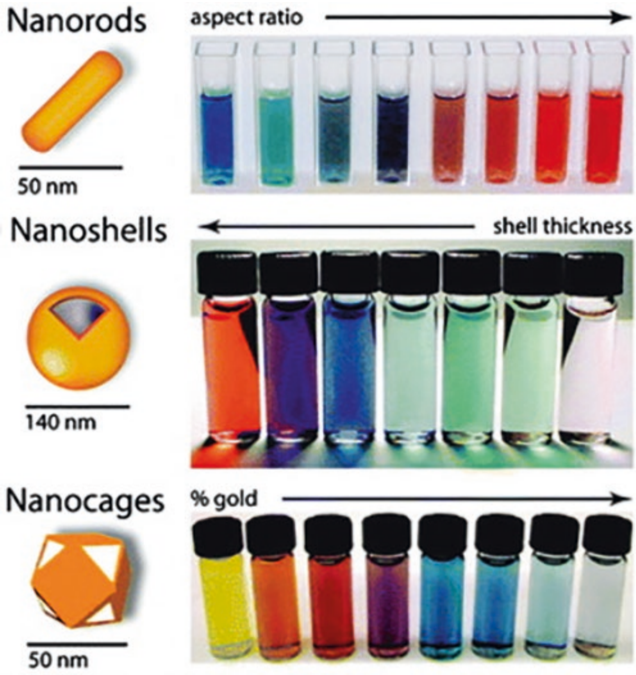

Fig. 3 Color dependence of AuNPs on size and shape. Reproduced from Ref. (Dreaden et al., 2012) with permission from the Royal Society of Chemistry

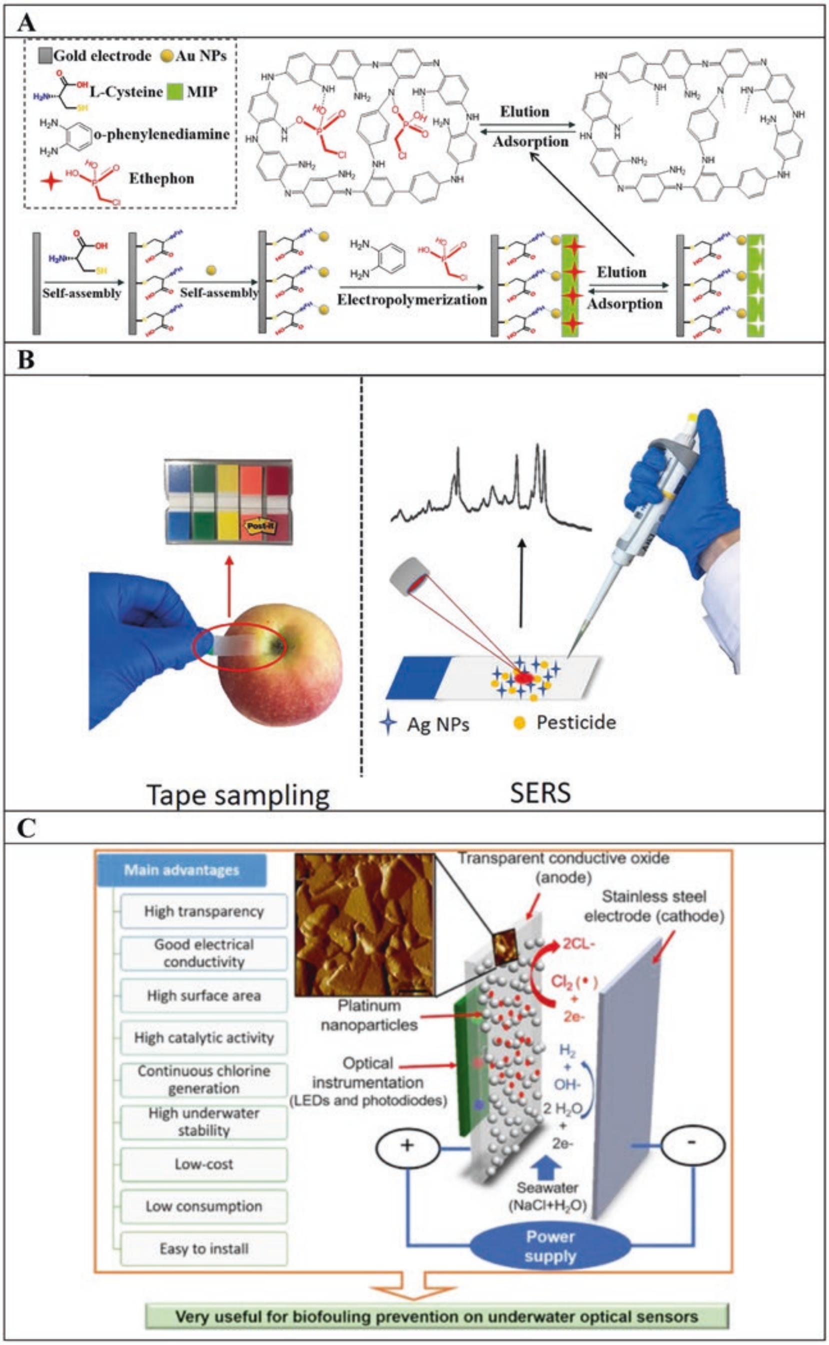

Fig. 4 (**a**) Procedure for fabricating the switch sensor to detect ethephon. Reprinted with permission from (Li et al., 2020), Biosensors and Bioelectronics, Copyright (2021) Elsevier journals. (**b**)

Silver nanoparticles (AgNPs) have also proven to be an important group of nanoparticles for biosensing approaches, due to their high conductivity and excellent biocompatibility. Indeed, highly sensitive and specific sensors based on silver nanoparticles created the possibility of developing novel analytical tools for the early detection of biological and infectious agents of plants. In some configuration, AgNPs have been optimized for coupling with optical detection techniques. It is the case of the simple and rapid method developed for pesticide detection on fruit surfaces by applying AgNPs directly on the surface of adhesive tape (Fig. 4b) and following the analysis by surface-enhanced Raman scattering (SERS) technique (Gong et al., 2019). This system was demonstrated to be capable of measuring triazophos on apple peels with a limit of detection of 25 ng/cm^2 in 5 min and without sample preparation.

Platinum nanoparticles (PtNPs) were also demonstrated to help improve the analytical performances of biosensors when coupled for example with optical transduction. In this case, an antibiofouling strategy was proposed using low-cost, transparent, and highly efficient electrodes based on platinum nanoparticles coated fluorine tin oxide (FTO) (Pinto et al., 2021). This combination of materials (Fig. 4c) demonstrated to be capable of creating high optical transparency and thus high catalytic properties, high durability, high stability, and low consumption (100–350 μW/cm^2).

2.3 Semiconductor Nanoparticles

Semiconductor nanoparticles are prepared exploiting different elements, resulting in GaN, GaP, GaAs, InP, and InAs from group III-V, ZnO, ZnS, CdS, CdSe, and CdTe from group II-VI of the periodic table, while silicon and germanium are mainly exploited from group IV. Clusters with a size between 1 and 100 nm^3 are considered as nanoclusters, nanocrystals, and quantum dots. Predominantly, when the size dimension ranges between ~1 and 10 nm, the term quantum dots (QDs) is usually exploited (Benoit & Choi, 2017). These nanoparticles show significant alteration in properties thanks to their wide bandgaps, which can be tuned to obtain desired features, as quantum size effects, nonlinear optical properties, and luminescence. For this reason, semiconductor NPs are suitable as labels, tracers, and reactants in the design of photo optics and electronic devices. A very recent biosensor exploiting QDs decorated with ad hoc designed biomimetics was described for atrazine recognition (Giardi et al., 2021). In particular, novel artificial peptides were designed and synthesized to mimic the plastoquinone binding niche of the D1

Fig 4 (continued) Schematic representation of the rapid SERS food safety screening method with adhesive tape sampling on fruit peels. Reprinted with permission from (Gong et al., 2019), Food chemistry, Copyright (2021) Elsevier journals. (**c**) Schematic representation of the new approach for biofouling prevention by seawater electrochlorination. The anode electrode is constituted by Pt nanoparticles coated transparent conductive oxide thin-film supported on glass substrate, responsible for chlorine generation in the sensitive area of the optical sensor. Reprinted with permission from Pinto et al. (2021), Chemical Engineering Journal, Copyright (2021) Elsevier journals

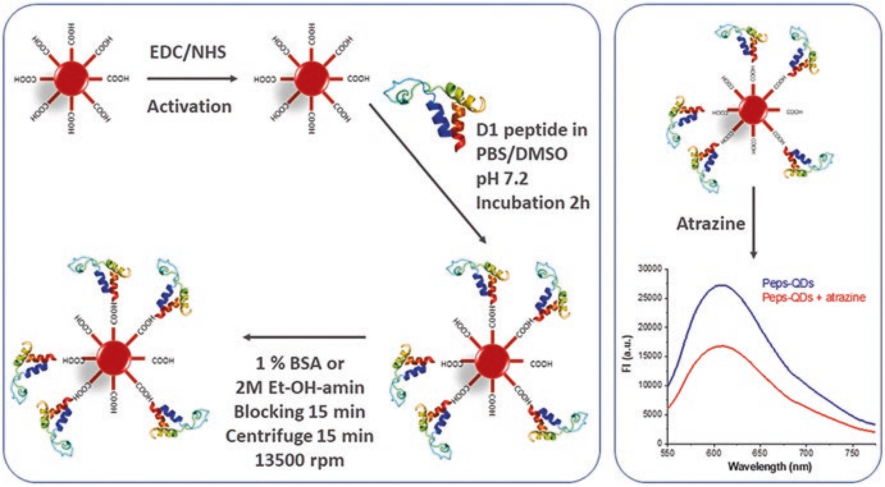

Fig. 5 Schematic representation of the approach used for the production of photosynthetic peptides-functionalized QDs (left). Fluorescence response of Peps-QDs to atrazine (right). Reprinted with permission from (Giardi et al., 2021), Talanta, Copyright (2021) Elsevier journals

protein from the green photosynthetic alga *Chlamydomonas reinhardtii* also able to bind herbicides. Such peptides were functionalized with QDs for the design of a hybrid optical biosensor for atrazine (Fig. 5), with detection limits in μg/L concentration, meeting the requirements of E.U. legislation. In this study, carboxylated QDs were exploited, being versatile, stable, and cost-effective nanomaterials. In addition, they are able to confer water solubility, making the hybrid molecule-nanoparticle flexible also in different biological environments.

3 Nanoparticle Synthesis

A plethora of strategies are now available for the synthesis of nanoparticles. The traditional classification of synthesis methods identifies two main categories: top-down approaches and bottom-up synthesis. The formers essentially consist of reducing the size of bulk materials down to obtaining nanomaterials. In contrast, the bottom-up methods produce nanomaterials by using chemical strategies that enable an atom-by-atom assembly.

Recently, the biological synthesis of nanoparticles (synthesis mediated by micro-organisms or in the presence of naturally occurring molecules) is gaining increasing attention as green and affordable methods for nanoparticle preparation. Indeed, the development of synthesis protocols compliant with green chemistry principles is highly desired. However, many efforts are still required to implement green methods for producing high-quality nanocrystals appropriate for precise applications.

The following section intends to briefly introduce some examples of top-down approaches and provides a deeper description of bottom-up synthesis, focusing on solution-based methods. They can provide higher degrees of freedom in nanomaterial design and preparation in terms of chemical compositions, crystallinity, morphology, and surface chemistry. Moreover, bottom-up synthesis approaches enable the fabrications of high-quality nanocrystals uniform in size, shape, and with high crystallinity. As a consequence, the obtained nanomaterials are regarded as valuable building blocks for the development of a variety of sensors and biosensors.

3.1 Top-Down Methods

Top-down methods consist of the progressive and controlled desegregation of bulk material down to a nanostructure. Mechanical milling, such as ball milling, is a typical example of a top-down method. This process performs a grinding of bulk material in smaller particles, reducing the size by the progressive attrition of the bulk material. It is a time-consuming and energy-consuming method, and produces nanostructures with broad size distribution and a non-uniform morphology (Virji & Stefaniak, 2014). Conversely, nanoparticles extremely uniform in size and shape can be achieved by laser ablation (Szuromi, 2017). Laser ablation makes use of pulsed lasers (nanosecond pulsed laser) to remove and vaporize material up to obtaining nanoparticles.

A laser beam focused on a solid target causes a temperature increase on the area where the light is focused, resulting in the vaporization of the target material and in the generation of ions and electrons (due to the collisions involving the vaporized species). Thus, electrons and ions forming the plasma plume coalesce and aggregate promoting the formation of nanoparticles.

The resulting nanoparticles can be generated in gas phase, liquid phase, and can potentially be deposited from the plume onto a defined substrate. However, the preparation of nanostructures, directly on a defined substrate, can be achieved also by lithography.

The production of nanoparticles by lithography can occur via the controlled deposition of a coating or by the controlled ablation of layers, from a specific substrate (Jose Varghese et al., 2019).

3.2 Bottom-up Syntheses

3.2.1 Solution-Based Methods for Nanocrystal Growth

Bottom-up syntheses are chemical approaches, allowing to build nanocrystals atom by atom. The bottom-up methods and, in particular, solution-based methods enable a high control over the chemical-physical properties of nanoparticles, including size, shape, surface chemistry, crystallographic structure, and exposed crystal facets. This makes possible an a-priori nanocrystal design for the specific application. The morphological control can be achieved by using static and dynamic templates, used for directing the size and morphology of the resulting nanocrystals, and preventing uncontrolled growth. Static templates are host materials that are exploited to grow nanoparticles in a nanoscopic constrained environment (Jeong et al., 2005). They include host zeolite, porous membranes, and carbon nanotubes that can be removed after the nanocrystal synthesis step, resulting in a nanostructure of a defined shape (van Bommel et al., 2003).

Undoubtedly, the use of static templates for nanocrystal preparation enables excellent morphological control; however, from an application point of view, greater opportunities arise from colloidal nanocrystals. Colloidal nanocrystals are crystalline solids, whose dimensions (ranging from 0 to 100 nm) and their surface chemistry make them perfectly dispersible in liquids (likewise the well-known colloids). Moreover, due to their peculiar surface chemistry, colloidal nanocrystals can be easily engineered, for instance, by properly modifying their surface by introducing new functionalities, suitable for the desired application as discussed in Sect. 4.

For the synthesis of colloidal nanocrystals, the colloidal strategies often exploit dynamic templates as shape directing agents. Dynamic templates are organic molecules able to control the nanocrystal growth directly in solution. Micelles and inverse micelles can be regarded as dynamic templates that, in the course of the synthesis process, can behave as “nano-reactors”, yielding to nanocrystals whose shapes resemble those of the micelles themselves.

However, high-quality colloidal nanocrystals can be effectively prepared by using surfactants, namely amphiphilic molecules characterized by a hydrophilic part such as a polar or a charged functional group, and a hydrophobic moiety, as one or more hydrocarbon chains.

Important, the hydrophilic moiety of surfactants, commonly used for colloidal synthesis of nanocrystals, should preferably bear a functional group characterized by a lone pair such as alkyl thiols, amines, carboxylic and phosphonic acid, phosphine, phosphine oxides, phosphate, and phosphonates. These functional groups are able to chemically coordinate the *monomer*, namely the reaction intermediate generated from the decomposition of the chemical, suitably selected as a *precursor* of the desired nanocrystals. Such a process is the key step of the colloidal synthesis routes suitable for achieving colloidal nanocrystals and nanocrystal-based heterostructures (Cozzoli et al., 2006).

Several colloidal routes are reported in the literature for nanocrystal synthesis including precipitation methods, co-precipitation methods, and thermal decomposition in coordinating solvents and seed-mediated techniques. As previously mentioned, the general scheme for nanocrystal synthesis involves three components: precursors, organic surfactants, and solvents. In some cases, the organic surfactants can also be used as a reaction solvent.

At a suitable temperature, the precursor transforms into the active atomic species or into the molecular species (monomers coordinated by the surfactant). The monomers are then converted into nanocrystals, whose growth is governed and controlled by surfactants and by reaction temperature. From a kinetic standpoint, the nanocrystal formation is regarded as a two-step process involving the nucleation of initial "seeds" (step 1) and the growth of nuclei (step 2).

In the nucleation step, precursors decompose forming monomers, after that, a burst of nanocrystal nucleation occurs. These nuclei grow by incorporating additional monomers still present in the reaction medium.

As the growth proceeds, a concentration gradient of supplying material from the bulk of the solution occurs, therefore the system enters a diffusion-limited growth regime, where the growth rate is given by the following Eq. 1.

$$\frac{\delta r}{\delta t} = K_d = \left(\frac{1}{r} - \frac{1}{d}\right) \cdot \left(\frac{1}{r^*} - \frac{1}{r}\right) \tag{1}$$

that illustrates the nanocrystal growth rate ($\delta r/\delta t$) as a function of mean nanocrystal size (r). In this equation, K_d includes the diffusion coefficient, d is the thickness of the diffusion layer around the particles, and r^* is the critical radius, namely the size at which the nanocrystal surface energy is such that nanocrystals neither grow nor shrink, therefore the growth rate is zero.

The critical radius value r^* depends on the monomer concentration. When the monomer concentration is high, and $r > 2r^*$ smaller nanocrystals grow faster than the larger ones therefore the nanocrystal mean size is uniform, the size distribution is narrow, and the system is under the so-called focusing regime (red track in Fig. 6). Conversely, the "defocusing regime" occurs when the monomer concentration determines: $r^* < r < 2r^*$. In this condition (blue track, Fig. 6), the larger nanocrystals grow faster than the smaller ones determining a wide size distribution. Moreover, when $r < r^*$ Ostwald ripening occurs: the larger particles get further enlarged at the expense of the smaller ones that, in fact, progressively dissolve.

As a consequence, the goal to produce high-quality nanocrystals with a uniform size distribution can be achieved by maintaining the focusing regime and, therefore, by keeping high and uniform the monomer concentration. This is possible by separating in time the nucleation step from the growth step so that nucleation must occur on a short time scale, and the growth can occur while monomers are slowly released in the reaction mixture (Jeong et al., 2005; LaMer, 1952; Yin & Alivisatos, 2005).

Such strategies are exploited in a colloidal synthesis technique known as "hot-injection in coordinating solvent" or "hot-injection" technique.

3.2.2 The "Hot-Injection" Technique

The hot-injection techniques enable the production of highly crystalline, monodisperse colloids by realizing a discrete nucleation event followed by a slower controlled growth on the existing nuclei, ensuring at the same time a constant reservoir of monomers.

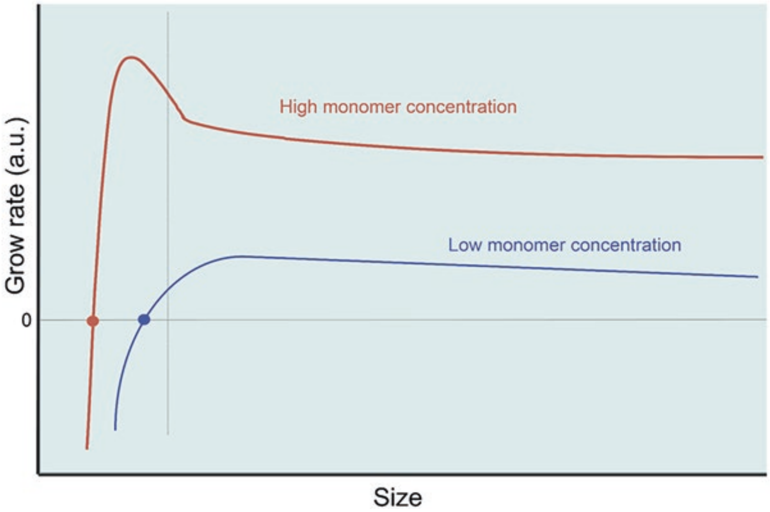

Fig. 6 According to the monomer concentration, nanocrystals can grow in "focusing" and "defocusing" mode and, therefore with a narrow or a broad size distribution, respectively. The value of the critical size depends on monomer concentration. The red track qualitatively indicates the particle growth rate as a function of their size at a high monomer concentration. In this condition the critical size is small and smaller particles grow faster than larger ones, resulting in a uniform (narrow) size distribution labeled as "focusing regime". On the contrary, when the monomer concentration is low (blue track) smaller nuclei growth is slower than the growth of bigger nuclei, thus causing a broad size distribution indicating a "defocusing regime"

The method involves the injection of the solution of precursor molecules (at room temperature) into a high temperature (100–350 °C) mixture of surfactants that also behaves as a reaction solvent. The rapid injection causes instantaneous nuclei formation, raising the monomer species concentration above the nucleation threshold. The precursor injection causes a temperature drop that stops the nucleation event, keeping it temporally separated from the successive growth stages. Moreover, in these conditions, the growth proceeds at a temperature lower than the injection temperature, so that the monomers are slowly released in the reaction mixture, and the system is kept in the focusing regime for a long time, thus resulting in narrow size distribution.

In this process, the surfactants play an essential role as reaction solvents that at the same time control the nanocrystal morphology in terms of size and shape. The surfactants, by dynamically coordinating the forming nanocrystals' surfaces, form a steric barrier for reactants that effectively stabilize the growing clusters, prevent them from agglomerating, and enable the slow addition of monomers to the particle surface ensuring a uniform size distribution.

Remarkably, selecting a suitable surfactant or a mixture of surfactants is essential to drive the resulting nanocrystals' shape.

Surfactants, indeed, can selectively absorb on a specific surface of the nanocrystal at the initial stage of its growth. In this way, surfactants minimize the surface

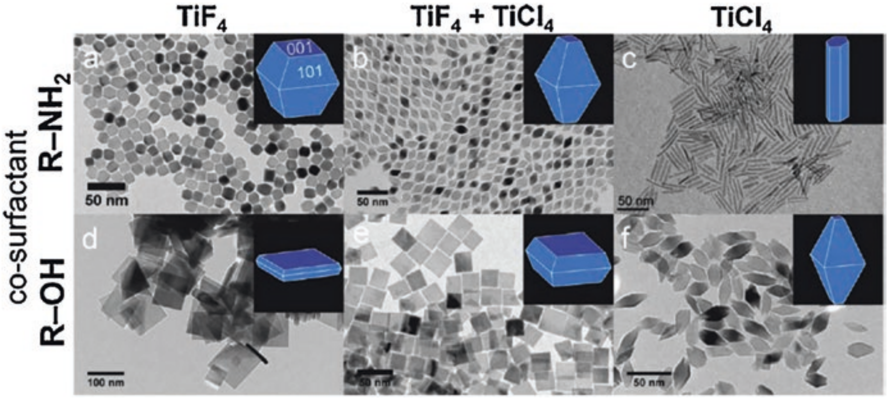

Fig. 7 TEM micrographs of TiO_2 nanocrystals that show how it is possible to control the size and the shape (dominant crystal facets) by selecting appropriate precursors or mixture of precursor (from **a** to **c**). The TEM micrographs demonstrate also how the proper combination of surfactant and precursor affects the resulting shape of nanocrystals. The comparison of micrographs **c** and **f** shows that if $TiCl_4$ is selected as a TiO_2 nanocrystal precursor, amine terminating surfactants promote the growth of nanorods, while hydroxyl terminating surfactants induce the growth of nanobypyramids. The micrographs d and e highlight the effect of using a pure precusor (TiF_4 in **d**) and a mixed precusor (TiF_4 and $TiCl_4$ in **e**) with a while hydroxyl terminating surfactant. Reprinted from (Gordon et al., 2012), Copyright 2021

energy of the crystal facets where they bind, minimizing their growth, and thus promoting the growth of other nanocrystal surfaces that, instead, have higher surface energy values, because they are not stabilized by the surfactant(s). In other words, the strategy for achieving nanocrystal shape control relies on the different surface energies possessed by the different crystallographic facets of the forming nanocrystals, and by the possibility to control this energy through a careful selection of surfactants and additives in the synthesis designing.

Some examples of colloidal nanocrystals with a uniform size distribution, defined morphologies, and controlled crystalline facets are reported in Fig. 7.

Besides the “hot-injection” techniques a lot of methods are extremely effective for preparing nanocrystal with tailored chemical-physical properties. Among these methods it is important to mention sol-gel methods, co-precipitation methods, hydrothermal and solvothermal techniques (Petronella et al., 2019).

3.2.3 Growth Mechanisms of Hybrid Nanoparticles

The importance of colloidal techniques for the nanocrystal production relies also on the possibility to prepare hybrid nanomaterials, namely composite nanocrystals that merge in a single nano-object the properties of two or more individual materials. The resulting hybrid nanostructures, besides carrying the chemical-physical properties of the components, display new properties that arise from the combination of the selected moieties (Truppi et al., 2017).

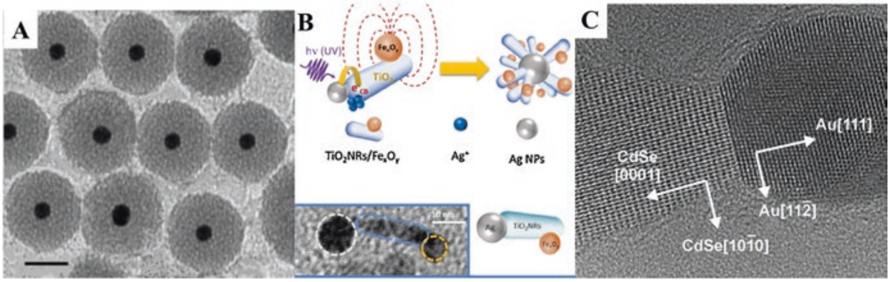

Fig. 8 TEM micrographs of nanocrystal-based heterostructures that merge different domains in one entity. Au nanospheres functionalized with a silica nanoshell (**a**), reprinted from (Fanizza et al., 2013). Copyright 2021. TiO_2 nanorods with a metallic domain (Ag nanoparticles) and a magnetic domain (iron oxide nanoparticles) growth at two different tips of TiO_2 nanorods (**b**) reprinted from (Petronella et al., 2017), Copyright 2021. CdSe/Au dumbbell-like heterostructures combining in one unit a photoluminescent nanocrystal with a plasmonic nanocrystal (**c**) reprinted from Figuerola et al. (2010), Copyright 2021

The three main growth mechanisms for hybrid nanoparticles are: (a) surface nucleation and growth of a second phase on a seed nanoparticle, (b) surface nucleation followed by surface diffusion of the metal phase or an inward diffusion, and (c) simultaneous nucleation and growth of both materials. Hybrid nanostructures can be prepared by exploiting reaction conditions that promote the heterogeneous nucleation (nucleation of the new component on the surface of the pre-existing component) over the homogeneous nucleation (independent nucleation of new nanoparticles). Relevant examples of hybrid nanoparticles are reported in Fig. 8.

4 Post-Synthesis Functionalization

One of the most fascinating features of colloidal nanocrystals is the possibility to perform surface functionalization procedures to endow nanocrystals with new properties or with specific instructions. This added value of colloidal nanocrystals arises from the occurrence of a one (or more) layer of surface stabilizing molecules (capping agents) that, in the synthesis step, control the growth and the shape of the resulting nanocrystals, and once that the nanocrystals are suitably isolated from their synthesis medium, provide colloidal stability in the selected solvent. The post-synthesis surface functionalization is extremely effective for nanocrystals due to their high surface-to-volume ratio that results in a high number of surface-active sites available for accepting the new (or the additional) capping agent.

Several methods are reported in the literature for post-synthesis functionalization. Chemical exchange procedures are very effective and are based on the replacement of pristine capping agents thermodynamically forced by a strong excess of the new capping agent, under suitable temperature, time, and stirring experimental conditions. Such an approach is often used for converting lipophilic nanocrystals in hydrophilic (for biological applications) ones (Pellegrino et al., 2004; Sivaram et al., 2018; Yüce & Kurt, 2017) and vice versa (for incorporating nanoparticles in suitable polymers (Corcione et al., 2018) or in liquid crystals (Pezzi et al., 2015)).

A further strategy for surface functionalization implies the construction of a polyelectrolyte (polymers with ionizable groups) multilayers on nanocrystal surface to modifying and controlling the nanocrystal surface charge for the preparation of stimuli-responsive nanoparticles (Zheludkevich et al., 2007).

Nanocrystal post-synthesis functionalization with biological entities including peptides, enzymes, proteins, oligonucleotides, and antibodies is particularly relevant for sensing-related applications. It can be achieved both by physical and chemical approaches. The most used physical approaches include avidin-biotin interactions, π-stacking interactions, and rely on hydrophobic and/or electrostatic attractions between nanoparticles and biomolecules. Chemical approaches such as modification with thiol compounds or cross-linking reactions through carbodiimide chemistry (Sivaram et al., 2018; Yüce & Kurt, 2017) aim at achieving a covalent bond between the nanoparticle capping agent and the biomolecule.

To fully exploit nanoparticle properties for designing and realizing biosensors the post-synthesis surface functionalization is a pivotal step. Indeed, as described in Sect. 2.3, a fluorescent probe for qualitative and quantitative determination of atrazine was developed by binding semiconductor quantum dots to artificial peptides able to recognize the analyte, by exploiting the carbodiimide chemistry (Giardi et al., 2021).

As metal nanoparticle solutions are characterized by shining colors, as depicted in Fig. 4, that can change according to particles morphology, interparticle spacing, and variation of the refractive index (as discussed in Sect. 5.3.2) they are often exploited as building blocks for the development of colorimetric sensors. This class of sensors identifies the occurrence of an analyte by observing (at naked eye and by absorption spectroscopy) a drastic color change triggered by the recognition of the analyte that induces the aggregation of gold nanoparticles, provided that a suitable instruction is imparted to nanoparticles by a surface functionalizing agent. Zhang et al. functionalized gold nanoparticles with an ionic liquid. Such a system, in presence of the pesticide imidaclopril triggered electrostatic attractions among nanoparticles that induce gold nanoparticle aggregation and a consequent color change that can be appreciated at naked eye, and can be related to the imidaclopril amount by a proper absorption spectroscopy investigation (Zhang et al., 2014).

Recently, gold nanoparticles functionalized with the anti-PA (anti-pantothenic acid) monoclonal antibody were prepared by exploiting the carbodiimide chemistry for achieving the anti-PA bioconjugation. The resulting functionalized nanoparticles were used for the development of a gold nanoparticle-based lateral flow immunoassay (LFIA) for the determination of the PA (Zeng et al., 2021).

5 Characterization

5.1 *Morphological and Structural Characterizations*

The morphology is a pivotal feature of nanocrystals, having a dramatic impact on nanocrystal properties, essential for sensing-related applications such as optical properties (Alivisatos, 1996; Eustis & El-Sayed, 2006), redox properties (Karim et al., 2016; Kamat, 2008), and refractive index sensitivity (Link & El-Sayed, 2005). Electron microscopy (EM) is a very powerful tool to investigate the morphology, the structure, and the elemental composition of nanocrystals and nanocrystal-based heterostructures. Indeed, EM techniques rely on the interaction between high-energy electrons and the sample under investigation, resulting in a range of information including size, shape, surface features, structure, and composition. Important, the EM is the only technique able to provide a direct image of nanostructured materials as other techniques (X-ray diffraction analysis, dynamic light scattering, and optical spectroscopy) allow to study indirectly the particle morphology. The present section aims at providing a general overview of the working principles of EM along with some relevant examples of nanocrystal characterization by EM with the goal to show the huge potential of these techniques. A final paragraph introduces X-ray diffraction analysis to investigate nanocrystal crystallographic structure and provide chemical and morphological information.

Compared to optical microscopy, EM enables to visualize nanosized objects as it displays higher performance in terms of resolution, magnification, and depth of field. The resolution is the ability to discriminate two different objects and is inversely proportional to the wavelengths interacting with the sample. While optical microscopy relies on the use of visible light, resulting in a resolution power of 0.2 mm, in EM an electron beam interacts with the sample, providing, consequently, resolution values of 0.1 nm for transmission electron microscopy (TEM) and 1.5 nm for scanning electron microscopy (SEM).

The magnification is the ability of producing an image of an object on a larger scale. In EM the magnification is achieved by exploiting electromagnetic lenses which focus the beam to a spot of the specimen or toward the detector. In EM it is possible to reach magnifications in a range from 10X to 1MX for SEM and in a range from 50X to 1.5 MX for TEM.

Moreover, SEM and TEM show a depth of field, which is the vertical range in which sample features remain in focus, of 1 μm for SEM and 0.2 μm for TEM.

In EM, an electron gun generates electrons in high vacuum conditions. These electrons are directed toward the sample by a positive electron potential. The electron beam is controlled by metal apertures and electromagnetic lenses that allow to obtain a focused and monochromatic electron beam. Electromagnetic lenses include condenser lenses, to generate a small and coherent electron beam and objective lenses to focus the electron beam to a defined area of the sample in the case of SEM and to focus the scattered electron toward the detector in TEM.

Stigmators (rings of electromagnet located around the beam) are also used in EM as correction tools avoiding the production of astigmatic (distorted) images.

At this stage, once the coherent and focused electron beam reach the specimen several physical interactions occur in the area of incidence. The detection system (fluorescent screens, scintillators, CCD cameras) catches and converts these interactions into an image.

In particular, in SEM the detection system produces an image that follows the topography of the sample, as it arises from voltage signals from electrons and photons emitted from the sample surface, following the impact with the electron beam. In TEM, the detection system analyses electrons transmitted by the sample after the impact with the electron beam from the electron gun, producing a real space image of the atom distribution in the nanocrystal (NC) and on its surface (Comparelli et al., 2013; Wang, 2000; Yao & Wang, 2005).

Figure 9 summarizes some relevant applications of SEM, for the investigation of inorganic nanocrystals, heterostructures, and nanocomposites. SEM shows topographic information relevant for understanding nanoparticle size and shape as demonstrated in Fig. 9a, as well as the morphology of coatings prepared with nanoparticles suitably embedded in polymers (Fig. 9b). Moreover, the investigation of backscattered electrons allows to obtain information regarding the phase composition of the investigated sample (Fig. 9c). The scanning electron microscope and

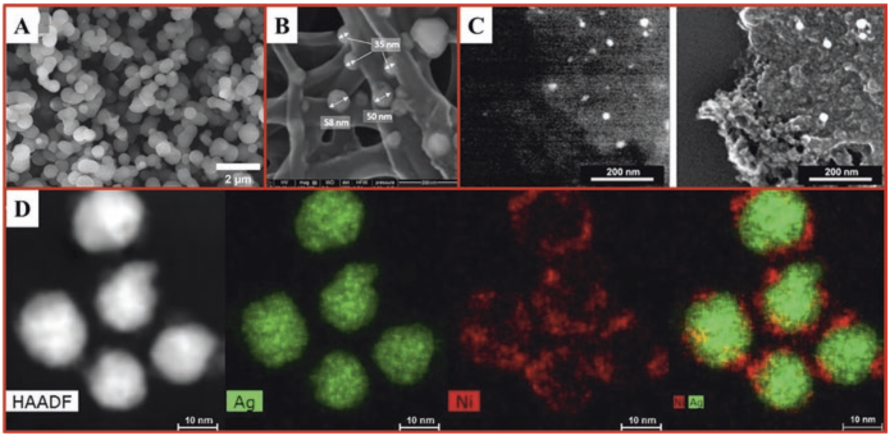

Fig. 9 Investigation morphology of nanocrystals and nanocomposite by SEM. SEM allows to identify the morphology of nanocrystals (**a**, reprinted from (Hwang et al., 2021) Copyright 2021), even when they are embedded polymers matrix (**b**, reprinted from (Zienkiewicz-Strzałka et al., 2020), Copyright 2021). The analysis of backscattered electrons (BSE) provides the sample topography sensitive to its chemical composition: in **c** (right, reprinted from (Petronella et al., 2013), Copyright 2021) the SEM images acquired with the BSE detector allowed to discriminate silver nanoparticles (bright spots) form the TiO_2 nanorods (particles with lower contrast) that compose the investigated hybrid heterostructure. In **d** is possible to observe a false color map, acquired with the EDS detector that shows the domains of elements that form the spherical nanostructure Ag element identified by green spots and Ni element identified by red spots (reprinted from (Vykoukal et al., 2019), Copyright 2021)

the transmission electron microscope can also be equipped with a detector, suitable for performing the energy dispersion spectroscopy (EDS). EDS provides the elemental analysis of the sample under investigation, (Fig. 9d) resulting in a false color map that identifies the element distributions in samples.

TEM is an extremely powerful EM technique for the investigation of nanostructured materials, as electrons after interaction with the sample carry a set of information including particle size, shape, crystallinity, and chemical composition. TEM technique allows to discriminate nanocrystal size and shape, and high-resolution TEM provides relevant information on crystallinity as it is possible to identify different crystalline domains. Moreover, the selected area diffraction (SAD) is a TEM technique able to provide a diffraction pattern of a selected area (with high density of nanocrystals) of the specimen that, in the case of nanocrystals, appears as a series of concentric ring due to the random orientations of the investigated nanoparticles. After a suitable and careful sample preparation, TEM allows to understand the interaction of nanocrystal with biological entities. Indeed, Fig. 10 (courtesy of the group of Professor L. De Sio) reports a TEM micrograph of keratine-capped gold nanospheres (identified with high contrast spherical spots) that are internalized in glioblastoma cells (Siyabonga et al., 2020; Guglielmelli et al., 2020).

Atomic force microscopy (AFM) is regarded among the main techniques suitable to perform the morphological characterization of nanoparticles. Although the

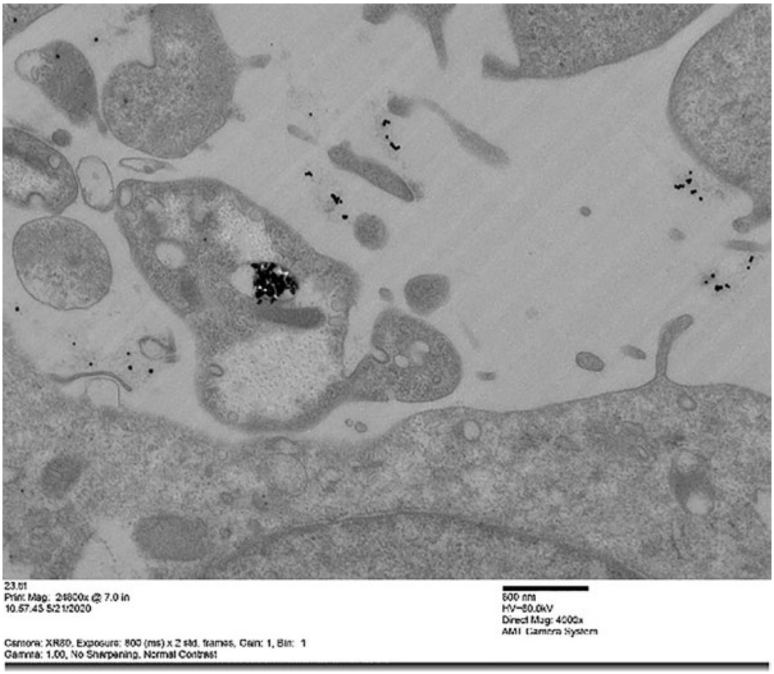

Fig. 10 TEM micrograph of biomimetic Au nanospheres (high contrast spherical spots) functionalized with keratin internalized in glioblastoma multiforme (U87) cells. Courtesy of the group of Professor L. De Sio

lateral resolution of the atomic force microscope is limited for a careful analysis of nanoparticle morphology, AFM is an excellent technique to investigate nanocrystal deposited on surfaces (Petronella et al., 2018), nanocrystals incorporated in polymeric matrices (Di Mauro et al., 2014), and nanocrystals functionalized with biological macromolecules (Li & Chen, 2014).

Understanding the crystallographic structure of nanocrystals is essential to predict and elucidate their properties and their chemical and physical behavior. X-ray diffraction analysis is one of the most used characterization techniques to achieve this goal as it gives access to several information including crystal atomic structure, qualitative and quantitative composition of crystalline phases, chemical composition, nanocrystal morphology, and it allows to investigate nanocrystal-based assembly (Giannini et al., 2016). However, the X-ray diffraction analysis of nanomaterials requires suitable techniques that account for the reduced dimensions of nanocrystals, the nanocrystal size distribution, the high rate of surface atoms, and, in the case of colloidal nanocrystal, the presence of the surface-stabilizing molecules (capping agents) that cause strain on surface atoms. A powerful tool for the X-ray diffraction analysis of nanocrystal relies on the use of the Debye formula that allows to analyze both small (SAXS) and wide (WAXS) angle X-ray scattering data. The former provides morphological information, the latter structure information (Giannini et al., 2020). The X-ray diffraction analysis of nanomaterials performed by using the Debye formula is more precise than that which would be obtained with the Debye-Scherrer equation that, instead has been designed for single crystals, and does not account for size distribution and stress associated with nanocrystals, but however is often used to provide information regarding the crystallite sizes.

5.2 Particle Size and Surface Area Characterization

The surface is the portion of nanocrystals that interacts with the external environment. For nanostructured materials the surface plays a relevant role, because the percentage of surface atoms is a high fraction of the total and possesses high energy value. It follows that to understand the chemical-physical behavior of nanocrystals a specific surface characterization with suitable techniques is strictly required. Important, the surface characterization techniques are also needed to monitor the post-synthesis nanocrystal functionalization often used especially for sensing-related applications as described in Sect. 4. This section will provide a concise summary of the main techniques used for nanocrystal surface characterization.

5.2.1 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a commonly used technique for the spectroscopic identification of organic compounds. It allows to identify organic molecules by analyzing the bands of the FTIR spectrum that can be often regarded as fingerprints of defined functional groups, because FTIR bands are generated from molecular vibrations (mainly stretching and banding) whose vibrational frequency depends from the mass of the involved atoms and from the force constant of the bond as described by the Hooke's law.

FTIR is a powerful technique for analyzing the surface of nanocrystals. Indeed, as described in Sect. 3, the surface of colloidal nanocrystals synthesized by solution-based methods is coordinated by surfactants that stabilize the nanocrystals in the desired solvent resulting in optically clear colloidal dispersions that can be easily characterized by optical spectroscopy (see Sect. 5.3). FTIR spectroscopy is often used for detecting the organic molecules that coordinate the surface of nanocrystals and for identifying the functional groups involved in the coordination bond.

Furthermore, FTIR is extensively used to monitor and to assess the post-synthesis functionalization as a variation of the FTIR spectrum is expected, upon the introduction of a new chemical entity on the nanocrystal surface (Cozzoli et al., 2003).

5.2.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a spectroscopic technique for the chemical analysis of a surface, with the further advantage to identify the oxidation state of elements laying on the sample surface. The XPS relies on the emission of electrons from their original energy level (core electrons), occurring following X-ray absorptions. The kinetic energy of the emitted electrons (photoelectrons) is related to the binding energy of atoms that have emitted photoelectrons. The XPS survey spectrum reports the intensity as a function of the binding energy values of the sample under investigation. As the binding energies of various orbitals are characteristics of an element, the analysis of the XPS spectrum (survey spectrum) allows to identify elements on the sample surface. Further analysis allows also to detect the element oxidation states and to obtain quantitative information. XPS is often used both for the surface characterization of nanocrystals and to investigate the doping of nanosized semiconductors (Petronella et al., 2014).

5.2.3 Dynamic Light Scattering

Dynamic light scattering (DLS) is a technique used to measure the hydrodynamic radius namely a parameter that indicates how the particles diffuse in a defined medium. It is based on the analysis of the speed at which particles move due to their Brownian motion. Particles are irradiated by a laser producing a speckle pattern revealed by a detection system. The speckle pattern will show dark areas, associated with disruptive interferences of scattered light and bright areas caused by constructive interferences of the scattered light. The constructing interferences are constantly evolving, generating new speckle patterns and therefore new intensity fluctuation over time, due to Brownian motion. The rate at with the intensity fluctuations occur will depend on particle hydrodynamic size. The small particles cause the intensity to fluctuate more rapidly than the large ones. The temporal evolution of the intensity of the scattered light is described by the correlation function. Suitable algorithms extract the mean size (z-average diameter) and an estimate of the width of the distribution (polydispersity index) from the correlation function. DLS instrument allows also to perform electrophoretic mobility measurements that are essential to understand the Z-potential, a value that is a measure of the electric charge on nanoparticle surface and provides information regarding the colloidal stability of nanoparticle dispersions. Hydrodynamic radius measurement and Z-potential measurement are extremely helpful for monitoring the nanoparticle surface functionalization with biomolecules including proteins, oligonucleotides, antibodies, or with polymers such as polyelectrolytes (Yüce & Kurt, 2017).

5.3 Optical Characterizations

5.3.1 Optical Characterization of Semiconductor Nanoparticles

One of the most interesting physical phenomena that describes the behavior of nanocrystalline semiconductors is the quantum size effect or quantum confinement that consists of a variation of the density of electronic energy levels as a function of the NC dimensions. In a semiconductor, the energy gap (Eg) is the difference between the energy of the highest occupied electronic states (valence band, VB) and the energy of lowest unoccupied states (conduction band, CB) and it is the minimum energy required for exciting the semiconductor and generating the electron/hole pairs. As the semiconductor NC size decreases the Eg increases, and more and more defined energy levels at the band edges are observed.

The variation of the Eg as a function of size can be clearly observed by investigating the optical behavior of semiconductor nanoparticles of a proper dimension, namely in the quantum size effect regime. In particular, the threshold energy for optical absorption is shifted to shorter wavelengths, as the nanoparticle size decreases, and discrete spectral features (associated with the allowed optical transitions) can be detected in the spectrum. Therefore, the position of the absorption peak is correlated with the nano-semiconductor dimensions.

Concomitantly, in the quantum size effect regime, also the photoluminescence properties of semiconductor nanoparticles can change with size: as the nanoparticle size decreases, the Eg increases, and as a consequence, the emission peak shifts toward higher energies.

Therefore, the investigation spectroscopic behavior of semiconductor nanoparticles is a fundamental characterization tool as it provides insight on nano semiconductor size, and size distribution. Further for nanosized semiconductor-based heterostructure, a proper optical characterization allows identifying possible charge transfer phenomena, occurring between the components of the nanosized heterostructure. This is particularly relevant for sensing-related applications based on the spectroscopic behavior of semiconductor nanocrystals (Alivisatos, 1996).

5.3.2 Optical Properties of Noble Metal NPs: Surface Plasmon Absorption

The optical properties of metallic nanoparticles, of a suitable size, rely on the phenomenon of localized surface plasmonic resonance (LSPR). The macroscopic evidence of the LSPR phenomenon is the vibrant colors observed for colloidal solutions of metallic nanoparticles. Light wavelength greater than metal nanoparticle size (typically visible light), when interacting with metallic nanoparticles, determines the standing oscillation of free electrons: the electron density in the particle is polarized to one surface, generation dipoles that oscillate in resonance with the incident light frequency.

The shape of metallic nanoparticles affects the density of the electric field on the nanometal surface. As a consequence, the frequency of oscillation of surface electrons is altered, and different cross-sections for light absorption and light scattering are generated. For this reason, the LSPR properties are extremely dependent on nanoparticle size and shape, according to the Mie theory which describes the spectroscopic behavior of spherical metallic nanoparticles, and to the Gans theory which predicts the spectroscopic behavior of anisotropic nanoparticles. Anisotropic nanoparticles as gold nanorods or gold nanopyramids show a peculiar spectroscopic behavior characterized by two plasmon bands: the transverse band typically centered at 520 nm and the longitudinal plasmon band typically centered at a higher wavelength. The former is generated from the oscillation of dipoles in the transverse direction (the shorter dimension of the nanorod) while the latter is associated with the oscillation of electrons along the longitudinal direction (long side of the nanorod). The position of the longitudinal plasmon band depends on the aspect ratio of gold nanorods: as the aspect ratio increase, the longitudinal plasmon band shift toward higher wavelengths.

The variation of the absorption profiles as a function of metal nanoparticle shape is described in Fig. 11 for gold nanoparticles. The spectra b and c and the respective TEM micrographs clearly highlight that spherical metallic nanoparticles show one absorption peak (plasmon band) that shifts toward higher wavelengths as the nanosphere size increases. The spectrum e in Fig. 11 (green track) describes the typical spectroscopic behavior of gold nanorods that, due to their anisotropy, show two plasmon absorption bands: the transverse and the longitudinal one in the near-infrared wavelength range. The absorption spectra f, g, h, and i, and the respective TEM micrographs of gold nanopyramids clearly point out how the longitudinal band shifts to higher wavelengths, as the aspect ratio of nanopyramids increases.

Remarkably, Mie theory and Gans theory point out that the position of the absorption peak, namely the plasmon absorption band, is significantly affected by the refractive index of the surrounding medium.

Such a feature makes metallic nanoparticles excellent candidates for sensing-related applications. In particular, the longitudinal plasmon band of anisotropic metal nanoparticles such as nanorods and nanobypyramids is extremely sensitive to the variation of the refractive index of the surrounding medium (Eustis & El-Sayed, 2006; Liz-Marzán, 2020).

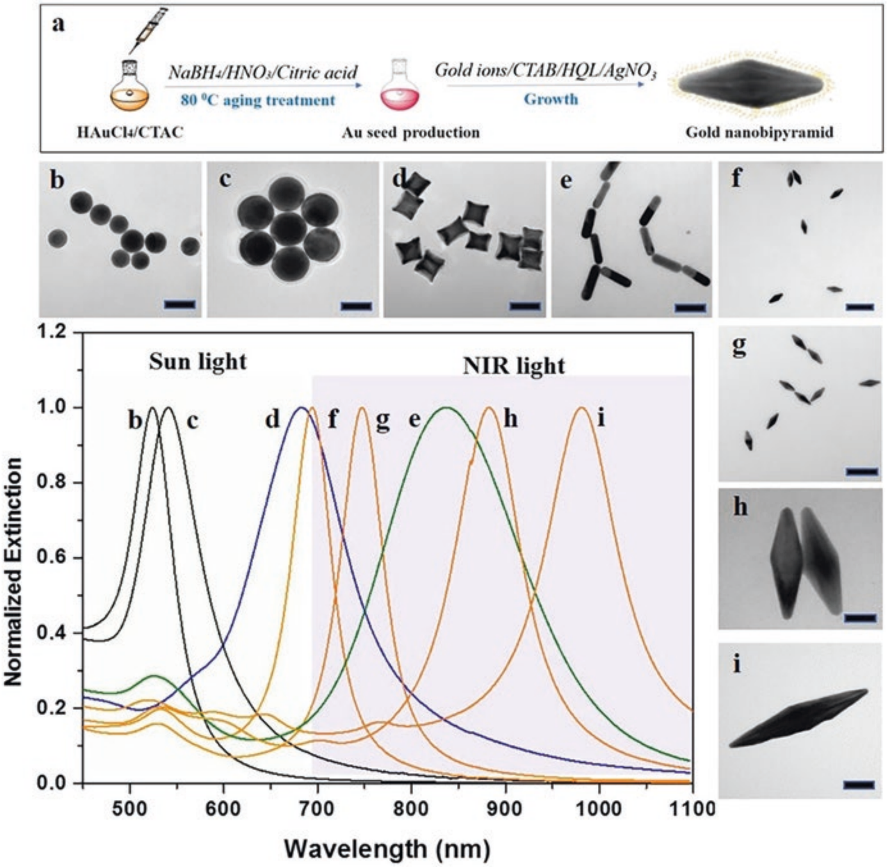

Fig. 11 Synthesis (**a**) and properties of plasmonic gold nanoparticles. Representative TEM micrographs of Au nanoparticles with different shapes and their corresponding normalized extinction spectra: (**b**, **c**) nanospheres, (**d**) nanocubes, (**e**) nanorods, and (**f-i**) nanopyramids with different aspect ratios starting. Scale bars: 50 nm. Reprinted with the permission of (De Sio et al., 2020) Copyright 2021

6 Applications of Nano(Bio)Sensors in the Agrifood Sector

The global agrifood system is expected to request for reliable and inexpensive methods for the management of food quality and security from the field to the fork. Nano(bio)sensor technology offers the chance to fulfill this need as ideal counterparts to the conventional analytical methods (e.g., HPLC, GC, and MS), being able to provide simple, fast, reliable, and cheap multi-analyte detection, as well as high degree of automation, on-line measurements, and high-throughput analysis along the whole food chain. Furthermore, taking advantage from nanotechnology, new opportunities of improvement of the current technology have been investigated (Arduini et al., 2020; Antonacci & Scognamiglio, 2020; Scognamiglio & Arduini, 2019). Indeed, coupling the high specificity of bioreceptors with the unique optical, electrical, and electrochemical properties of nanomaterials provides novel stimulating analytical features as improved sensitivity, specificity, robustness, and the performance in general (Srivastava et al., 2018; Pradhan et al., 2015).

Thanks to these astonishing advantages, nano(bio)sensors find several applications in each segment of the agrifood system, from the management of the field crop (e.g., detection of pesticides, nutrients, pathogens) to the monitoring of the food processing (e.g., detection of sugars and amino acids), food packaging as well as food quality and safety assessment.

6.1 Crop Field Monitoring of Pesticides, Nutrients, and Pathogens

In the last decades, the strong pressure exerted by the increase in population and by the demand for ever higher production, even more diagnostics is required for the monitoring of chemical and biological parameters of the crop field, including pesticides, nutrients, pathogens, and humidity to guarantee high yield while protecting the environment.

Pesticides are extensively used in agriculture to increase crop yield, and their analysis needs cutting-edge technologies for their discrimination in complex agricultural matrices as soil, water, and crop. To this purpose, nano(bio)sensors display numerous benefits as sensitivity, rapidity, stability, and robustness. Many nano(bio) sensors have been reported in the literature to monitor pesticides in water and food, based on nanomaterials, like carbon nanotubes, quantum dots, gold nanoparticles, Prussian Blue nanoparticles, carbon black, and nanocomposites (Antonacci et al., 2018).

In this context, soil analysis is an interesting challenge, since it represents a complex matrix, characterized by low homogeneity and retention of toxic substances, such as pesticides. For all these reasons, soil state analysis requires pre-treatment procedures and multiple sampling. Despite the hurdles above described, interesting solutions have been proposed by the literature including the biosensor based on tyrosinase/TiO_2 nanotubes for atrazine detection designed by Yu and colleagues (Yu et al., 2010). In particular, a nanobiosensor was developed exploiting vertical growing of TiO_2 nanotubes with a large surface area for the immobilization of tyrosinase enzyme. This planning resulted in higher sensitivity and robustness of the system, providing reliability even in real samples measurements, after their pre-treatment (e.g., air-dried, grinding with pestle, sieve, vacuum-dried, and solubilization with acetone), reaching the detection range of atrazine from 0.2 ppt to 2 part-per-billion (ppb).

Fertilizers are also largely exploited in agriculture to enhance plant growth and thus productivity. Nevertheless, they show important environmental impacts on surface and groundwater. For this reason, a wise fertilization procedure is extremely needed in correct weather conditions, at appropriate crop growth period, and at a precise amount. Nano(bio)sensors can support a comprehensive and accurate analysis of fertilizers in soil and water to better adjust their use, fostering sustainable practices, supporting farmers to obtain information about spatial and temporal variations of fertilizer concentrations, including soil organic matter or total carbon content, soil salinity, sodium content, residual nitrate, phosphate, and urea.

To report an example, nitrate detection in soil was accomplished by Azahar Ali and co-workers (Ali et al., 2017) by realizing an impedimetric sensor based on graphene oxide (GO) nanosheets and poly (3,4-ethylenedioxythiophene) nanofibers (PEDOT-NFs). This PEDOT NFs-GO composite was capable to host the enzyme nitrate reductase to measure nitrate ions in water samples extracted from soil of a *Zea mays* farm, in a wide concentration range of 0.44–442 mg/L and with a limit of detection of 0.135 mg/L.

Several nano(bio)sensors were reported also for monitoring urea and phosphate (Szuromi, 2017); however, they are similarly limited to the analysis of river water, tap, river, and lake waters.

Pests, weeds, and pathogens may also influence crop yield, and nano(bio)sensors can contribute to detect infectious diseases in plants due to these agents. In particular, some nanomaterials played a leading role in this field, such as the luminescent semiconductor quantum dots (QDs), widely exploited for their broad excitation spectra. In this context, different quantum dots FRET-based biosensing systems have been conceived to detect viruses and pathogens of plants, e.g., for *Polymyxa betae,* responsible for Rhizomania disease in sugar beet, and for synthetic oligonucleotide of *Ganoderma boninense*, with a LOD of 3.55 × 10–9 M (Safarpour et al., 2012; Bakhori et al., 2013).

Other nanomaterials, e.g., carbon nanotubes, graphene, nanowires, and nanocomposites, as well as nanoparticles, widely supported the generation of nanosensing platforms for pathogens and mycotoxins, fostering the user friendly and assured diagnostic kits for farmers. All these researches are aimed at preventing, managing, and counteracting epidemic diseases, and hence at avoiding significant economic losses.

Gold nanoparticles have been very successful in these applications, in particular for sensors functionalization thanks to their high surface-to-volume ratios and to their peculiar optical and electrochemical properties, making possible lower detection limits and higher specificity in comparison with traditional approaches (Wang et al., 2010). A relevant example is the electrochemical enzyme-linked immunoassay based on gold nanoparticles developed by Zhao and colleagues to detect *Pantoea stewartii subsp. Stewartia*, a bacteria plant (detection limit of 7.8 × 10^3 CFU/mL) (Zhao et al., 2014). In terms of sensitivity, another intriguing example of nanobiosensor based on gold nanoparticles was the label-free SPR immunosensor for the detection of *Cymbidium mosaic* and *Odontoglossum ringspot* viruses designed by Lin and colleagues (pg/mL range) (Lin et al., 2014).

The electrochemical biosensor based on ZnO nanoparticles/chitosan nanocomposite-modified gold electrode developed by Siddiquee et al. (Siddiquee et al., 2014) is certainly part of these innovative nano-biosensing tools useful for fungi detection. This device was designed to identify the crude DNA of *Trichoderma harzianum* with a LOD of 1.0×10^{-19} mol L^{-1} in the concentration ranges of 1.0×10^{-18}–1.82×10^{-4} mol L^{-1}.

However, during the development of a biosensor, it would be restrictive to limit the usefulness of nanotechnology only to functionalization, labeling, and immobilization of bioreceptors. In fact, this new technology also performs fundamental functions in the microfluidics, instrumentation, robotics, and remote control of the sensing device.

6.2 Food Processing

The food processing industry accounts for 32% of the total food market (Thakur & Ragavan, 2013). This entails among many processes also the food quality and safety assessment during the manufacturing process, through the monitoring of biological, chemical, and/or physical status of the food. Many sensing configurations were described for the real-time continuous monitoring of compounds in the production chain of industrial processes, like food fermentation, which produces beverages (wine, beer, cider, and kefir) or food (cheese, yogurt, bread, sausage, vinegar, pickled cucumbers, and soy sauce olives). Such methods usually analyze physicochemical parameters like pH, temperature, and pressure, as well as food freshness and composition (alcohols, sugars, amino acids, vitamins, fermentation products) and contaminants (pesticides, heavy metals, nitrites, pathogens, toxins, antibiotics, allergens, and hormones).

Microbiological analysis is also compulsory to guarantee high quality in microorganisms-based production and for food safety issues. For example, *Saccharomyces cerevisiae* is the most relevant industrial yeast, commonly exploited in wine production being able to complete fermentation of sugars to alcohol, carbon dioxide, and secondary end-products (Doyle et al., 2020). Nevertheless, it should be removed after fermentation to avoid uncontrolled growth at the re-fermentation stage, and thus alteration of the chemical composition and organoleptic properties of wine. Conventional methods for microbial monitoring are time-consuming and often inappropriate for decision making during alcoholic fermentation. Falcao and co-workers reported an effective nanobiosensor (Jimenez-Falcao et al., 2020), able to identify living *S. cerevisiae* cells in the range of 8×10^2–4×10^8 CFU/mL. In particular, the system senses the local pH modifications due to the invertase activity, an enzyme naturally synthetized by the yeast and involved in the hydrolyzation of sucrose to fructose. This nanobiosensor design was equipped with a nanovalve in capped benzimidazole-functionalized mesoporous silica nanoparticles with β-cyclodextrin-coated gold nanoparticles containing adatamantane-modified glucose oxidase as a bioactive element. As a consequence of pH modifications, the pores on nanovalve are opened and a dye is released activating the colorimetric sensing approach. Non-enzymatic nanosensors have been also reported in the literature, based on electrodes nanomodified with spherical gold-nickel nanoparticles with a core-shell architecture (Au@Ni) (Gao et al., 2020). This nanosensor combines the high electrocatalytic activity, good selectivity, and biological compatibility of Au with the remarkable tolerance of Ni for chlorine ions (Cl^-) and poisoning intermediates in catalytic oxidation of glucose. This nanosensor was able to electrochemically monitor glucose at a low operating voltage of 0.10 V vs in a linear range from 0.5 mmol L^{-1} to 10 mmol L^{-1} and a detection limit of 0.0157 mM with a fast response time of 3 s.

6.3 Food Packaging

The fast nanotechnology progress is furnishing several chances for the design of novel sensing solutions for food packaging, to extend shelf-life, diminish waste, evaluate safety, and increase food quality. Nanomaterials are exploited in food packaging design to reinforce mechanical strength, improve gas barrier properties, provide water repellence as well as antimicrobial and scavenging activity. Indeed, nanomaterials can be integrated into chemical and biological sensors to assess freshness and detect allergens, toxins, or pathogens (Mustafa & Andreescu, 2020). This allows for the design of the so-called smart or intelligent packaging. Smart packaging monitors the quality and safety of food from the producers to the costumers, as well as freshness, pathogens, leakage, carbon dioxide, oxygen, pH, time or temperature, control of weight, volume, color, and appearance (Kuswandi et al., 2011).

Numerous intelligent packaging involves nano(bio)sensors to monitor physical parameters (humidity, pH, temperature, light exposure), gas mixtures (e.g., oxygen and carbon dioxide), pathogens and toxins, or to assess freshness (e.g., ethanol, lactic acid, acetic acid) and decomposition (e.g., putrescine, cadaverine). Among them, biogenic amines (BA) are a crucial example of the result of microbial metabolism that may be affected by temperatures and storage conditions, and their level represents a safety/quality indicator of food. Vanegas and colleagues (Vanegas et al., 2018) realized electrodes functionalized with copper microparticles and diamine oxidase graphene for biogenic amines sensing, providing good electrochemical performance, a detection limit of 11.6 μM and a response time of 7.3 s.

6.4 Food Quality and Safety Analysis

Currently, the word “agrifood” encompasses a complex reality, consisting of diversified concepts as innovation, development, and globalization. However, two important issues remain pivotal, namely the quality and safety of products, which have a direct impact on the environment and human health. Food quality and safety are guaranteed when appearance, freshness, taste, texture, nutritional value content, and chemical are monitored and protected. Hence the need to monitor the entire production chain from an analytical and legislative point of view is highly sought after. For all these reasons, innovative, specific, sensitive, rapid, easy to use, and reliable methods of investigation are highly required in the monitoring of organoleptic qualities, as well as in the detection of both chemical and biological contaminants. The use of nanomaterials for (bio)sensor design further contributed to enhance the analytical performances of such systems, when exploited as catalytic tools, immobilization platforms, or optical or electroactive labels. Among various nanoparticles, carbon dots (CDs) are recently emerging as smart nanoparticles for (bio)sensor design for monitoring food quality related analytes, with appealing merits such as ease of preparation, low cost, non-blinking, low cytotoxicity, excellent biocompatibility, and high resistance to photo-bleaching (Luo et al., 2020). As described by Ahmed and co-workers (Ahmed et al., 2015), CDs exhibited good analytical potential as sensing probes for tannic acid determination, in the linear concentration range from 0.1 to 10 mg L^{-1} with a limit of detection equal to 0.018 mg L^{-1}. The nanosensor was able to monitor tannic acid also in red and white wine samples, with recoveries in the range 90–112.5%. Food safety has been also accomplished by CDs-based sensors, as reported by Weng et al. (Weng et al., 2015). In this study, mannose-modified fluorescent carbon quantum dots (Man-CQDs) were synthetized from solid ammonium citrate and mannose, and used to bind the FimH lectin unit in the flagella of the wild-type 1 *Escherichia coli* K12 strain. These CDs had an average particle diameter of 3.1 ± 1.2 nm, showed highly solubility and a quantum yield of 9.8% at excitation and emission wavelengths of 365 and 450 nm, respectively. The specific mannose binding allowed bacteria detection at 450 CFU mL^{-1} in lab samples also in real samples as tap water and apple juice.

7 Regulatory Aspects and Consumer Perception

Safety of nanomaterials has been largely discussed by regulatory agencies (e.g., Scientific Committee of the European Food Safety Authority, EFSA) through many recommendations and novel guidelines should be stated to set associated risks and regulate their exploitation in commercial products, like cosmetics, food ingredients, pesticides, and pharmaceuticals. Due to the lack of specific regulations, more research is required to set new standards as well as novel methods for their toxicity evaluation.

In particular, the use of nanoparticles in the agrifood system, from the agricultural field to feed and food, regards applications in food additives and food contact materials, including additives, biocides, pesticides, and food packaging. Legislation on these materials is incomplete and limited are also the records of toxicity assessments.

Despite the fast trends and early acceptance of nanomaterials in many agrifood application, the potential adverse effects on human health and ecosystems have not yet been established. Indeed, the impact of nanoparticles is expected to increase, being such materials able to organize and aggregate depending on their size, curvature, shape and surface characteristics charge, functionalized groups, and free energy, thus generating adverse biological effects. Furthermore, due to the nanodimensions of such particles, there is a high tendency to cross barriers like skin, lung, body tissues, and organs, causing oxidative stress, organelle damage, asthma, and cancer.

Crucial concerns regard also (a) the acceptance and willingness for nano-fertilizers, nano-food, and nano-packaging, being consumers reluctant to accept food and food-related products that incorporate nanoparticles, as well as (b) the need of nano-products to exhibit labels reporting the use of nanoparticles and that such products meet safety standards. For example, the European Parliament and the Council have requested through Regulation 1169/2011 that foods containing nanomaterial-based ingredients need to be labeled (EU Regulation, 2011).

For these reasons, further efforts on both toxicity assessment of nanoparticles as well as more specific regulatory aspects are strongly required.

8 Conclusion

The agrifood system represents one of the most important economic sectors worldwide, and the exploitation of biosensing devices enables monitoring and management of the whole chain, from the field to the fork. Moreover, nanoparticles have become important components in the design of analytical tools, being capable to significantly improve biosensor performance in terms of sensitivity, efficiency, and stability. Nano(bio)sensors demonstrated their ability in several agrifood applications, from crop field management (e.g., detection of pesticides, nutrients, pathogens) to food processing monitoring (e.g., detection of sugars and amino acids), food packaging as well as food quality and safety assessment.

However, many aspects still need to be considered especially regarding the acceptance of nano-products and their potential toxicity on human wellbeing and the environment. As stated by Antonacci et al. (Antonacci & Scognamiglio, 2020) "*several criticisms emerged regarding the use of nanomaterials. The main issue is related to their most important aspect, the nano-size. Indeed, while this feature determines high reactivity and great capacity, it could become potential lethal factor by inducing adverse cellular toxic and harmful effects*". For this reason, further investigations are required to establish the toxicological effects as well as legislations needed to set safety standards of nanoparticles.

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Box 1 History as Magistra Vitae: The Current Success of Nanomaterials

The advantages of nanomaterials were already smelled in the most ancient times. In fact, the advent of nanomaterials in human society has been testified already 4500 years ago concerning the use of asbestos nanofibers in the manufacture of ceramic matrixes. Moreover, historical sources report the use of a multifaceted mixture of $CaCuSi_4O_{10}$ and SiO_2 (both glass and quartz) in the community of ancient Egypt for the production of “blue of Egypt” color, the first case of synthetic pigment in history for decorative purposes.

The first attempts of chemical synthesis were dated in the XIV century BC, when Egyptians and Mesopotamians began to produce glass in the presence of metal particles. In particular, the gold and silver decoration in glass processing has shown particular optical properties, as the metal nanoparticles display iridescent bright green and blue colors under particular reflection conditions. This technology has been widely used in the subsequent cultures all over the world, up to the XIX century in Japan where a similar approach has been used to produce the Satsuma glass with ruby color.

Proceeding along the timeline of history, in Italy archaeological finds, dating back to 1200–1000 BC and colored by surface plasmon excitation of Cu nanoparticles, have been discovered, as well as analogous Celtic red enamels from 400–100 BC. However, the most famous and studied finding containing nanoparticles, dates back to the IV century BC, with the glass cups of Lycurgus. In particular, with modern technologies the composition of the alloy and the relative ratio between the materials used (silver/gold in the ratios of 7:3 and 10% copper) has been traced.

The empirical approaches described by ancient history have been probably replaced by a scientific method in 1857, when Michael Faraday, for the first time, reported the synthesis of a colloidal gold nanoparticles solution, as well as he observed their peculiar optical features. This represented a milestone in the evolution of nanomaterial, from which their use and study have grown exponentially and conquered many sectors of the market. The reasons why even today nanomaterials remain in vogue are many, as for example they can improve the intrinsic proprieties of bulk materials (durability, strength, lightness, and conductivity), as well as provide additional useful properties (antibacterial, self-healing, anti-freezing, and self-cleaning). In addition, nanomaterials are also widely used as a passive material in the production of nanocomposite, for example, in the automotive, household appliances and paint industries.

Recently nanomaterials conquer also medical and pharmaceutical sectors, despite the important scientific debates and concerns regarding their toxicity for environment and human health.

Box 2. Next-Generation Nanomaterials: The Green Era

In the last decades, the affirmation of nanomaterials in many sectors is undeniable; however, major concerns have emerged concerning the risks and side effects, especially in the medical and agrifood sectors, for possible environmental and medical toxic effects. For these reasons, the science is focusing on new green methods for the synthesis of nanomaterials, enhancing the sustainability of production process, that means reduction of risks and costs, another sore point. The green nanotechnology represents a new and promising route with the aim of counteracting the use of harmful substances, as well as reducing the lifetime of materials, and thus making them less recalcitrant for the environment. In this context, nature has proved to be a strong inspiration; in fact, many nanomaterials are synthesized from different (micro)organisms, such as plants, algae, fungi, and bacteria. For example, several studies reported the production of gold nanoparticles in plants with significant improvements in terms of quality and environmental impact. The noble metal, with beneficial properties for the treatment of diseases (e.g., measles, smallpox, syphilis, and skin ulcers) already known in ancient times, today find interesting applications as a pacemaker, stent, in dental restoration, radiation enhancers in radiology, middle ear implant and biomarkers. In particular, gold nanoparticles have proved extremely useful in assisting cancer therapies by cell/protein labeling, hyperthermia treatment, and drug administration. In addition, the development of Aurimmune and AuroLase drugs, respectively, in phase I and in pre-clinical trials, are concrete and positive signs of the effectiveness of these materials. The literature reports several promising studies in terms of stability concerning the synthesis of gold nanoparticles with different shapes from various plant sources. In this context, Das and colleagues presented one of these intriguing examples of gold nanoparticles synthesis, ranging between 20 and 50 nm, reducing and capping potentials of ethanolic flower extract of *Nyctanthes arbortristis*. Instead, in Ramesh laboratory gold nanoparticles derived from *Diospyros ferrea* (70–90 nm in size) have been produced and tested for anticancer activity, suggesting hopeful results concerning the growth inhibition of the cancer cells.

Another green synthesis widely investigated covers copper oxide nanoparticles, principally due to their important antimicrobial activity versus different pathogens such as *E. coli, Bacillus subtilis, Vibria cholera, Pseudomonas aeruginosa, Syphillis typhus,* and *Staphylococcus aureus*. Several plant materials have been exploited for copper oxide nanoparticles production, for example, magnolia leaves and *Euphorbia nivulia* stem latex to obtain a non-toxic aqueous formulation useful for cancer therapy, or natural hydrocolloid gum karaya for antibacterial action. Moreover, algae cells were exploited to biosynthesize and characterize copper oxide nanoparticles (5–45 nm) with high antibacterial activity against Gram positive and negative.

(continued)

Box 2 (continued)

In particular, among the green possibilities to produce nanoparticles in a sustainable way, the microalgae present many advantages related to the easy and inexpensive growth conditions and the capability to survive in extreme conditions. In this context, some of the most species investigated were *Neochloris oleoabundans*, *Chlorella pyrenoidosa*, *Galdieria* sp., and *Dunaliella tertiolecta*. Moreover, the presence of hydrophilic surface groups (e.g., carboxyl, sulphate, and hydroxyl) on algae-mediated nanomaterials gives them peculiar features and specific application fields including the reaction catalysis.

As regards other microorganisms (e.g., bacteria, fungi, and yeast), they play an essential role in the minerals reprocessing, and hence they found huge importance in the production of metal and semiconductor nanoparticles.

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Physicochemical Properties of Inorganic Nanopesticides/Nanofertilizers in Aqueous Media and Tank Mixtures

Rafael Augusto Alves Ferreira, Marta Simão Kfouri, Rafael Pires-Oliveira, Augusto Cesar Gonçalves, and Poliana Cardoso-Gustavson

Abstract Nanotechnology is still pointed out as a promising technology in the crop protection market, mainly in a sustainable scenario of reducing the amount of active ingredient (AI) applied in the field. Although the benefits of this technology in terms of safety, efficiency, sustainability, and performance in the field are undeniable, a huge regulatory issue remains to be overcome. Apart from the several promises and challenges in the development, scale up, and use of the nanoformulations in the field, the global market shows a stable growth of this technology and a movement toward innovation by using sustainable components and new application models. All the known nanosystems' advantages are thoroughly explained by the physicochemistry of colloids. This technology might provide more stable formulations in terms of shelf-life, a higher field performance with a lower applied dose of the AI, and less issues in the tank mixtures. Indeed, a rising technology in precision agriculture is the application of nanoformulations through drones, which can finally overspread their use in the field. In this chapter, we provide an overview of the global market for nanofertilizers, besides deepening on the main physicochemical properties linked to the higher stability of nanoformulations over conventional ones, as well as their expected performance in the tank mix applications in the field.

Keywords Nanotechnology · Nanoparticles · Formulation · Fertilizer market · Pesticide market · Nanoparticle uptake · Tank mix compatibility

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1 Introduction

Agriculture is responsible for the production of food crops (cereals, vegetables, fruits, and edible oils) and non-food crops, also known as industrial crops. Industrial crops include the production of flowers, first- and second-generation biofuels (bioethanol, biodiesel, and biomass), natural fibers (such as cotton, linen, and industrial hemp, commonly used to produce paper, cloth, fabric, and rope), and sustainable raw materials (such as biopolymers, rubber, and building materials). The demand for these products is increasing with the global population growth, estimated to achieve over 9 billion in 2050 (United Nations, 2019). In order to ensure high productivity to supply the world needs, it is crucial to supply all macro- and micronutrients particularly required by each crop and to protect the plants against pest attack. In addition, some mineral nutrients, such as phosphate and potash, are facing a global source scarcity, leading to a disproportion in the supply/demand balance and hence affecting the fertilizers price (Scholz et al., 2013; Jung, 2021). Nanotechnologies enable more effective production of inorganic fertilizers and pesticides, safely reducing the dosage applied and preventing material loss or undesired residues in terms of environmental pollution, addressing the nutrients shortage as well. In this chapter, we examine the technological status of this sort of products, the patent's overall status, and a physicochemical overview to understand the formulation stability of nanosystems focused on shelf life and their behavior in tank mixtures.

2 Market, Intellectual Property, and Technology Analyses

A conceptual issue that has received attention from the market is the debate about the use of the term "nano" for nanopesticides, including nanofertilizers. This use is problematic because the definition based on size alone excludes the recently named nanofertilizer formulations and includes products that have been available in the market since a long time ago without posing clearly as a formulation based on nanosize scale, such as microemulsions[1]. So, to avoid customer confusions by including ingredients which were not characterized as nano, it is more useful to discuss nanoenabled or formulation technology instead focus on nanoparticles and their definitions. In addition, the absence of comprehensive studies in the literature that evaluates efficacy and environmental impact of nanofertilizers under field conditions and comparison with conventional fertilizers to assess economics limit a higher use and acceptance of nanotechnologies. This is a crucial knowledge gap and

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[1] Microemulsion is defined as a "dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm". (Slomkowski et al., 2011)

therefore more work will be necessary for a solid evaluation of the benefits that nanofertilizers represent in relation to existing products.

The fertilizers market has been virtually static in the last few years, and in this section, we analyze some figures from this market. The general fertilizer industry made a global production revenue of USD 250 billion in 2018, reaching 252 Mt. nutrients (International Fertilizer Association (IFA) Fertilizer Outlook 2019–2023 IFA Annual Conference 11–13 June 2019 Montreal (Canada)). The COVID-19 pandemic[2] is adversely affecting this market in conjunction with several global supply chain disruptions and severe macroeconomic turbulence, and it was expected to reach in 2020 a reduction of total sales to 247 Mt. (Fertilizer Outlook, 2020–2024 Market Intelligence and Agriculture Services). On the other hand, the controlled-release fertilizers global market, a portion of which may comprise nanofertilizers, is projected to grow at a compound annual growth rate (CAGR) of 6.3% in the forecast period (2020–2025) reaching USD 3.2 billion by the end of 2025 (Gupta, 2020). The drivers for this expectation are the increase in global population and economic growth. Indeed, the market of the emerging nations is growing with the support of the government in terms of incentives, loans, and tax waives in agricultural fertilizers, thus boosting the overall industry.

The restrictions of this market are linked to the environmental and health concerns, such as soil and water pollution, and fate of microplastics. The increasing use of biofertilizers and trend of organic food, besides the issues about government regulations and the political-economic scenario of the reduction of free trade, have also constrained the market for fertilizers – conventional and nano-enabled ones.

The sustainability claim for nanofertilizers has affected the market positively, acting as an incentive to this technology. Indeed, a more widespread adoption of nanofertilizers would reduce environmental risks, such as atmospheric and groundwater pollution, soil acidification, eutrophication, the decline of the level of soil fertility, and loss of biodiversity. Compared to other fertilizer technologies such as chemical or biofertilizers, nanofertilizers help in supplying nutrients in a more effective way, offering controlled release of active ingredients onto the soil, which in turn improves the crop yield. These are the main reasons for the rising demand for nanofertilizers in the next years, although this market seems not to forecast an aggressive increase, but a slower one following the establishment of the technologies to their production. Looking forward, the global nanofertilizers market is expected to continue its moderate but consistent growth during the next decade (IMARC Group, 2021).

From a global market point of view, the continuing driver for research and investment into nanofertilizers is the urgent need to increase nutrient uptake efficiency in order to decrease environmental harms from synthetic fertilizers. Advancements in nanotechnology have paved the way for large-scale production of nanoparticles that are used in the manufacture of nanofertilizer formulations. The market benefits of nanofertilizers are mainly linked to the slow/controlled release of nutrients,

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[2] The COVID-19 pandemic was declared in March 2020 by the World Health Organization.

reducing nutrient loss and increasing their bioavailability, and the specificity to be synthesized according to the objective, creating highly nutrient efficient crops. However, the lowlights of this technology include the high reactivity and variability, the environmental impacts of microplastics, and safety concerns for farm workers and consumers (Kah, 2015, Kah et al., 2018, Zulfiqar et al. 2019). The market for surfactants, and monomers/polymers to be applied in the formulations may follow a similar forecast compared to nanofertilizers, presumably due to the benefits of improving physicochemical aspects of the nanofertilizers' formulation. This forecast is expected to be even more positive for sustainable and low carbon footprint components. In addition, these components must be suitable for registration by regulatory agencies from the USA and EU to be applied in crop and even in organic markets, being convenient for customers of the surfactant industry to have at least one registration.

Key agrochemical companies figure as key players in the global pesticides and fertilizers market, such as Syngenta, Nanosolutions, Smart Agri-Tech Co. Ltd., Richfield Fertilizers Pvt. Ltd., Alert Biotech, Prathista Industries Limited, Lazuriton Nano Biotechnology Co., Sonic Essentials, Jinzhou City Jinchangsheng Chemical Co., UNO Fortunate Inc., Florikan, Bayer, BASF, Nutrien, Yara International, ICL, Haifa, and Mosaic, among others (Dimkpa & Bindraban, 2018; Pires-Oliveira et al., 2020a), but when nanosized products are taken into consideration, small companies also stand out. Nanotechnology is still not widespread in agricultural products nor clearly positioned by big players of the market. The main reasons are the lack of robust studies showing the environmental safety and benefits of nano-sized products in comparison to the conventional ones, and the challenge for a large-scale production in a competitive cost (Dimkpa & Bindraban, 2018; Kah et al., 2018). The same behavior is observed by patent landscape analysis (Figs. 1 and 2), which allows the understanding of the maturity, players, and most promising regions for commercialization of this technology.

The intellectual property analysis was performed using PatSnap IP Platform searched from 116 databases. We performed searches using different queries, adjusting the terms searched in the Title/Abstract/Claims/Description (original and machine translation) (TACD_ALL) and selecting the International Patent Classification (IPC) to recover the best results according to the objectives – for example, using the term "nano*" resulted in documents not related to nanotechnological products that only appeared due to terms "nanoseconds", "[wavelength] nanometer" (as a unit of UV-Vis measurements), etc. On the other hand, when the IPC B82 (Nanotechnology) was searched no relevant results were obtained. Therefore, the searches were performed using the search terms described in Table 1, and queries F1 and F4 recovered the best results for conventional and nano-enabled fertilizers, respectively. A similar analysis was performed separated for inorganic nanopesticides, using the queries shown in Table 2 and, in this case, most reliable results were recovered using queries P4 and P5 for conventional and nano-based inorganic pesticides, respectively.

Fertilizer is an old technology, with a significant number of patent applications per year since 1922 showing an expressive growth of patent application in 2000

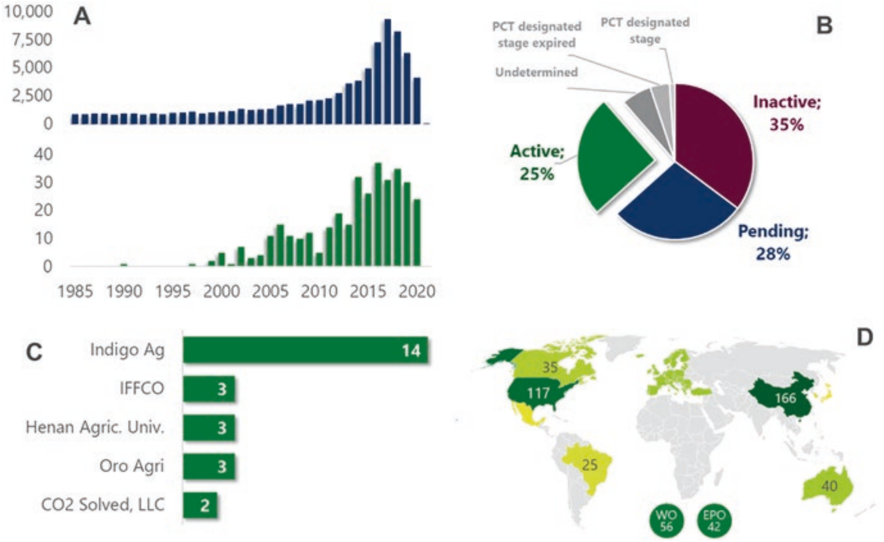

Fig. 1 Patent landscape analysis for nano-enabled fertilizers using query F4. (**a**) Patent application per year of nano fertilizers (green bars, query F4) in comparison to conventional fertilizers (blue bars, query F1). (**b**) Simple legal status breakdown of the technology field. (**c**) Highlight of the top 5 assignees with the largest patent portfolios in the technology field. (**d**) Geographic coverage of where patent applications have been filed

(Fig. 1a). Similarly, inorganic pesticides also display a constant patent applications per year until mid-1960s, when it grew reaching a plateau up until mid-2000s, when started to grow at a faster rate (Fig. 2a). This may be due to the development of more effective organic active ingredients replacing old inorganic compounds. Nanotechnology is a recent development and first patent applications in both technological fields were filed relative recently, around mid-2000s. From the patent applications, only about one-fourth are currently active (granted and alive) assuring the exclusivity of commercialization of that technology in a specific region for the assignee and in both nanotechnological fields the patent application is widespread all over the world and filed by multiple assignees.

According to the Nanotechnology Products Database, (2021), there are around 9000 nano-enabled products available for different market segments, but only a few are agricultural products (231 products from 75 companies, against 850 products from 244 companies available in the cosmetics market, for example). Nano-based products and technologies comprise mainly nanoparticles, such as metals, metal oxides, clays, nutrient or active ingredient impregnated in a polymeric or inorganic nano-sized matrix acting as a nanocarrier. Some products claimed as nanotechnological are also prepared by emulsification using surfactants or polymers as emulsifiers and stabilizers (Nuruzzaman et al., 2016; Mustafa & Hussein, 2020; Sikder et al., 2021), which can also be coacervated or polymerized in situ to form, respectively, a soft or a hard shell (Pires-Oliveira et al., 2020a). Fertilizers (102) account

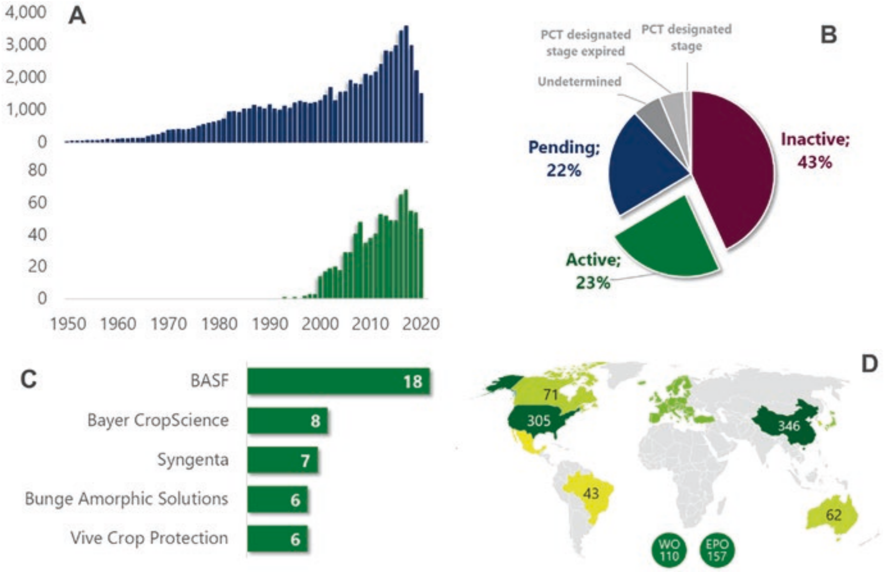

Fig. 2 Patent landscape analysis for nano-enabled inorganic pesticides using query P5. (**a**) Patent application per year of nanofertilizers (green bars, query P5) in comparison to conventional fertilizers (blue bars, query P4). (**b**) Simple legal status breakdown of the technology field. (**c**) Highlight of the top 5 assignees with the largest patent portfolios in the technology field. (**d**) Geographic coverage of where patent applications have been filed

for the main nanoagricultural products available with formulations, being divided mainly into the application mode (aeroponics, hydroponics, soil, or foliar applications) and type of nutrient, such as macronutrients (NPK), secondary macronutrients (calcium, Ca), and micronutrients, such as copper (Cu), iron (Fe), and zinc (Zn). Nanotechnological plant protection products comprise silver (Ag) and copper (Cu) nanoparticles and the landscape tends to focus more on technical challenges, mainly the scale up.

Inorganic matrices, such as nanoclays (Chevillard et al., 2012; Zhang et al., 2020), mesoporous silica nanoparticles (Plohl et al., 2021; Xu et al., 2021), and other nanocomposites (Pancera & Wengeler, 2015; Kottegoda et al., 2017; Zhang et al., 2019; Eldridge & Rosa, 2020) are often used to produce a nanocarrier for pesticides and nutrients. Polymers, dendrimers, and surfactants are classes of organic compounds able to encapsulate and/or deliver nano-sized inorganic pesticides or fertilizers. In addition to a controlled release, these nanomaterials may also display further benefits: be a nutrient source providing N, P, and Si when decomposing. Moreover, smart nanomaterials can be generated by coating the nanoparticles, leading to a nanopesticide or a nanofertilizer responsive to light (Chen et al., 2018), pH (Hao et al., 2020), temperature (Yao et al., 2021), or even to a plant enzyme (Abdelrahman et al., 2021), releasing the active ingredient in a specific target or at a desired time. Another advantage of polymer coating is to provide adhesion of the nanoparticle onto the leaves' surface, guaranteeing the uptake of nutrients (Read et al., 2020).

Table 1 Searched terms used for queries related to conventional and nano-enabled fertilizers. TACD_ALL = search in Title/Abstract/Claims/Description (original and machine translation). IPC: A01N is related to pesticides, and A01C is related to fertilizers

Query	Search terms	Total	Simple families
F1	TACD_ALL:((leaf OR foliar OR foliage OR root) AND (fertiliz*)) AND IPC:(A01N OR A01C)	230,573	94,261
F2	TACD_ALL:((leaf OR foliar OR foliage OR root) AND fertiliz*) AND IPC:(A01C)	54,156	40,579
F3	TACD_ALL:((leaf OR foliar OR foliage OR root) AND (fertiliz*) AND (nano*)) AND IPC:(A01C)	1597	1007
F4	TACD_ALL:((leaf OR foliar OR foliage OR root) AND (fertiliz*)) AND TACD_ALL:("nanoscale" OR "nano-scale" OR "nanosize*" OR "nanomater*" OR "nanopar-tic*" OR "nano-particle" OR "nano-level" OR "nanosphere" OR "nano-powder" OR "nano-sphere" OR "nano-material" OR "nanotech*" OR "nanocaps*" OR "nanostruct*" OR "nano-tech*") AND IPC:(A01N OR A01C)	865	351
F5	(TACD_ALL:((leaf OR foliar OR foliage OR root) AND (fertiliz*) AND (("nanoscale" OR "nano-scale" OR "nanosiz*" OR "nanomat*" OR "nanoparticle" OR "nano-particle" OR "nano-level" OR "nanosphere" OR "nano-powder" OR "nano-sphere" OR "nano-material" OR "nanometer" OR "nano-copper" OR "nanotech*" OR "nanocaps*" OR "nanostruct*"))) AND IPC:(A01C))	442	253

Metal and metal oxide nanoparticles with potential application as pesticide or fertilizer can also be produced by the sol-gel method, which generates solid materials (*gel*) from small molecules in colloidal solution (*sol*) (Parashar et al., 2020), as described in several embodiments of patent documents from industries of the two different segments, for instance, BASF (Dreher et al., 2013) and Bunge Amorphic Solutions LLC (Foscante, 2018), besides universities (Duan et al., 2005; Santra, 2018; Santra et al., 2018). A composite of titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$) nanoparticles (Baker et al., 2020) applied to agricultural plants was developed to enhance CO_2 trapping from the air, as an attempt to reduce the concentration of greenhouse gases. Micronutrients, such as copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), boron (B), silicon (Si), and titanium (Ti), were combined with coordinating anions to produce 2D nanostructured compounds that can be used as nanofertilizers or nanopesticides showing an enhanced performance (Hamers & Borgatta, 2020). A similar system was produced neutralizing a water-soluble polyelectrolyte using an oppositely charged species, forming a collapsed polymer nanoparticle that entraps the active ingredient in its interior producing a controlled release (Li et al., 2020).

Amphiphilic copolymers have been widely used to produce nanocapsules of pesticides and fertilizers. Mulqueen et al. (2014) described a method for coating crystalline nanoparticle of an active ingredient using block copolymer micelles. The fungicide mancozeb was prepared in a nanoformulation comprising micelles of a poly(ethylene glycol)-based functionalized amphiphilic copolymers for targeted

Table 2 Searched terms used for queries related to conventional and nano-enabled inorganic pesticides. TACD_ALL = search in Title/Abstract/Claims/Description (original and machine translation). IPC: A01N is related to pesticides, B82 is related to nanotechnology, and C01 is related to inorganic chemistry

Query	Search terms	Total	Simple families
P1	TACD_ALL:((herbicid*) OR (pesticid*) OR (insecticid*) OR (fungicid*)) AND IPC:((A01N) AND (C01))	3045	1073
P2	TACD_ALL:((herbicid*) OR (pesticid*) OR (insecticid*) OR (fungicid*)) AND IPC:((A01N) AND (C01) AND (B82))	74	36
P3	TACD_ALL:((herbicid*) OR (pesticid*) OR (insecticid*) OR (fungicid*)) AND IPC:((A01N) AND (C01)) AND TACD_ALL:((“nanoscale” OR “nano” OR “nano-particle” OR “nano-scale” OR “nano-level” OR “nanosphere” OR “nano-powder” OR “nanomaterial” OR “nano-sphere” OR “nano-material” OR “nanometer” OR “nano-copper”))	347	131
P4	TACD_ALL:(((herbicid*) OR (pesticid*) OR (insecticid*) OR (fungicid*))) AND TACD_ALL:(“silver” OR “copper” OR “cupper” OR “zinc” OR “zinc-copper” OR “titanium” OR “silicon” OR “silicon oxide” OR “aluminium” OR “SiO2” OR “TiO2” OR “ZnO” OR “Al2O3”) AND IPC:(A01N)	261,856	74,769
P5	TACD_ALL:(((herbicid*) OR (pesticid*) OR (insecticid*) OR (fungicid*))) AND TACD_ALL:(“silver” OR “copper” OR “cupper” OR “zinc” OR “zinc-copper” OR “titanium” OR “silicon” OR “silicon oxide” OR “aluminium” OR “SiO2” OR “TiO2” OR “ZnO” OR “Al2O3”) AND TACD_ALL:(“nanoscale” OR “nano-scale” OR “nanosize*” OR “nanomater*” OR “nanopartic*” OR “nano-particle” OR “nano-level” OR “nanosphere” OR “nano-powder” OR “nano-sphere” OR “nano-material” OR “nanotech*” OR “nanocaps*” OR “nanostruct*” OR “nano-tech*”) AND IPC:(A01N)	2030	848

delivery of the active ingredient (Majumder et al., 2020). Using a nanoemulsion, Berg and Pullen (2016) created a lipid nanocarrier system for delivery of nutrients or active ingredients. Other nanocarrier for fertilizer and pesticide application is highly branched dendrimers, such as poly(etherhydroxylamine) (PEHAM) (Hayes et al., 2017) or poly(aminoamide) (PAMAM) (Bunderson et al., 2020), which enhance the water solubility of active ingredients and increase their bioefficacy. In this case the active ingredient is conjugated and entrapped in the dendrimer molecule.

Different materials and approaches can be employed to produce nanomaterials with potential use in agriculture. A wise combination of inorganic particles and polymers enables a prospective system to overcome current limitations in nanocarriers for agrochemicals. It is possible to design and control the polymer architecture generating a versatile functional component that allows to tune the transition trigger tailoring the nanostructure formed (Pires-Oliveira et al., 2020b), hence enabling a controlled delivery of the active ingredient (Sikder et al., 2021). Moreover, there are a number of monomers that can be selected to produce biodegradable polymers avoiding microplastics pollution. Further, these additional outer layers may provide physical stability of the nanoparticles in aqueous suspension, as discussed in the following section, ensuring long-term stability for an appropriate time between production, transportation, storage, and application. The ionic moieties of the coating polymer grant electrostatic repulsion between nanoparticles and the non-ionic groups, such as ethylene oxide chains, provide steric hindrance; both mechanisms avoid particle agglomeration and aggregation, eventually followed by a phase separation. Finally, with all these features together and taking into consideration the best feasible process for a large-scale production using ecofriendly raw materials, nanotechnology can be used as a cost-competitive alternative to increase the sustainability of the agriculture.

3 Physicochemical Concepts and Properties of Nanosystems

As previously mentioned, the development of new vehicles to deliver actives for different systems, aiming to deliver at a specific target or time and to increase bioavailability or stability is recurrent in several areas of industry. In agriculture, nanostructured systems such as microemulsions, nanocapsules, and nanoparticles are examples of strategies that can intensify uptake, promoting a sustained release, with enhanced residual effect or bioefficacy in the field. Usually, nanoparticles cover the range 10–200 nm diameter, being included within the colloidal range, between 1 nm and 1 μm (IUPAC, 2019). These particles start presenting properties completely different from their bulk counterparts. The observations of these size-dependent properties are intriguing because the entities that make up the micro and the nanoparticles are the same. So why are the properties so different? Other than the exponentially increased surface area, the shape or assembly of the atoms is enough to modulate the properties. Before understanding the field performance, the nanosystems present highlighted features in terms of formulation stability. The destabilization of a colloidal system in liquid media can occur by two main mechanisms: gravitational force and Ostwald ripening.

For the sake of understanding these phenomena, it is important to consider fine particles that are dispersed in a liquid medium and undergo Brownian motion. The Brownian motion is favorable in nanosystems, since it describes their random motion and the smaller the particle size, the faster their movement and the less likely it is to sink to the bottom, resulting in no creaming or sedimentation during storage (Tadros, 2016). On the other hand, the increase of motion triggers more collisions favoring Ostwald ripening, hitting each other and changing direction of motion in solution. Therefore, the Ostwald ripening is the main mechanism for the instability of nanoformulations (Tadros et al., 2004). This phenomenon is thermodynamically driven, a spontaneous process that occurs due to the larger particles being more energetically stable than smaller ones. The molecules of the surface are interacting with less molecules than those of the bulk. As the system tends to keep the lower energy, molecules from the surface of small particles detach and diffuse into the solution. The consequence is the increase of free molecules concentration in the solution and the supersaturation leads to the aggregation of them onto the surface of larger particles (Ratke & Voorhees, 2002). Thereby, the small particles have a decrease in their sizes whereas the big particles have an increase always trying to minimize the total surface area and thus minimizing the ratio surface area by volume. Then, the Ostwald ripening describes crystal growth. By the same reason described above, a decrease of particle size leads to an increase of solubility, consequently these molecules tend to circulate in the medium and to deposit onto larger particles. The different polymorphs of the insoluble particle may also drive this phenomenon once the solubility may be different among them.

The gravitational force triggers the sedimentation, flocculation, and creaming. Regarding sedimentation, it occurs when the sedimentation velocity (v_s) is greater than the thermal velocity (v_t) of Brownian motion. Both rates can be approximated to particle size-dependent functions (McClements, 2011):

$$v_s = \frac{2a^2 g\Delta\rho}{9\eta} \tag{1}$$

$$v_t = \sqrt{\frac{kT}{m}} = \sqrt{\frac{3kT}{4\pi a^3 \rho}} \tag{2}$$

Equation 1 describes the sedimentation velocity, and it is called Stokes' law, in which "a" is the particle radius, $\Delta\rho$ is the difference between the dispersed and continuous phase densities, g is the acceleration of gravity, and η is the viscosity of the continuous phase. Eq. 2, also called the Fokker-Planck equation, describes the thermal velocity of the particles in Brownian motion, where k is the Boltzmann constant, T is the temperature, m is the mass of a particle, and ρ is the density of the dispersed phase. Generally, nanoparticles suffer less influence of this phenomenon due to their small radius, but Ostwald's ripening is predominant for the same type of particles (Tadros, 2016). Another reason for destabilization is flocculation. The driving force for flocculation is van der Waals attraction, which for spherical particles at short distances of separation is proportional to the particle or droplet radius (Hamaker, 1937). This effect is less prominent in nanosystems since the radius is much smaller when compared to suspensions and emulsions, resulting in lower van der Waals attraction between the particles or droplets. Therefore, nanoparticles do not tend to flocculate by van der Waals attraction.

Considering application as nanopesticides or nanofertilizers, some properties, such as surface area, play an important role. The surface area for a given volume of nanoparticles is much larger than the surface area for the same volume of larger particles, thus considering that the application of agrochemical formulations is usually very inefficient, the increase in surface area by volume might be an interesting strategy to improve the efficacy of these formulations. Leaf uptake can be increased by the application of nanoparticles, considering their usual sizes. The entrance routes for these nanoparticles may include the cuticle and stomata, as shown in

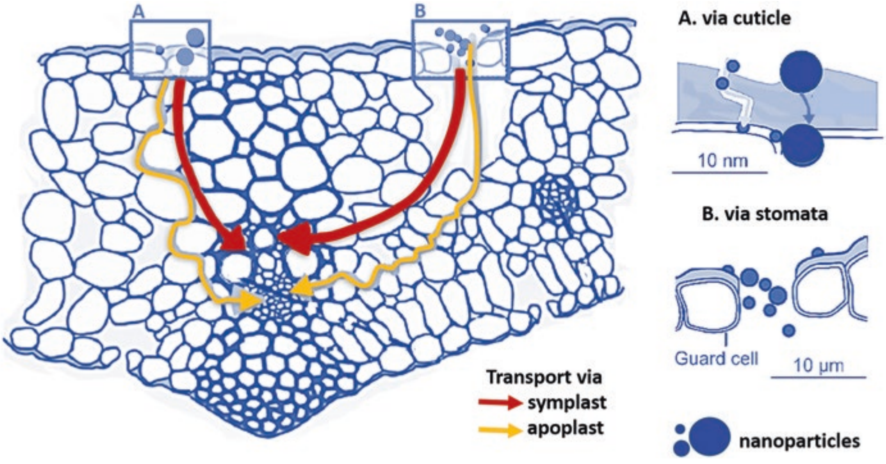

Fig. 3 Pathways for nanoparticles foliar uptake with transportation via symplast (red arrow) and apoplast (yellow arrow). Scheme depicting (**a**) the uptake via cuticle and (**b**) the uptake via stomata

Fig. 3, although these phenomena are still not fully elucidated to date (Avellan et al., 2019). It is usually assumed that the entrance through stomata seems more feasible due to the size difference between the nanoparticle and the stomata itself; however, it is more likely that nanoparticles are absorbed through the cuticle, even though cuticular pores are smaller than the nanoparticle sizes, similarly to the entrance of particulate matter from polluted environments. The entrance through stomata may occur, however alike particulate matter events, it may cause stomata clogging by nanoparticles. This clogging leads to an accumulation of reactive oxygen species at the substomatal chamber and adjacent cells, which may trigger a programmed cell death, morphologically observed as necrotic spots (phytotoxicity).

Particles of varying sizes, including nanoparticles, can also be used for emulsion stabilization, enabling the storage and use of formulations, as well as improved tank mixtures for application in the field, in the so-called Pickering emulsion (Pickering, 1907), named after Spencer Pickering but first observed by Walter Ramsden (Ramsden, 1904). In this type of emulsion, particles adsorb on the interface between the dispersed and continuous phases preventing them from coalescing and leading to more stable emulsions (Ortiz et al., 2020). The energy of the system (ΔG_d), represented in Eq. 3, is dependent on the particle radius (r), the contact angle between the phases (θ), and the interfacial tension between the oil and water (γ_OW) (Zhou et al., 2020). The nature of the particle is important for the stabilization ability, being amphiphilic particles, including Janus particles (Walther & Müller, 2013), the most effective ones because they interact well with the hydrophilic phase and the oil phase.

$$\Delta G_d = \pi r^2 \gamma_{OW} \left(1 - \left|\cos\theta\right|\right)^2 \tag{3}$$

Rheological properties of nanoparticle-containing solutions can vary from Newtonian to non-Newtonian according to the power-law as represented in Eq. 4 and Eq. 5 (Saedodin et al., 2019; Kessler et al., 2019).

$$\tau = m\ddot{Y}^{n} \tag{4}$$

$$\mu = m\ddot{Y}^{n-1} \tag{5}$$

where τ is the shear stress (Pa), μ is the dynamic viscosity (Pa·s), $\ddot{Y}$ is the shear rate (s^{-1}), n is the power-law index, and m is the consistency index ($Pa{\cdot}s^{n}$). When n is equal to 1, the behavior of the fluid is Newtonian (linear shear stress in terms of shear rate), whereas the fluid is non-Newtonian if n is different of 1 (having shear thinning when n is lower than 1 and shear thickening when n is greater than 1).

In terms of appearance of the nanoformulation, they can be transparent, translucent, or turbid depending on three main factors, namely the particle or droplet radius, the difference in refractive index between the dispersed phase and dispersion medium, and the volume fraction of the dispersed phase. As there are different types of formulation that apply nanotechnology, it is unspecific to list all the possible required protocols to be applied in order to evaluate the physicochemical performance. Our suggestion is that the formulator consults the FAO Guidelines and find the better kind of formulation to follow the requirements (microemulsions – ME, Capsule suspension – CS, among others). In general, the commonly recommended tests by CIPAC[3] are the following:

- Acidity and/or Alkalinity (MT 191) or pH range (MT 75.3).
- Pourability (MT 148.1).
- Spontaneity of dispersion (MT 160).
- Suspensibility (MT 184).
- Wet sieve test (MT 185).
- Persistent foaming (MT 47.2).
- Emulsion stability and re-emulsification (MT 36.3).
- Particle size distribution (MT 187).
- Accelerated storage (MT 46.3).

4 Tank Mix Compatibility

Tank mixture of two or more components is a usual and necessary practice adopted by farmers aiming to optimize resources in crop management. Time, costs, number of treatments, water, wear of agricultural implements, and energy are examples of parameters that can be optimized by combining and applying suitable products in a mixture. Furthermore, the combination of pesticides with different modes of action

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[3] CIPAC: Collaborative International Pesticides Analytical Council.

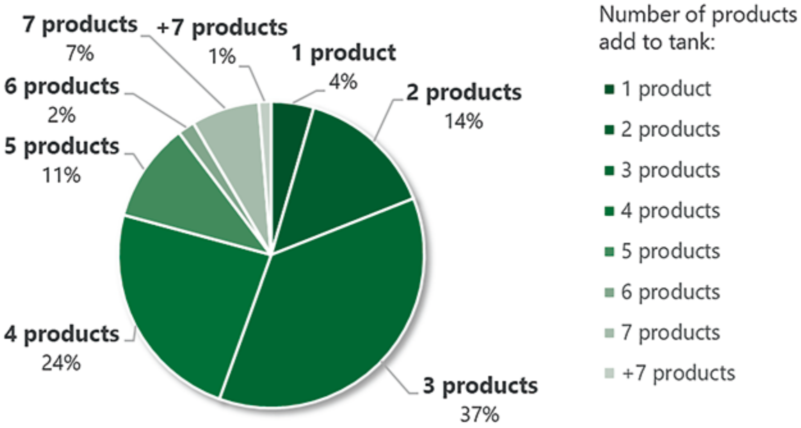

Fig. 4 Number of products added in a tank for applications in Brazil. It includes insecticides, fungicides, herbicides, foliar fertilizers, and adjuvants

can be synergistic, promoting a better result when compared to single and time elapsed application. However, although some mixtures are synergistic or neutral, it is important to pay attention to the antagonistic effect that may occur (Green, 1989). The global result of this equation is reflected in a substantial gain in profit, due to the optimized management and improved yield.

The tank mixture practice is very regionalized and customized due to obvious reasons. In Brazil, ca. 96% of the farmers apply tank mixtures, and in 86% of the cases the mixtures contain between two and five products, as shown in Fig. 4 (Gazziero, 2015). In the soybean crop, for example, 86% of the glyphosate applications are made by the combination of insecticides, fungicides, and other herbicides. The choice of the products to be mixed depends on the crop, seed germplasm, pests and diseases to be treated or prevented, weather conditions, application stage, and products available in the region. Resistant pests, weeds, and diseases are important drivers for the definition of which products will be mixed in each application.

In addition to the great variability presented above, there is a clear and constant trend on reducing the spray volume per hectare, which contributes to the autonomy of the agricultural to be implemented in both terrestrial and aerial applications, again impacting in the management costs. Ultra-low volume (ULV) applications through drones are a real and booming subject for both chemical and biological pesticides. In typical drone applications the spray volume varies from 5 to 10 liters/ha. The same terrestrial application would take about 100 to 300 liters/ha. There is a considerable difference in the preparation of tank mixture for terrestrial vs. drone's application.

Considering the variability of products, water quality, types of mixtures, pH of mixture, and volume/area, there is a great chance of having problems related to tank mixture compatibility. Difficulty in dissolving products, phytotoxicity on target crop, excess of foam, nozzle clogging, and precipitation of material are the most frequent problems of compatibility observed in the field. The order of addition of the products is another point of high relevance and can be determinant on the compatibility or not for a given tank mixture. As there are many variables involved and as the system becomes more and more complex by the sequential addition of products, it is a difficult (and almost impossible) task to define exactly which is the key point in a compatibility issue. For this reason, there are products in the market positioned as tank mix compatibilizers, which are in most cases water conditioners, acidifiers, buffers, chelation agents, and emulsifiers, in order to ensure compatibility and avoid problems.

When the subject of nanostructured pesticides or fertilizers is introduced, there is an additional point of attention regarding the compatibility of complex mixtures. However, there are interesting new perspectives about this incoming type of pesticides, that would help to achieve stable mixtures and new possibilities:

1. 59% of the tank mixture preparations in Brazil are made using the full dosage of the products (Gazziero, 2015).
2. Given the size range of nano-enabled pesticides, and the fact that the size impacts directly on the efficacy of the active ingredients due to better distribution and uptake, it is possible to apply reduced doses of active ingredients per hectare (De Oliveira et al., 2015);
3. As the lower the load in a tank, the lower is the risk of compatibility issues. Furthermore, lower doses of active ingredients are advantageous in terms of cost of formulation, environmentally friendly approach, and lower risks of remaining residues of pesticides on food.

The concept of nanoscale pesticides also includes hybrid micromaterials (size >200 nm) that contain substructures attached in the nanoscale. These substructures can be: (a) nanoscale coatings, (b) additives, and (c) fertilizers (Mikkelsen, 2018). Much of the tank compatibility problem comes from the surface of a given active ingredient particle that interacts with electrically charged components present in the system, giving rise to clusters of increased size, which results in aggregates that precipitate and culminate in nozzle clogging. The possibility of implementing nanocoating on the surface of a given problematic active ingredient particle can lead to a surface modification which can avoid the aggregation process and related complications. Furthermore, it can modulate the delivery kinetics of the active to the target, which can be of interest regarding residual effect, for example.

When applied in the ionic and soluble form, fertilizers or inorganic pesticides act as electrolytes in the spraying solution. The presence of charged components can result in attraction forces between ions and particles, causing instability and precipitation. Insoluble salts can be formed between ions in solution, representing another risk to the mixture. The application of formulations based on nanoparticles suggests an interesting approach to overcome issues of this nature, once they are not ions, but the particle size is of comparable dimension. As new nanopesticides and nanofertilizers emerge as product options, the results in the field practice will naturally be explored and become an alternative tool for the market toward complex mixtures. The advantages we can prospect are based on the lower doses combined with the nanosized particle that makes them more available compared to current microparticle's formulations.

5 Final Remarks

The countless benefits of nanosystems are exhaustively described in the literature for diverse fields of science. For agriculture, it is not different. In this chapter, we overviewed the main technologies used and market for this application, highlighting the physicochemical properties that ensure a relevant performance of nanopesticides and nanofertilizers in terms of formulation stability and their behavior in tank mixtures. When we refer to nanotechnology for inorganic pesticides or fertilizers the possibilities are extensive, since inorganic matrices and aggregates are formed by polymers, dendrimers, and surfactants, which can be smart and functional materials, and formulated as products classified as microemulsion (ME) or capsule suspension (CS, ZC). This approach of modern products for agriculture is growing and we expect to see an increased number of studies and patents on this technological field, followed by new products launched in the market comprising nano-enabled fertilizers and pesticides.

In this scenario, it is common to occur merges of startups with big global companies. Due to the specific technology that is currently under development, it needs a big effort to control, characterize, and scale up the process, normally the mergers are the better strategy to incorporate the technology by the big ones, once their assets scarcely can absorb the specific demand for nanosystems.

Besides that, farmers need to be convinced about the benefits of this kind of technology that probably will not deliver the load of actives nor there is a need for it, due to their nanotechnology ability to present similar performance in the field with less concentration of active ingredients or fertilizers.

Other obstacle to overcome is the regulatory issues, there are several studies proving the absence of great toxicological problems, but the regulatory agencies must position themselves about that when they carefully understand the toxicity aspects.

In contrast to several steps to overcome, the great number of studies, patents, and some products that already exist in the market prove the importance of nanotechnology for agriculture.

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Inorganic Nanoparticles to Promote Crop Health and Stimulate Growth

Carlos Tamez, Nubia Zuverza-Mena, Wade Elmer, and Jason C. White

Abstract As global food needs grow to keep pace with an ever-growing population, increased stress will be placed upon agricultural output. Current agriculture practices are wasteful and inefficient, especially with regard to fertilizer application. Inefficiency in plant uptake of nutrients leads to repeated over application, which in turn causes increased runoff of NPK into the environment. Recent developments in nanotechnology can enable more effecient delivery and uptake of vital nutrients to plants when they are needed. Published research has shown that targeted delivery of micro and/or macronutrients at critical development stages can boost plant growth, improve crop yields, increase nutritional content, or aid in disease suppression. Although further work is necessary to completely understand the mechanisms and implications of their use, the application of nanoparticles in agriculture can provide the changes needed to keep the world fed.

Keywords Biostimulation · Agriculture · Sustainability · Plant growth

The exposure of agricultural crops to nanoparticles (NPs) has long had a stigma of potential negative effects, and this is highlighted by the initial studies into the phytotoxicity of nanoparticle exposure to plants of agricultural interest. Results demonstrating reduced seed germination, diminished root and shoot growth, increased oxidative stress activity, or even complete yield losses were common—as were

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excessively high application doses. However, as engineered nanoparticles are developed and the phytotoxicity studies evaluating their effects have matured, the research has begun to show several beneficial aspects associated with metal and nonmetal-based nanoparticles. Studies spanning the entire life cycle of plants, grown in soil-based media or in field plots, and with exposure to environmentally relevant conditions have demonstrated the ability of NPs to stimulate crop growth and photosynthetic output, improve plant health, and bolster defenses against pest and disease—often outperforming bulk or conventional material equivalents. Consequently, the use of nanoparticles is gaining momentum for applications in agricultural settings such as nanoscale fertilizers or other crop amendments, and recent studies have demonstrated their efficacy for enhancing disease suppression, modifying nutrient accumulation and distribution, and increasing crop yield. As the global population is expected to surpass 9.5 billion by 2050 and food demand will nearly double (Zhao et al., 2020), conventional approaches to agriculture will most certainly prove inadequate. In fact, the lack of sustainability of many of the current agricultural practices is contributing to environmental problems that will limit arable land in the near future. The projected global demand for NPK fertilizers in 2020 was estimated to be over 200 million tons (FOA, 2017). It is also widely known that certain applied agrichemicals are persistent in soil, often affecting vital soil functions such as nutrient content, pH, and soil microbiota health (Mandal et al., 2020; Meena et al., 2020; Prashar & Shah, 2016). The adoption of nanotechnology in agricultural practices can help alleviate this burden. Herein, we describe some of the sustainable and practical uses where different nanoparticles can positively and sustainably impact agriculturally relevant crops (Fig. 1).

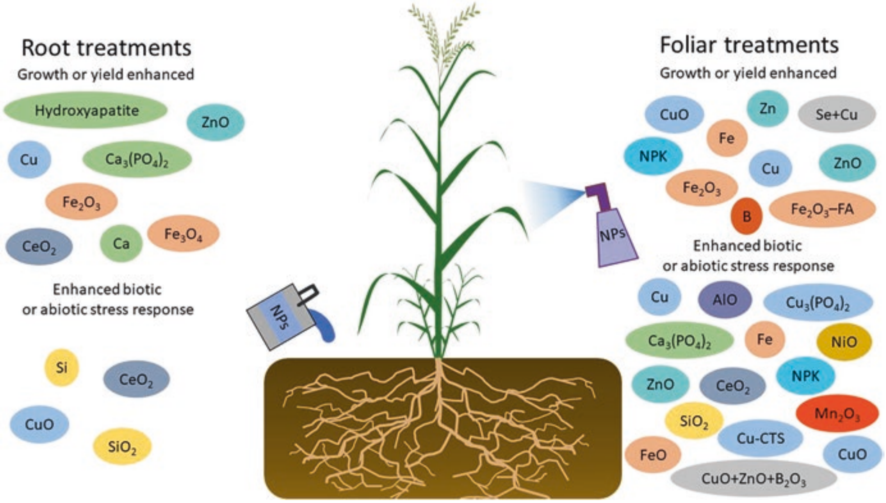

Fig. 1 Inorganic-based nanoparticles have been shown to enhance crop performance. Exposure has increased crop performance by modulating nutrient accumulation or triggering the activation of certain plant defense mechanisms. This has led to increased growth, better yields, and/or enhanced disease tolerance

1 Nanoparticles to Enhance Plant Growth and Increase Yield

One desirable outcome from the application of NPs to agricultural crops is increased growth and improved yield, although this clearly depends on the type of NPs utilized and the crop, as well as the environmental conditions (e.g., biotic and abiotic stressors). Nutrient deficiencies in agricultural soils are common due to soil erosion, over-production, and monoculture cultivation; so, a starting point could be with the application of nanoscale or nano-fertilizers when mineral fertilizers would otherwise be employed. Among the nutrients that plants require in order to maintain healthy functions, nitrogen (N), phosphorous (P), and potassium (K) are applied in the greatest amounts. However, the use efficiency of applied N, P, and K fertilizers is less than 50%, 10%, and 40%, respectively, with the vast majority of nutrients remaining in the soil to be washed away or volatilize (Baligar et al., 2001). Therefore, overfertilizing is a common and non-sustainable agricultural practice. For example, the excessive use of N might be necessary to meet production goals, but N amendments lead to water pollution from runoff and nitrous oxide (N_2O) emissions to the air, a greenhouse gas more potent at trapping heat than CO_2 (Woodbury & Wightman, 2017). Alternatives to reduce the amounts of agrochemicals include optimization of irrigation practices (e.g., drip irrigation to avoid runoff), improved fertilization regimes (delivery rate and times), and cultivation of nutrient-efficient plants. An approach under investigation is the use of nanofertilizers which often show enhanced efficacy at lower amounts than typical salts. Foliar application of nano NPK to cucumber plants improved yield by over 50%, compared to conventional mineral NPK fertilizer (Merghany et al., 2019). The treatment (foliar) of wheat with nano NPK, combined with conventional NPK, was effective at boosting plant growth and enhancing grain yield (Abdelsalam et al., 2019). Treating bean with foliar nano NPK at the flowering stage of growth significantly increased yield 133%, while treating at any growth stage improved yield 61% (Mohsen et al., 2020). Meanwhile, nano NPK foliar application to chickpea plants significantly enhanced seed weight (12%), seed yield (25%), and biological yield (14%), compared to non-fertilized controls (Drostkar et al., 2016). Potato foliar-treated with chitosan-coated NPK (CTS-NPK) showed growth increases of 18.5–36.5%, 17% greater yield, and improved nutrient content over conventional mineral NPK (Elshamy et al., 2019). Spraying chitosan-coated nano NPK enhanced the growth of bean and coffee and augmented the mineral nutrient content of coffee (Ha et al., 2019; Hasaneen et al., 2016).

As nanotechnology advances, researchers are developing smart or tunable engineered nanomaterials or pairing NP with conventional treatments. For example, the application of ZnO NPs applied with mineral NPK fertilizer increased sorghum grain yield and modified NPK accumulation versus the use of NPK fertilization alone (Dimkpa et al., 2017b). Combined NPK-Zn treatments led to increased grain yield with higher levels of K and Zn in the plants, regardless of the form (nanoscale or salt). Additionally, NPs applied as mixtures (ZnO, CuO, and/or B_2O_3) increased soybean branching, number of flowers, shoot dry weight, and N uptake. However, this is a distinct composite effect; when B_2O_3 NPs were omitted, only increased shoot growth was noted (Dimkpa et al., 2019). Likewise, soybean treated with ZnO, CuO, or B NPs separately showed only increased biomass (Peréz et al., 2020). This suggests that combined NPs have different effects than when applied individually. The foliar application of Fe, Zn, and NPK was able to increase the number of branches in chickpea plants; however, when NPK was removed and only Fe and Zn were sprayed, plants achieved the highest seed yield and seed weight of any of the tested treatment combinations (Drostkar et al., 2016). Meanwhile, improvements were reported when both Cu NPs and Se NPs were applied at varying concentrations (Se 1–20 mg L^{-1}, Cu 10–250 mg L^{-1}), including increased vitamin C content, firmer tomato fruit, and 25% heavier fruit (Hernández-Hernández et al., 2019). On the other hand, Elmer et al. (2021) found that a single application of CuO NPs was superior to combinations with Mn_2O_3, and/or ZnO at increasing the yield of eggplant and suppressing the Verticillium wilt disease. Importantly, the benefits of many NPs are, among other significant factors, concentration-dependent. For instance, wheat plants treated with ZnO NPs at low concentrations (~2 mg kg^{-1}) showed increased shoot growth and a non-significant trend toward higher yield (Dimkpa et al., 2020). However, when wheat was separately exposed to treatments of 10–200 mg kg^{-1}, yield was increased by up to 56% (Du et al., 2019). Priming wheat seeds in ZnO NPs before sowing increased plant growth, biomass, and grain weight (Rizwan et al., 2019). Others have demonstrated that ZnO NPs increased the plant height, branching, and seed yield of chickpea (Drostkar et al., 2016); plant height, stem diameter, biomass, yield, and capsaicin content of habanero pepper (García-López et al., 2019); biomass and leaf area of mung bean (Patra et al., 2013); and biomass and photosynthetic activity of coffee (Rossi et al., 2019). These benefits could be attributed to the slow release of Zn ions. For example, application of NPs—either by foliar treatment or seed coating—provides a long-term surface attached source of Zn ions that can enter via roots, the stomata, or ruptures in the leaf surface. Easy access of Zn ions to the leaf promotes improved photosynthesis, as a positive interaction between ZnO NP application, carbon assimilation, and stomatal conductance has been observed (Rossi et al., 2019). Seed priming activates certain metabolic pathways that lead to the promotion of plant growth, such as photosynthetic pathways and reactive oxygen species (ROS) scavenging enzymes (Rizwan et al., 2019). Research into the benefits of seed priming has shown the technique activates vital protective functions, including antioxidant defense, that protect the plant from DNA/RNA damage (Buchman et al., 2019; De La Torre-Roche et al., 2020).

More recently, applying NPs of different forms and at lower doses under different regimes have produced positive effects. In many cases, nano-treatments improve growth parameters in comparison to ordinary amendments and therefore, studies to optimize the use of nano-formulations are also taking place. A study on maize revealed that nano NPK at lower ratios of 12-12-36 was superior than higher percentages (20-20-20) at stimulating growth and increasing yield in maize (Alzreejawi & Al-Juthery, 2020). Maize grown in soil amended with sulfur-enhanced nano NPK

(NPKS) provided better growth promotion than standard nano NPK (Dhlamini et al., 2020). The application of a nanoscale NPK, containing two sources of N (nitrate and urea), at a rate of 15 kg N ha^{-1} allowed for a 40% reduction in the amount of traditional N fertilizer applied without any adverse effects on wheat kernel weight (Ramírez-Rodríguez et al., 2020). Moreover, foliar application of CuO NPs and $Cu_3(PO_4)_2$ nanosheets increased total chlorophyll content and carotenoids in the leaves of watermelon plants (Borgatta et al., 2018). Metallic Cu NPs have been successful at improving the production of tomato fruit, with foliar applications increasing fruit firmness, lycopene, and vitamin C content (López-Vargas et al., 2018; Pérez-Labrada et al., 2019). Applications of Cu NPs at low concentrations of 30 ppm enhanced the yield of wheat by increasing number of spikes, number of grains per spike, and overall grain weight (Hafeez et al., 2015). Firmer tomato fruit could be the result of increased lignin formation, enhanced by the accumulation of Cu in plant tissues (López-Vargas et al., 2018); increased wheat performance has been attributed to NPs ability to better deliver ions over an extended period of time. Additionally, copper nanowires were successful at improving root and shoot length, and biomass of exposed alfalfa (Cota-Ruiz et al., 2020). Although the application of copper-based NPs provides negligible to slightly beneficial effects when applied to unstressed crops, the opposite effect has been observed in plants experiencing biotic or abiotic stress (refer to the section "Engineered Nanomaterials for Plant Disease Management").

Like other metallic NPs, iron (Fe) NPs have demonstrated the ability to enhance crop growth and promote yield. Specifically, iron-based NPs such as Fe_2O_3, Fe_3O_4, and metallic Fe NPs have been used in agricultural settings with notable success. Fulvic acid coated onto Fe_2O_3 NPs caused a significant increase in soybean N fixation by increasing the weight of root nodules by 120%, leading to a 91% and 49% increase in root and shoot biomass, while the use of bare Fe_2O_3 NPs increased biomass by approximately 60% compared to conventional Fe-EDTA fertilizer (Yang et al., 2020). Iron oxide NPs (Fe_3O_4) used to prime wheat seeds significantly improved plant height (35%) and spike length (49%), and increased the dry weight of roots, shoots, spikes, and grains by an average of 67% (Rizwan et al., 2019). Wheat germination and shoot length were also improved when seeds were primed with Fe_2O_3 (Sundaria et al., 2019). Similarly, metallic Fe NPs have shown promising results in chickpea, significantly increasing plant height and enhancing production by nearly 23%, compared to control (Drostkar et al., 2016). Similar results are achieved when chickpea seeds were primed with FeS_2 prior to sowing. Treated chickpeas produced denser roots with larger nodules, which led to increased yield and nutrient accumulation (Jangir et al., 2020).

A number of other elements have been investigated for similar applications. Equally promising is the application of Si-based NPs to promote crop growth. SiO_2 NPs successfully increased wheat shoot growth and enhanced grain yield and 1000-grain weight (Behboudi et al., 2018). Similarly, Si NPs increased cucumber yield while simultaneously improving nitrogen content, chlorophyll production, and growth (Alsaeedi et al., 2019). Other NPs, such as those based on B and Ca, have also shown promise for increasing crop growth. The use of a B nano-fertilizer significantly increased shoot growth of lettuce by 55% and zucchini by 14% compared to the application of a conventional boron fertilizer, in boron-deficient media (Meier et al., 2020). Calcium-based NPs such as $Ca_3(PO_4)_2$ (CaP NPs) and nanohydroxyapatite (nHA) have also demonstrated the ability to enhance the performance of rice, rye, and tomato (Marchiol et al., 2019; Sun et al., 2018; Upadhyaya et al., 2017). Nanoscale CaP was shown to increase rice growth at low concentrations ($\leq$20 mg L^{-1}), increasing root and shoot length by 5%, and root and shoot biomass by 10%. The application of nHA at rates of 200–2000 mg L^{-1} significantly increased the root elongation of hydroponically grown tomatoes. Collectively, the body of evidence suggests that nanoscale nutrients provide a unique and tunable source of necessary ions to sustainably increase the performance of crucial cellular functions, resulting in greater plant growth. Importantly, these positive impacts are rarely evident with conventional nutrient formulations, highlighting the importance of nanoscale size to the observed benefit.

2 Nanoparticles to Boost Plant Nutrition

Improving nutrient availability to plants can help enhance response to external factors and can also lead to enhancement in the nutritional value of edible tissues. Plants require essential elements such as N, P, K, S, Ca, Mg, Mn, Cu, B, Zn, Fe, Ni, and Mo to activate a complex set of metabolic functions leading to the production of carbohydrates, antioxidants, proteins, and other important biomolecules (Datnoff et al., 2007). Often plants are grown in environments that are lacking in some or many of these crucial nutrients, requiring the soils to be amended exogenously with fertilizers. However, the efficiency of delivery and utilization of conventional fertilizer formulations is often quite low (<25%), resulting in overapplication to maintain growth but that also leads to secondary and potentially significant environmental damage over the long term (Hofmann et al., 2020; Kah et al., 2018; Lowry et al., 2019). The use of nanomaterials has shown significant promise for enhanced delivery efficiency as part of a sustainable agriculture framework, by using less chemicals to increase productivity with fewer impacts on the environment. The application of conventional mineral fertilizers is plagued by poor availability in non-acidic soils and low basipetal translocation with foliar treatments. However, the application of nano-based fertilizers can increase the mobility of nutrients in plant tissues (Elmer & White, 2016; Peréz et al., 2020). Increased availability of nutrients could allow for a reduction in agrichemicals, wasting fewer resources from production, saving the grower money, reducing environmental impact, and lowering the risk of exposure to farmworkers.

With respect to potentially fortifying edible tissues, the application of ZnO NPs has been shown to significantly increase Zn content in edible tissues of species such as wheat, soybean, and sorghum (Dimkpa et al., 2020; Dimkpa et al., 2017a; Dimkpa et al., 2017b). The technique of seed priming is a promising method for fortifying crops in the field. The use of ZnO or Zn-chitosan NPs significantly increased Zn content in the edible parts of rice, maize, and pinto beans (Choudhary et al., 2019; Mahdieh et al., 2018; Rameshraddy et al., 2017). Seed treatment of wheat with Fe_2O_3 NPs increased Fe content in the grains by 45.7% in a high-iron genotype (IITR26) and by 26.8% in a low-iron genotype (WL711) (Sundaria et al., 2019). This technique has also been successful at increasing the concentration of the applied element in other plant tissues, thereby promoting overall crop health. Peanut seeds coated with ZnO NPs had increased Zn content in leaves and kernels by 100 and 84%, compared to control, and 42 and 24%, compared to $ZnSO_4$ (Prasad et al., 2012). Similarly, coating seeds of maize, soybean, pigeon pea, and ladies finger with ZnO NPs increased Zn in shoots to a greater extent than $ZnSO_4$ or the bulk equivalent (Adhikari et al., 2016). Additionally, chickpea seeds primed with FeS_2 increased the content of Fe in the more densely produced roots (Jangir et al., 2020).

However, data on the effect of NPs treatments on the accumulation and distribution of other macro- and micronutrients is fragmented and less clear. The foliar application of CeO_2 NPs on tomato increased fruit concentrations of K, P, and S by an average of 27%; and Ca content by 261% (Adisa et al., 2020). When citric acid-coated CeO_2 NPs were applied via soil, Al accumulation in roots and leaves of tomato increased by 175% (Barrios et al., 2016). Seed priming has also been successful in providing a significant increase in the uptake of additional nutrients, as illustrated with chickpea primed with FeS_2; mature plants contained increased root concentrations of Mo, Mg, P, K, Mn, and Ca—ranging from 80 to 415%—compared to no priming (Jangir et al., 2020). Seed priming chickpea with FeS_2 also increased leaf concentrations of Mo by 300%, Mg by 98%, and doubled Ca content. The application of copper-based NPs has led to mixed results. Foliar application of CuO NPs increased leaf content of P, Ca, and Mn; however, it decreased Na, Fe, and Zn concentrations (Pérez-Labrada et al., 2019). In some cases, particle morphology and composition affect the accumulation of nutrients. For example, the application of CuO NPs (round edges, ~30 nm) to watermelon decreased uptake of Si, Mn, Mg, and Fe; while the application of $Cu_3(PO_4)_2 \bullet 3H_2O$ in the form of nanosheets (flat sides, sharp edges, ~151 nm) increased the amounts of these elements (Borgatta et al., 2018). These accumulation patterns are also a function of plant species; Zn, P, and Mn were decreased with CuO NPs in watermelon but increased in tomato (Ma et al., 2019). Several types of NPs have been shown to increase the uptake of either N or K, with subsequent growth promotion (Alsaeedi et al., 2019; Dimkpa et al., 2017a; Dimkpa et al., 2017b; López-Vargas et al., 2018; Peréz et al., 2020; Yang et al., 2020). Additionally, there are instances where the application of NPs does not significantly alter nutritional content in the edible tissues (Elmer et al., 2021; Elmer & White, 2016), but provides plant protection (see Plant Disease Management). Last, for some NP applications, it is difficult to assess their impact on the plant nutritional profile because the overall elemental analysis is lacking in some studies that report only the element present in the treatment. For example, calcium NPs increased the content of tomato crude protein, crude fiber, and crude fat while SiO_2 NPs increased wheat protein content (Azeez et al., 2020; Behboudi et al., 2018). However, in general, these types of nutrient analyses are lacking in many studies. In addition, given that elemental analyses are destructive, the pattern of nutrient accumulation over the course of the plant life cycle is rarely known; an understanding of that process could inform the design of optimized materials and treatment regimens. The elucidation of this could be accomplished through techniques like portable X-ray fluorescence (pXRF), which would allow for real-time monitoring of key nutrients (Montanha et al., 2020).

3 Engineered Nanomaterials for Plant Disease Management

Fungi, bacteria, viruses, and parasites are pathogens that threaten plant health (Elmer & White, 2018; Worrall et al., 2018). Although management options do exist for most pathogens, strategies are plagued by a range of shortcomings such as low overall efficacy, high cost, lack of sustainability, and induced pest resistance. Interest in the use of nano-enabled strategies in crop disease management has increased significantly in the last 5 years (Table 1). Nanomaterials can be engineered as sensors to detect disease, as agrichemical delivery carriers to inhibit or mitigate infection, as nano-enabled pesticides that directly inhibit the pathogen, or as nanoscale micronutrients that indirectly protect the host by stimulating host defense (Elmer & White, 2018). Metal oxide micronutrient nanoparticles have consistently provided positive results on a variety of crops infected with several soil-borne diseases, such as Fusarium wilts, Verticillium wilt, and Black Scurf disease. Convincing evidence has been published on the efficacy of foliar-applied CuO NPs, used alone or in combination with other NPs, to suppress soil-based pathogens. Foliar treatments carrying only a few milligrams of Cu in 2–3 mL of solution consistently provide effective long-term protection. The spatial separation between treatment (foliar) and infection (root) and the fact that conventional forms of Cu are ineffective highlights the importance of unique nanoscale properties in this strategy. Foliar application of CuO NPs has been shown to decrease the severity of Fusarium diseases on watermelon, tomato, and soybean; Verticillium wilt on eggplant; and Black Scurf Disease on potato (Borgatta et al., 2018; El-Shewy, 2019; Elmer et al., 2018, 2021; Elmer & White, 2016; Ma et al., 2019, 2020; Peréz et al., 2020). More specifically, foliar treatment with CuO NPs at 500 mg L^{-1} in watermelon suppressed Fusarium wilt and restored fruit yield to levels recorded in healthy controls; root and/or foliar-dip treatment with 1000 mg L^{-1} (of which less than 3 mL are retained in the tissues, resulting in a low dose) reduced area under the disease progress curve (AUDPC)—a metric for monitoring disease progress—by 53% (Borgatta et al., 2018). In a greenhouse study on the foliar application of Al_2O_3, CuO, Fe_2O_3, MnO, NiO, and ZnO NPs against Fusarium wilt, CuO, MnO, and ZnO were found to be the most effective in treating tomatoes (Elmer & White, 2016). CuO NPs provided the greatest Fusarium wilt suppression, with AUDPC being reduced 34%, while MnO and ZnO NPs reduced disease by 28% (Elmer & White, 2016). Foliar treatment of eggplant with CuO NPs reduced disease by 69% and ZnO NPs reduced AUDPC by 36%. The treatment of eggplants with MnO NPs had no impact on disease progression. Foliar application of Al_2O_3, Fe_2O_3, and NiO also reduced AUDPC in tomato, but did not

Table 1 Selected treatment outcomes of inorganic nanoparticles applied to agricultural crops to enhance disease tolerance

Disease	Crop	NP	Outcome	References
Fusarium wilt *Fusarium oxysporum* f. sp. *Lycopersici*	Tomato *Solanum lycopersicum*	Al_2O_3, Fe_2O_3, NiO	Foliar treatment significantly reduced disease progression.	Elmer and White (2016)
		CuO	Foliar spray led to a 30% drop in disease and a 33% increase in yield.	
		MnO, ZnO	Foliar spray caused a 30% reduction in disease severity.	
		CeO_2	Up to 57% reduction in disease.	Adisa et al. (2018)
		CuO	Foliar dipping caused a 31% reduction in disease.	Ma et al. (2019)
		$Cu_3(PO_4)_2 \bullet 3H_2O$	Foliar dipping caused a 31% reduction in disease, resulting in a 50% increase in biomass.	
	Eggplant *Solanum melongena*	CuO	Foliar treatment resulted in a 69% reduction in disease, a 64% increase in biomass, and a 34% and 73% increase in yield.	Elmer and White (2016)
		ZnO	Foliar treatment caused a 36% reduction in disease.	
Fusarium wilt *Fusarium oxysporum* f. sp. *niveum*	Watermelon *Citrullus lanatus*	CuO	53% reduction in disease when treated with a foliar "dip" or via root treatments. There was a 23% reduction in disease with a foliar spray treatment and a 40% increase in biomass.	Borgatta et al. (2018)
		$Cu_3(PO_4)_2 \bullet 3H_2O$	Foliar dipping caused a 58% reduction in disease, leading to a 261% increase in biomass. Foliar spray reduced disease by 25% and increased biomass by 40%.	
		CTS-MSN, MSN	Foliar dipping led to a 27 and 40% reduction in disease.	Buchman et al. (2019)
		SiO_2	Supplied silicic acid as NPs dissolve mitigating disease and enhancing fruit yield ~80%.	Kang et al. (2021)
		B, CuO, MnO, SiO_2, TiO_2, ZnO	CuO outperformed the other NPs overall giving higher yields. CuO in the presence of fusarium upregulated PPO gene expression and activation of PPO enzyme.	Elmer and White (2018)

(continued)

Table 1 (continued)

Disease	Crop	NP	Outcome	References
Verticillium wilt *Verticillium dahliae*	Eggplant *Solanum melongena*	CuO	In greenhouse studies, foliar dipping resulted in a 40% reduction in disease and a 47% increase in biomass. In field experiments, treatments caused a 28% reduction in disease and a 33% increase in yield.	Elmer et al. (2021)
		ZnO, Mn_2O_3	Foliar treatment had no effect on disease, but increased yield 21 and 17%.	
		CuO + ZnO	Combined foliar treatment of CuO and ZnO (greenhouse) led to a 47% reduction in disease and a 52% increase in biomass.	
Black scurf disease *Rhizoctonia solani*	Potato *Solanum tuberosum*	$Ca_3(PO_4)_2$, CuO, SiO_2	Soaking tuber followed soil drenching mature plants. All NPs at 150 ul/L mitigated disease like a commercial fungicide. NPs activated defense-related enzymes.	El-Shewy (2019)
Sudden death syndrome *Fusarium virguliforme*	Soybean *Glycine max*	CuO, ZnO, Mn_2O_3	Foliar dipping resulted in 18.9, 24.7, and 17.1% less root rot.	Peréz et al. (2020)
		CuO (NP or NS), $Cu_3(PO_4)_2$	Foliar dipping caused an increase in biomass of up to 50%. Disease severity was reduced due to the activation of plant defense mechanisms upon treatment.	Ma et al. (2020)
Curvularia leaf spot *Curvularia lunata*	Maize *Zea mays*	CTS-Cu	Foliar treatment significantly reduced disease up to 25%.	Choudhary et al. (2017)
Cucumber mosaic virus	Cowpea *Vigna unguiculata*	Mg-Al layered double hydroxides (MgAl–LDHs)	Nanosheets as carriers of CMV-dsRNA, reduced the number of infected plants.	Mitter et al. (2017)
Pepper mild mottle virus	Tobacco *Nicotiana tabacum*	MgAl–LDHs	Nanosheets supplied dsRNA from PMMoV, protected tobacco plants for 20 d from viral infection.	Mitter et al. (2017)
Phytophtora/ bacteria	Tobacco *Nicotiana tabacum*	Ag	Biosynthesized Ag NPs mitigated disease without causing apparent toxicity in tobacco seedlings.	Ali et al. (2015)

(continued)

Table 1 (continued)

Disease	Crop	NP	Outcome	References
Xanthomonas perforans (bacteria)	Tomato *Solanum lycopersicum*	Cu/Zn hybrids	Nanohybrids reduced disease by 80% in a Cu-tolerant species where traditional treatments are inefficient.	Carvalho et al. (2019)
		MgO	MgO suppressed disease without being toxic to the plants.	Liao et al. (2019)

perform as well as CuO, MnO, or ZnO NPs. In field trials, none of the tested NPs reduced disease occurrence; however, CuO NPs increased eggplant yield 40% and 73%, compared to untreated control, for two consecutive seasons.

In a separate study, greenhouse-grown eggplant infected with the Verticillium wilt fungus had AUDPC values reduced 40%, and biomass increased 47%, when plants were foliar-treated with CuO NPs at 500 mg L^{-1} (Elmer et al., 2021. Interestingly, when this treatment was combined with ZnO NPs at 500 mg L^{-1}, there was no added benefit. Similarly, when studies were performed in the field across multiple seasons, CuO NPs lowered disease ~27%, and increased biomass and fruit mass. In addition, CuO NPs increased eggplant yield 17 and 33% during two growing seasons. Once again, the combined treatment of CuO and ZnO NPs had no effect on disease progression, but did increase yield by 15%, which, to a grower, could be a considerable increase of marketable produce from disease-impacted plants.

Fusarium wilt in watermelon has also been successfully treated with CuO NPs, where diseased plants showed significantly less disease severity than untreated controls (Elmer et al., 2018). Equivalent doses of MnO and TiO_2 were less effective at treating wilt disease. Additionally, watermelon plants treated with CuO NPs were significantly larger than both control plants or plants that received MnO, SiO_2, TiO_2, or ZnO NPs. However, when the greenhouse-based experiment was repeated, only CuO NPs were effective at treating Fusarium wilt (decreased by 35%). Field trials with CuO, MnO, B, and ZnO NPs were all effective at significantly reducing disease ratings, although CuO NPs were the most effective and increased yield from 35% to 53% compared to no treatment.

Similarly, the use of CuO, SiO_2, or $Ca_3(PO_4)_2$ NPs at concentrations of 150 and 200 µl L^{-1} was found to significantly reduce the incidence and severity of Black Scurf disease in potato, with 200 µl L^{-1} completely eliminated evidence of disease (El-Shewy, 2019). However, amendment with other nutrients may play a role in the efficacy of the treatment, as has been shown with sudden death syndrome in soybean. Plants fertilized with 50 µg N mL^{-1} and foliar-treated with CuO, Mn_2O_3, or ZnO NPs at 500 µg mL^{-1} significantly reduced root rot, but when fertilization was increased to 100 µg N mL^{-1} the treatments were less effective (Peréz et al., 2020). Treatment of Soybean Sudden Death Syndrome was most effective with ZnO or CuO NPs (24.7% and 18.9% less root rot); however, increasing the concentration of CuO NPs to 1000 µg mL^{-1} reduced the treatment's effectiveness by over 40–60%, regardless of nitrogen fertilization. Note that strategically, even though these are high concentration treatments, only a small volume of 2–3 mL is transferred to the leaves of young seedlings, resulting overall in low doses (Borgatta et al., 2018; Elmer et al., 2018; Peréz et al., 2020; Shen et al., 2020). These low doses were applied to very young plants, but provided long-term protection, with positive effects observed over the full life cycle of the plants. These results confirm that treatment of plants when in the early stages of growth provides the most effective treatment against soil-borne diseases. The life cycle long protection is a nanoscale-dependent phenomenon; the responses to these specific plant-nanoparticle interactions are under investigation (Pagano et al., 2017).

Several studies have begun to explore how tuning the chemistry of Cu nanomaterials could be used as a strategy to optimize benefit (Fig. 2). For example, work has been done with $Cu_3(PO_4)_2•3H_2O$ nanosheets (NS)—Ma et al. reported that either CuO NPs or $Cu_3(PO_4)_2•3H_2O$ NS reduced Fusarium wilt by an average of 31% in tomatoes (Ma et al., 2019). This study also found that $Cu_3(PO_4)_2•3H_2O$ NS delayed the visual symptoms of Fusarium wilt until day 14, and by the end of the experiment (day 21) signs of disease among infected plants were equivalent to uninfected controls. The application of $Cu_3(PO_4)_2•3H_2O$ NS also increased biomass in diseased plants by nearly 50%, an effect also seen with CuO NPs. Further work with Fusarium-infected soybean showed that $Cu_3(PO_4)_2•3H_2O$ NS, CuO NS, and CuO NPs were all effective treatments, with CuO NS having the greatest impact (Ma et al., 2020). Moreover, analysis of two dozen plant defense and stress-related genes confirmed foliar application of these materials provoked a Cu-induced increase in plant immunity. Conversely, in Fusarium-infected watermelon, $Cu_3(PO_4)_2•3H_2O$ NS reduced AUDPC values to a similar degree as CuO NPs, but at doses that were 100 times lower (Borgatta et al., 2018). Additionally, foliar treatment of tomato with CuO NPs or $Cu_3(PO_4)_2•3H_2O$ NS demonstrated Cu form controls the rate of uptake and internalization; simultaneously, treatments were equally effective as a single dose to seedlings as were multiple doses applied over a period of weeks (Shen et al.,

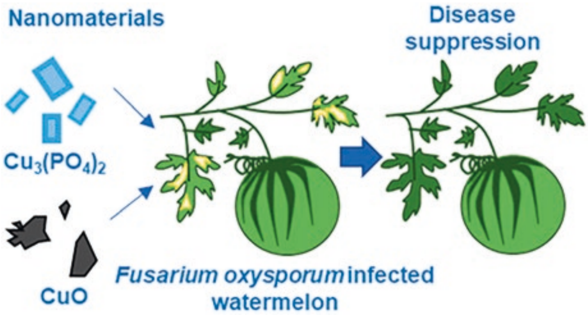

Fig. 2 Foliar treatment of crops infected with Fusarium wilt treated with copper-based nanoparticles showed improved disease tolerance due to treatments enhancing plant defense responses. Figure used with permission from Borgatta et al. (2018)

2020). The mechanism of this action remains unknown, but treatment timing to seedlings is critical to maximize benefit and reduce waste. Chitosan-coated copper NPs (CTS-Cu NPs) have been effective against Curvularia leaf spot (CLS) disease in maize. When maize seeds were soaked in suspensions of CTS-Cu NPs at concentrations ranging from 0.04 to 0.16% (w/v), then foliar-treated 35 days later, visual symptoms were delayed twice as long as untreated controls and disease severity was reduced by 24–22% (Choudhary et al., 2017). The mechanism against CLS appears to be 2-pronged: direct, in vitro exposure caused up to 50% inhibition of mycelia growth; and indirect, with Cu amendment stimulating SOD activity—increasing plant defense activity.

Other successful reported treatments for Fusarium wilt include mesoporous silica nanoparticles (MSN), chitosan-coated MSN (CTS-MSN), and CeO_2 NPs. To treat Fusarium wilt in watermelon, seeds were vacuum-infused in suspensions of 250 or 500 mg L^{-1} MSN or CTS-MSN and, subsequent to germination, had their aerial tissues dipped in corresponding solutions of MSN or CTS-MSN at 500 mg L^{-1}; AUDPC was reduced 40% with MSN and 27% with CTS-MSN compared to untreated plants (Buchman et al., 2019). Kang et al. (2021) also showed that MSN synthesis chemistry could be tuned to release silicic acid at a range of desired rates; faster rates were superior to conventional MSN at increasing biomass, yield, and Fusarium wilt suppression in watermelon. Interestingly, silicic acid controls had no such benefit. Suppression of Fusarium wilt in tomato with NPs CeO_2 was equally effective when applied either through the soil (decrease of 53%) or by foliar spray (decrease of 57%) (Adisa et al., 2018). However, treatment of diseased tomato plants with CeO_2 NPs did impact the fruit (Adisa et al., 2020). Specifically, foliar application of CeO_2 NPs increased fruit dry weight by 67% but decreased total sugars by 50%; while root treatments with NPs CeO_2 increased fruit total sugars by an average of 58%, lycopene by 9%, and the micronutrients Cu and Mn by 51 and 59% respectively.

Mechanistically, it is important to highlight the fact that these foliar amendment strategies are not directly targeting the pathogen but serving to modulate plant nutrition and defense as a strategy to suppress disease damage. For example, in-vitro studies show that the concentration of 500 mg L^{-1} of CuO NPs does not have a fungicidal effect. Importantly, for the in vivo work, although a dose of 500 mg L^{-1} may be applied foliarly, only 2–3 ml of the solution is transferred to the plant, yielding an actual dose of only a few mg. Therefore, CuO NPs may act as a more active and available nanoscale supply of Cu for the host plant which uniquely activates an entire range of defense pathways and enzymes (Elmer & White, 2016; Lopez-Lima et al., 2021). The end result is disease management at doses that may be orders of magnitude below conventional treatment options. Conversely, certain metal-based NPs have been shown to be bactericidal (Carvalho et al., 2019; Liao et al., 2019). This is important as a number of strains of bacteria that cause crop diseases have become resistant to conventional copper-based treatments (Lamichhane et al., 2018). In vitro work with *Xanthomonas* spp. demonstrated that hybrid nanoparticles of Cu and Zn were effective at inhibiting bacterial growth and reducing the severity of tomato spot disease by up to 80%, as compared to Kocide 3000, Kocide

3000 + Mancozeb, and untreated controls (Carvalho et al., 2019). In this study, the authors point to a significant reduction in xanthomonadin—a pigment present in the cell membrane—as a possible mechanism for the bactericidal effect. Similarly, MgO NPs were effective in inhibiting the growth (in vitro) of *Xanthomonas* spp. and significantly decreased the severity of tomato spot disease in an in vivo study compared both to controls and conventional treatments (Liao et al., 2019). Other studies with pathogenic bacteria include silver (Ag) nanoparticles (Dimkpa et al., 2011; Ding et al., 2017). Unlike the above studies where the foliar application of low masses of micronutrients to seedlings points to an indirect mechanism of action, Ag NPs act by disrupting the pathogen cell membrane on contact, or through the generation of ROS, either from the nanoparticles themselves or the ions they release, leading their direct bactericidal effect (Levard et al., 2012; You et al., 2012).

Another strategy against disease is the indirect use of nanoscale materials to supply defense agents such as herbicides, hormones, and antimicrobials (Worrall et al., 2018). For example, Xu et al. used an electrospinning approach to coat seeds with nanoscale biopolymer fibers that were pre-loaded with Cu and that provided enhanced germination and growth of lettuce and tomato in the presence of disease (Xu et al., 2020). In addition, NPs are being engineered and tested also as carriers of nucleotides for purposes of gene silencing, which inhibits the replication of viral pathogens. This RNA interference (RNAi) mechanism is inherent to plants, and in order to activate these processes, genetic material of the pathogen needs to enter the plant. The host will detect these nucleic acids and code for destruction instead of replication of the disease agent. However, unprotected nucleotides are prone to degradation before entering the plant or can denature once inside. Therefore, there have been efforts to utilize nanomaterials as nucleotide protectors and carriers to activate RNAi pathways (Elsharkawy & Mousa, 2015; Mitter et al., 2017; Schwartz et al., 2020). Disease management is essential in agriculture in order to mitigate or avoid crop losses; other chapters in this book cover the role of NPs as pesticides (Chap. 6 and Chap. 10), and their performance as nanocarriers (Chap. 11) in greater detail; please refer to those sections for additional details on these important topics.

4 Nanoparticles to Alleviate Environmental Stressors

As the effects of climate change begin to worsen, it is clear many crops will have to be grown under increasingly marginal conditions. For example, drought conditions will become more prevalent across the globe, limiting crop production, and decreasing arable land. The use of NPs to mitigate the detrimental effects of drought stress in crops has shown promise. Wheat treated with SiO_2 NPs, either via soil or through foliar spray, were able to better tolerate drought conditions (Behboudi et al., 2018), having increased chlorophyll (SPAD) content, relative water content (RWC), and greater yield; the soil treatment route provided significantly better 1000-grain weight and yield than foliar treatment. Although treatment with SiO_2 NPs improved some agronomic parameters, SOD activity increased upon treatment under drought conditions compared to non-drought controls. Under drought conditions, fertilization of soil with ZnO NPs increased the emergence of wheat sprouts by 5 days, and increased chlorophyll and Zn content in the shoots and grain (Dimkpa et al., 2020). Compared to controls, the foliar application of a mixture of NP ZnO, B_2O_3, and CuO to drought-stressed soybean increased yield by 33% and shoot growth by 36%, while also increasing leaf area and leaf number (Dimkpa et al., 2017a). The application of Fe, Cu, or Co NPs improved soybean drought tolerance and increased shoot dry weight under drought conditions when compared to untreated control, while the application of Fe NPs also increased shoot length (Linh et al., 2020). The relative water content was enhanced with the application of either Fe or Cu NPs, and biomass was increased with Fe or Co NPs. Priming maize seeds with Cu NPs have also been reported to increase seed yield and weight of drought-affected plants two-fold (Van Nguyen et al., 2021).

Agricultural crops can be susceptible to salinity—which can alter vital plant functions, affecting growth, photosynthesis, and yield. Importantly, select nanoscale amendments have been shown to enhance tolerance to or alleviate damage from salinity. Cucumber was grown under salt stress, with varying amounts of additional water stress, and was then treated with Si NPs (Alsaeedi et al., 2019). The addition of Si NPs at 200 mg kg^{-1} improved growth and productivity, regardless of drought status, by increasing the leaf area, total chlorophyll, and plant height, compared to water-stressed controls. Additionally, Si NPs lowered the uptake of Na, while increasing K content in all tissues. This action reduced the Na/K ratio in favor of improved salt tolerance. Moreover, the addition of Si NP—especially at 200 mg kg^{-1}—increased cucumber yield under all watering conditions. Foliar application of nanoscale NPK to hydroponically grown peas exposed to salt stress showed increased growth parameters, including leaf area, leaf number, and shoot length (El-Hefnawy, 2020). Cellular analysis of roots from nanoscale NPK treated plants showed a reduction in chromosomal abnormalities, compared to untreated controls. Tomato plants grown under salt stress suffered reduced growth and a decrease in the yield of up to 50% (Pérez-Labrada et al., 2019). Importantly, foliar application of Cu NPs had no impact on growth under saline conditions; chlorophyll content and fruit yield were unchanged. However, treatment did increase vitamin C content in the tomato fruit. Wheat seeds treated with sulfur (S) NPs and planted in saline conditions experienced improved growth—increasing root and shoot fresh/dry weight, and leaf area—compared to untreated salt-stressed plants (Saad-Allah & Ragab, 2020). Treatment with S NPs alleviated the increased catalase, superoxide dismutase, ascorbic peroxidase, and polyphenol oxidase activities that were elevated due to salt stress. Additionally, leaf pigment concentrations were increased; uptake of N, P, and K was increased; uptake of Na was reduced; and growth was restored to near unstressed control levels. Biochemical indicators of stress, such as malondialdehyde (MDA), H_2O_2, and electrolyte leakage were also reduced—with S NPs being more effective with lower salt concentrations (100 mM NaCl) versus higher (200 mM NaCl) for most endpoints. Given this limited yet promising data, it is clear that select nanoscale treatments have the potential to sustainably increase crop tolerance to environmental stresses anticipated from a changing climate; future work should focus on uncovering the mechanisms of plant response to these unique nanoscale effects, as well as on the ability to tune material properties to further optimize the observed benefits (An et al., 2020). High-throughput studies have already begun to reveal some mechanisms behind increased photosynthesis upon exposure to metal NPs. Spinach chloroplasts exposure to Mn_3O_4 or Fe NPs for 2 h showed increased photocurrent and electron transport, resulting in a 23 and 43% increase in quantum yield and ATP synthesis (Wang et al., 2020).

5 Future Implications

The use of NPs on agronomic crops plants will be a subject of continuous research, as new materials are introduced, and as current materials are transformed by the environment after their application. Also needed are insights into potential drawbacks arising from the desire to over apply NPs to maximize beneficial results. For example, if a grower decided to increase the dose of an NP to further promote already enhanced growth, they may not receive the desired effect. Exposure of barley to increasing concentrations of CeO_2 NPs resulted in greater biomass accumulation, but the enhancement was all directed at vegetative growth and mature plants failed to produce grains (Rico et al., 2015). Further research will also be needed into the implications of increased NP release into the environment, especially those containing elements not typically found in agricultural soils (e.g., Ce and Ti). Still, there are concerns about the ramifications of prolonged NP application on the food web and how extended ion release could impact the soil and plant microbiomes. Further investigation is also needed on the potential interactions of NPs with the myriad of agrichemicals currently in use and ubiquitous in the environment (Zhao et al., 2019). Great care must be taken with the use of NPs in agriculture, any perceived negative implication may cause rejection by the general public (Hofmann et al., 2020). As with all the outcomes presented, the observed effects are dependent on the type of NP employed and so far, published research has not shown that effects induced by the application of NPs affect the propagation of later generations of crops. In fact, application of ZnO NPs to soil-grown kidney bean produced nearly no residual effects when the subsequent generation was cultivated without amendment (Medina-Velo et al., 2018). Additionally, concerns over the implications on the use of NPs to promote crop performance should not be limited to the effects on the target plants. The use of NPs should be considered on a life-cycle basis, evaluating their total impact on the system in which they are being applied. Consideration must be given to the total environmental impact of scaling up the application of NPs from the laboratory to the field. A recent study evaluated total embodied energy of the manufacture of several NPs, including ZnO, CuO, and CeO_2, and found that at the currently applied research doses, NPs were not a sustainable alternative to conventional practices as a means of N replacement (Gilbertson et al., 2020). However, as presented above, there are numerous uses for NPs in agriculture other than supplanting the application of N fertilizers, and in some cases, better performance is obtained from utilizing both. This study did report that both ZnO and CuO NPs used as seed coatings (i.e., seed priming) and ZnO used as a foliar treatment were promising from an embodied resource standpoint. Additionally, some areas will be too remote or lack the infrastructure to mass produce NPs for agricultural applications; it is therefore critical to invest heavily in economical, green synthesis methods. Such approaches utilize more environmentally conscious materials (e.g., plant material, bacteria, or algae) and produce fewer toxic byproducts (Saratale et al., 2018).

6 Conclusion

In conclusion, a rapidly growing body of literature has demonstrated the beneficial qualities of NPs application onto agriculturally relevant plants. This includes a demonstration of how NPs can be utilized to improve disease suppression, drought, and salinity tolerance while improving crop yields. Further, the application of NPs onto non-stressed plants has been shown to provide a performance-enhancing effect. It is clear that current agricultural practices are inadequate to address future predicted food demands and predicted challenges on agriculture from a changing climate. A paradigm shift to more technologically advanced, environmentally sound agricultural practices is needed and has begun. The move to nanoscale-based crop amendment strategies can be critical to sustainably increase food security while reducing our impact on the surrounding environment.

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Metal- and Metalloid-Based Nanofertilizers and Nanopesticides for Advanced Agriculture

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Abstract Globally, huge crop yield losses are observed due to soil degradation accompanied by insufficient nutrient content needed for healthy plant development and growth. Therefore, soil or foliar applications of essential metal micronutrients to plants in formulations providing their sustained and controlled release for a longer period are desirable. On the other hand, zeolites, nanoclays, or montmorillonite with unique pore structures of molecular dimensions can serve as an excellent carrier for enriching soils with macroelements when used as slow-release fertilizers. Even nutripriming using solutions containing nanoparticles of essential metals results in a significant improvement in plant growth and, like fertilization, can contribute to the biofortification of crops with essential metals. However, massive yield losses are also caused by harmful pests, and therefore metal- and metalloid-based NPs with a strong ability to generate oxidative stress are frequently used in plant protection as insecticides or as effective agents against a wide range of phytopathogens. In contrast to many synthetic pesticides, the use of such inorganic nanoparticles does not induce the development of resistance in treated insects and harmful phytopathogens and, in addition, also has a beneficial effect on plants attacked with insects or infected with phytopathogens. This chapter provides a comprehensive overview of the findings on metal- and metalloid-based nanoparticles/nanocomposites used as nanopriming agents, nanofertilizers, nanoinsecticides, and nanosized agents against viral, bacterial, and fungal phytopathogens, including the

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corresponding mechanism of action. In addition, slow-release fertilizers using zeolites, nanoclays, or montmorillonite as carriers of macronutrients are discussed as well.

Keywords Crops · Nanoparticles · Nanopriming · Metal nanoparticles · Aluminosilicates · Fertilizers · Insecticides · Phytopathogens · Plant protection · Mechanism of action

1 Introduction

Considering the urgent need to ensure sufficient healthy food for a growing human population, the United Nations General Assembly declared 2020 as the International Year of Plant Health (IYPH) (FAO, 2020). Since the second half of the twentieth century, agriculture focused on industrial crop production based on the overuse of synthetic fertilizers, synthetic pesticides, and monocropping resulting in soil degradation, continual increase of man-made inputs, which contributed to climate change. Due to climate change, groundwater is declining, or heavy rainfall is occurring, resulting in further degradation of poorly cultivated fields/soils by wind drifting or flushing the soil with heavy rainfall, leading to further soil degradation, demineralization, humus and nutrient loss, and impaired water retention (Hunting et al., 2016; Lal, 2020; Menzies Pluer et al., 2020). All these factors adversely affect the growth and nutritional quality of crops. In addition, various pests, such as insects and other phytopathogens, also cause huge yield losses (Donatelli et al., 2017; Savary et al., 2019). Therefore, continued climate change accompanied by extreme weather events and a gradual reduction in agricultural land area, together with the above-mentioned decrease of soil quality and increased contamination by anthropogenic activities require effective strategies to increase crop yields without using excessive agrochemicals.

Fortunately, with the twenty-first century, innovative technologies have emerged to harness the potential of nanoparticles (NPs). In addition to industrial materials and biomedical applications, nanomaterials are also gaining ground in agriculture and the food industry. One of the excellent properties of NPs associated with their small size is that they can penetrate better into target organs and their specificity to target organs can be ensured by appropriate surface functionalization. Thus, it is possible to achieve a higher utilization of nutrients by plants, and treatment of plants with these nanosized nutrients is advantageous, because a lower dose can be used to achieve the same or significantly better effect compared to conventional fertilizers (Jampílek & Kráľová, 2017a, 2019a, 2019b; Rana et al., 2019; Zulfiqar et al., 2019; Kráľová & Jampílek, 2021b).

The nanosized particles of essential metals, such as Cu, Zn, Fe, Mn, or Mg, which are essential for the healthy development and growth of the plants, proved to be highly effective in improving crop yields when used as nanopriming agents or nanofertilizers. In addition, their use can result in the biofortification of crops with these metals, which are also essential for humans, and their deficiency in food products can result in serious health problems (Rizwan et al., 2017; Chen, 2018; Jampílek & Kráľová, 2019a; Shang et al., 2019; Mittal et al., 2020; Kráľová & Jampílek, 2021b; Kráľová et al., 2021). Optimized tailor-made nanofertilizers with the required composition of active ingredients can achieve improved nutrient utilization efficiencies, reduce environmental impact and ensure effective crop yields, and their use in smart and accurate nanotechnology-based agriculture is a prerequisite for global food safety (Raliya et al., 2018). In addition to nanofertilizers using essential metals, some other nanosized metals and metalloids (e.g., AgNPs, SeNPs, TiO_2 NPs, SiO_2 NPs, Ca-based NPs) used at low concentrations also show strong stimulating effects on plant growth. In general, metal-based NPs exhibit hormetic effects characterized by the biphasic dose-response phenomenon when application of a low dose leads to stimulation, but high doses cause inhibition. Therefore, it is especially important to use appropriate doses of these inorganic NPs as fertilizers (Kráľová et al., 2019, 2021; Kráľová & Jampílek, 2021b). However, in addition to essential nutrients, the plant also requires macronutrients such as nitrogen, phosphorus, and potassium, which can be supplied to the soil using appropriate inorganic carriers such as zeolites, nanoclays, or montmorillonite, which have unique porous structures of molecular dimensions. Due to their cation exchange capacity and porosity, these carriers can be used as slow-release fertilizers that release nutrients over a long period of time and prevent nutrient leaching, and in addition to plant-growth stimulating effects can significantly improve soil quality and water retention capacity. For effective fertilization, a controlled and sustained release of nutrients over a substantially longer period than with conventional fertilizers is desirable to avoid the need for frequent re-fertilization. This can be achieved by encapsulating mineral micronutrients in biodegradable polymeric matrices of natural origin or by suitable polymeric coatings (Guo et al., 2018; Biswas et al., 2019; Jahangirian et al., 2020; Mikula et al., 2020; Nanografi Nano Technology, 2021; Sivarethinamohan & Sujatha, 2021).

Another beneficial property of metal- and metalloid-based NPs is their ability to reduce the adverse impact of various abiotic stresses on plants, such as drought, salinity, high temperature, waterlogging, contamination with toxic metals, etc. As a result, their use under environmental stress conditions can effectively contribute to improved crop yields. The beneficial impact of metal-based NPs used as nanopriming agents or nanofertilizers is due to their ability to activate plant antioxidant defense systems by enhancing activities of antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), or ascorbate peroxidase (APX) and levels of non-enzymatic antioxidants (Gupta et al., 2018; Samart & Chutipaijit, 2019) and reducing levels of oxidative stress in plants lead to improved efficiency of photosynthetic processes and ultimately to improved plant growth and performance (Kráľová et al., 2019, 2021; Kráľová & Jampílek, 2021b).

Metal- and metalloid-based NPs are also frequently used as pesticides, predominantly as insecticides, bactericides, fungicides, and antiviral agents in plant protection. Compared to conventional synthetic pesticides, their use is favorable due to the lower required dose for the same biological effect, less impact on non-target organisms, and reduced soil contamination. In addition, with long-term use of synthetic pesticides, insects and other phytopathogens may have developed resistance to given organic chemicals, while the use of metal- and metalloid-based NPs minimizes this risk. Such nanosized inorganic pesticides can penetrate through insect cuticle and outer membranes of phytopathogens and subsequently induce increased production of reactive oxygen species (ROS) that cause oxidative stress, resulting in cell membrane damage, increased lipid peroxidation, decreased enzyme antioxidant activities and genotoxic effects, leading ultimately to death of insects/phytopathogens. Moreover, the application of metal-based NPs against phytopathogens not only reduces the severity of viral, bacterial, and fungal diseases of plants, but also has a beneficial effect on infected plants and improves their performance and resistance to phytopathogens (Egusa et al., 2015; Alonso-Diaz et al., 2019; Cumplido-Najera et al., 2019; Quiterio-Gutierrez et al., 2019; Ahmed et al., 2020; Elsharkawy et al., 2020a, 2020b; Li et al., 2020b; Sofy et al., 2020; Tauseef et al., 2021).

In general, metal-based NPs for agricultural use are mostly green synthesized, i.e., prepared using plant extracts or fungal filtrates as reducing and capping agents. Such phyto- or mycosynthesized metal NPs have functional groups on their surface that contribute to improved biological activity compared to NPs produced by conventional methods (Ali et al., 2020; Ameen et al., 2021; Bahrulolum et al., 2021; Hong et al., 2021; Kráľová et al., 2021).

Although many studies have recently been conducted into the beneficial impact of metal- and metalloid-based NPs on plants, as well as their ability to kill insects and reduce the severity of plant diseases infected with various pathogens, most of these studies are performed in the laboratory or greenhouse rather than in the field (Gusev et al., 2016; Jampílek & Kráľová, 2017b, 2019a; Acharya et al., 2020; Jampílek et al., 2020; Kráľová & Jampílek, 2021b; Kráľová et al., 2021). Therefore, it is necessary to pronouncedly extend field experiments, including the investigation of the transgenerational effects of NP on plants, to develop effective nanoformulations with sufficient stability and efficiency that can be produced on a large scale. On the other hand, the use of such NPs is safe. Ten years ago, EPA issued a proposal to use the provisions of the Federal Insecticides, Fungicides and Rodenticides Act (FIFRA) to gather information on the application of nanomaterials in pesticide products (EPA, 2011).

This chapter provides a comprehensive overview of the findings on metal- and metalloid-based NPs used as nanopriming agents, nanofertilizers, nanoinsecticides, and nanosized agents against viral, bacterial, and fungal phytopathogens, including the corresponding mechanism of action. In addition, slow-release fertilizers using zeolites, nanoclays, or montmorillonite as carriers of macronutrients are discussed.

2 Nanofertilizers

Higher agricultural productivity requires the supply of appropriate amounts of nutrients, which are indispensable for healthy development and growth of crops. In general, nutrient use efficiency by crops under conditions of intensive agriculture using conventional fertilizers is lower than 50% (Baligar & Fageria, 2015) and application of excess amounts of chemical fertilizers or irrigation of crops with contaminated water has negative impact on the environment and causes great damage to agriculture (Singh et al., 2021). Therefore, the use of convenient fertilizers, which help to maintain soil fertility, increase nutrient use efficiency, and improve crops tolerance against abiotic stresses, is desirable and for this purpose nanofertilizers are particularly suitable (Sanivada et al., 2017; El-Ramady et al., 2018; Zulfiqar et al., 2019). However, improved seed germination and ameliorated plant growth resulting in improved plant productivity can be also achieved using nanopriming, i.e., treatment of seeds with priming solution containing nanoscale nutrients, which improve water uptake, increase activities of antioxidant systems and alleviate adverse impact of abiotic stresses on plants (Saboor et al., 2019; Prajapati et al., 2020).

Nutrient nanofertilizers are applied whether alone, as nanocomposites with biodegradable polymers, or bound to nanoscale adsorbents via foliar and soil routes. They are characterized with controlled and prolonged nutrient release, are target-oriented with improved targeted delivery efficiency and lower amount of nutrient is required compared to conventional fertilizers (Chhipa & Joshi, 2016; Chhipa, 2017; Elemike et al., 2019; Zulfiqar et al., 2019). Using nanofertilizers can contribute to reduce environmental contamination along with improved plant productivity, which is necessary with respect to fast-growing human population associated with increasing food demand (Raliya et al., 2018; Saldivar et al., 2018; Adisa et al., 2019). On the other hand, using nutrient nanofertilizers biofortification of crops with nutrients can be achieved, which is desirable for healthy nutrition of population (Elemike et al., 2019). Besides nanoscale essential micronutrients used as nanofertilizers favorable impact on crop production can also exhibit NPs/nanocomposites (NCs) of other minerals stimulating plant growth, such as Ag, Ca, Se, Si, SiO_2 of TiO_2 (Masarovičová et al., 2014; Jampílek & Kráľová, 2017a, 2019a, 2019b; Kráľová et al., 2019, 2021; Kráľová & Jampílek, 2021a, 2021b).

Liu & Lal (2017) classified the nanofertilizers into (i) macronutrient nanofertilizers (e.g., apatite $Ca_5(PO_4)_3$ (F, Cl, OH) NPs, $CaCO_3$ NPs, and MgO NPs); (ii) micronutrient nanofertilizers (e.g., Fe_3O_4 NPs, MnO NPs, ZnO NPs, and CuO NPs); (iii) nutrient-loaded nanofertilizers (zeolites, SiO_2 NPs, and carbon nanotubes (CNTs)); and (iv) plant growth stimulating nanomaterials (TiO_2 and CNTs). On the other hand, Mikula et al. (2020) divided the fertilizers into four basic groups: (a) low-solubility fertilizers; (b) fertilizers with external coating; (c) bio-based fertilizers; and (d) nanofertilizers, nevertheless all groups show controlled release of microelements. Benefits of the application of nanosized nutrient fertilizers for improvement of crop production and biofortification of food crops

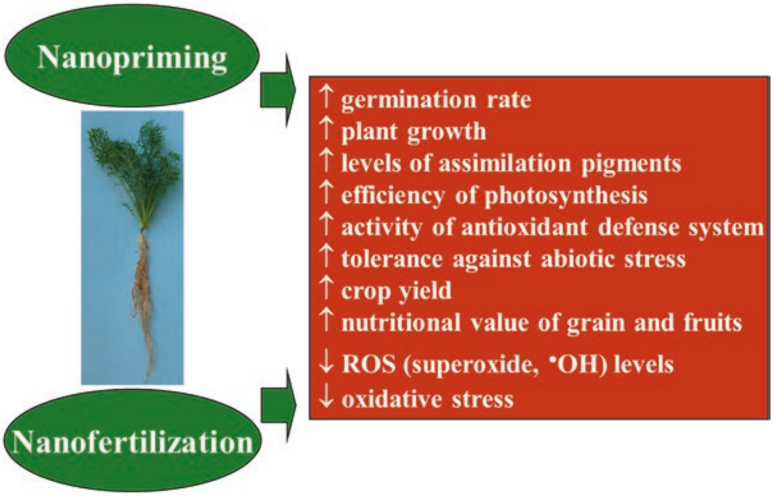

Fig. 1 Beneficial impact of nanopriming and micronutrient nanofertilizers on plants

deficient in these nutrients were discussed by Elemike et al. (2019). The beneficial impact of nanopriming and micronutrient nanofertilizers on plants is shown in Fig. 1.

2.1 *Nanopriming*

Using priming solution to hydrate seeds results in increased metabolic activities and improved germination without the protrusion of radical (Paparella et al., 2015). However, seed priming also has beneficial impact on plant growth, can contribute to increased plant productivity, and can help to alleviate adverse impact of abiotic stresses on plants, including metal stress (Saboor et al., 2019; Prajapati et al., 2020). Hence, nanopriming is a simple inexpensive environment friendly seed treatment which can greatly contribute to improved crop yields also under their exposure to various abiotic stresses. For nanopriming frequently metal NPs are used (Kráľová & Jampílek, 2021b; Kráľová et al., 2021). At NPs application in priming solution to induce seed germination, nanopores improving water uptake are formed, reactive oxygen species (ROS)/antioxidant systems in seeds are restarted and of •OH species can cause cell wall loosening or fastening starch hydrolysis (Mahakham et al., 2017). Metal-based NPs used in nanopriming activate the antioxidative defense systems via enhancing activities of antioxidant enzymes (e.g., SOD, CAT, POD, APX) as well as the levels of non-enzymatic antioxidants (Gupta et al., 2018; Samart & Chutipaijit, 2019) and thus contribute to reduced oxidative stress in plant, improved plant growth, enhanced levels of assimilation pigments as well as improved nutritional quality of grains due to increased content of essential metals and increased resistance to abiotic stresses (Mohamed et al., 2017; Maswada et al., 2018; Kasote et al., 2019; Rizwan et al., 2019; Choudhary et al., 2019; Mansoor et al., 2019). Application of nanopriming can be very favorable especially for aged seeds (Mahakham et al., 2016, 2017). Khalaki et al. (2021) comprehensively overviewed the recent findings related to the beneficial impact of priming with various nano-sized particles on seed germination, seedling growth, and enhanced resistance against environmental stress of forage and medicinal plants, discussing also the potential adverse effects of nanopriming on plants.

Priming of wheat seeds with 10 ppm ZnO NPs showing hexagonal wurtzite structure considerably increased growth characteristics of plants, including number of spikelets per spike, spike length, and number of grains per spike compared to control and treatment with bulk ZnO. Moreover, via priming with 10 ppm ZnO NPs increases in total phenolic content (TPC), Zn content in roots, and Fe grain concentration by 60.37%, 88.9%, and 113% were achieved suggesting improved nutritional quality (Mansoor et al., 2019). Priming of wheat seeds with ZnO NPs (50, 100, and 500 mg/L) improved growth characteristics, photosynthetic pigments, and photosynthetic efficiency of plants exposed to 150 mM NaCl and induced changes in electrophoretic profiles of shoot proteins (Abou-Zeid et al., 2021). Priming of wheat seeds with ZnO NPs (20–30 nm; 25–100 mg/L) or Fe_3O_4 (50–100 nm; 5–20 mg/L) for 24 h increased growth characteristics and improved photosynthesis in plants grown on Cd-contaminated soil; priming with these NPs also reduced electrolyte leakage and SOD and POD activities in leaves of Cd-stressed plants, and greatly reduced accumulation of Cd in plant organs, whereby in grains the observed Cd concentration was <0.2 mg/kg. Moreover, treatment with ZnO NPs increased Fe content, while exposure to Fe_2O_3 enhanced Zn content in plant organs, including grains (Rizwan et al., 2019). After priming with 50 mg/L ZnO NPs, the 20 days old plants, which were subsequently exposed to 100 mM NaCl for 10 days, showed better tolerance of photosynthetic apparatus to salt stress due to the enhanced trapped energy flux and electron transport flux, increased activities of phosphoglucomutase and cytoplasmic invertase stimulating biosynthesis of sucrose in leaves under salt stress and showed higher shoot dry biomass than control plants. The improved salt tolerance of plants was due to activated antioxidant system reducing oxidative stress and increasing efficiency of photosynthetic electron transport and sucrose biosynthesis in leaves under salt stress (Wang et al., 2020). Priming of *Zea mays* seeds with ZnO NPs at doses from 20 to 80 mg/L Zn showed dose-dependent improvement of germination and seedling growth compared to control achieving by 12% higher dry biomass production than the control at a dose 80 mg/L, whereas growth characteristics of plants primed with bulk ZnO were comparable with those of the control (Neto et al., 2020). *Zea mays* seeds primed with 100 mg/L ZnO NPs more effectively improved growth characteristics of plants compared to hydropriming or priming with $Zn(CH_3COO)_2$ and normal hydroprimed control, whereby ZnO NPs were adsorbed on the endosperm regions of seed suggesting that nanopriming can increase Zn content and alleviate zinc deficiency (Itroutwar et al., 2020a). Improvement of agronomical characteristics of rice via priming *Oryza sativa* seeds with ZnO NPs green synthesized using extract of *Turbinaria ornata* brown seaweed was reported by Itroutwar et al. (2020b). Priming of *Phaseolus vulgaris* seeds with 10 mg/L ZnO NPs (40 nm) increased seedling, weight by 7.3% compared to control, whereas at exposure to 5000 mg/L it was by 12.7% lower than the control. Most absorbed Zn was found in seed coat and small portion in biotransformed form was detected in cotyledon, where Zn complexes with citrate, malate, and histidine-like compounds were observed. ZnO NPs exhibited slow Zn release and reduced phytotoxicity compared to $ZnSO_4$ (Savassa et al., 2018). Priming of *Lupinus termis* seeds with 60 mg/L ZnO NPs stimulated growth of lupine plants cultivated 20 days and exposed to 150 mM NaCl, increased the levels of chlorophylls (Chls), Chl*a* and Chl*b*, and carotenoids, non-enzymatic antioxidants (TPC, ascorbic acid) and Zn and activities of antioxidant enzymes (SOD, CAT, POD, and APX) over salinized control plants along with reduction of malondialdehyde (MDA) levels suggesting that priming with ZnO NPs improved salt tolerance of lupine plants (Latef et al., 2017).

Priming of *Zea mays* seeds with CuNPs positively affected drought stress tolerance of maize plants, and the plants exposed to water deficit showed higher leaf water content and plant biomass as well as enhanced levels of anthocyanin, Chl, and carotenoids than plants treated with water along with reduced ROS content and improved activities of antioxidant enzymes. Moreover, priming with CuNPs resulted in higher total seed number and grain yield under drought stress conditions (Van Nguyen et al., 2022).

Priming of seeds of aromatic rice cultivar (cv. Gobindabhog) with 10–80 mg/L Fe^0NPs showed positive impact on growth and photosynthetic pigment content of 14 days old plants, whereby highest activities of hydrolytic and antioxidant enzymes were achieved using a dose 20 mg/L Fe^0NPs. On the other hand, priming with 160 mg/L Fe^0NPs induced oxidative stress in plants along with the highest Fe levels (Guha et al., 2018). Priming of Pusa basmati rice seeds with 20 mg/L FeO NPs green synthesized using *Cassia occidentalis* L. flower extract enhanced some growth characteristics of seedlings up to 50%, and markedly promoted contents of soluble sugars, enhanced α-amylase activity and Fe accumulation compared to control; considerable increase of antioxidant enzymes activities over control and priming with $FeSO_4$ was observed as well (Afzal et al., 2021). Priming of *Sorghum bicolor* seeds with 10 mg/L Fe_2O_3 NPs improved the germination, while priming with 50 and 100 mg/L Fe_2O_3 NPs most effectively enhanced growth of 12 days old plants. On the other hand, priming with 500 mg/L Fe_2O_3 NPs was able to protect sorghum plants from adverse impact of excess salinity (150 mmol NaCl) via increasing efficiency of photosystem II, Chl levels, photosynthetic rate and relative water content (RWC), and decreasing lipid peroxidation, which was reflected in increased growth of 45 days old plants (Maswada et al., 2018). Whereas seed priming of high-iron and low-iron wheat genotypes with 400 and 200 ppm Fe_2O_3 NPs, respectively, considerably enhanced germination percentage and shoot length, exposure to 25 ppm demonstrated pronouncedly increased grain Fe levels by 26.8% and 45.7% in low- and high-iron genotype, respectively, suggesting beneficial impact of nanopriming on biofortification of grains with this essential metal (Sundaria et al., 2019). Baltazar et al. (2021) investigated the first generation of seeds (S_1) harvested in wheat plants whose seeds (S_0) were hydroprimed and nutriprimed with 4 and/or

8 mg/L of Fe and/or Zn using $ZnSO_4$ and $FeSO_4$ and found 100% germination and lower mitotic irregularities in all S_1 offsprings suggesting mitigation of cytotoxicity. S_1 showed better yield components compared to S_0, suggesting that positive impact of priming with metal salts on S_0 seeds was further ameliorated in S_1 offspring through seed provisioning and by the epigenetic inheritance of DNA hypomethylation patterns, which were estimated in the S_0 generation. Priming of diploid and triploid watermelon seeds with Fe_2O_3 NPs (19–30 nm) clearly altered the metabolome of corresponding seedlings, considerably modulated the 12-oxo phytodienoic acid level in both types of watermelon seedlings, improved nonenzymatic antioxidant potential, and induced jasmonates-linked defense responses in *Citrullus lanatus* seedlings (Kasote et al., 2019).

Nanopriming with Mn_2O_3 NPs considerably enhanced the root growth of *Capsicum annuum* plants grown under normal conditions as well as those exposed to salt stress (100 μM NaCl). It was found that the Mn_2O_3 NPs penetrated through the seed and NP-corona complex was formed. However, Mn_2O_3 NPs did not affect redistributions of Mg, Na, K, and Ca contents between the shoot and root occurring due to salt stress (Ye et al., 2020).

Priming of *Hibiscus sabdariffa* L. seeds with 0.01% Al_2O_3 NPs showed beneficial impact on growth characteristics, levels of Chl*a*, Ch*lb*, soluble sugars, protein, amino acid and proline content and antioxidant enzymes SOD, CAT, POD, APX, and reduced MDA levels in treated plants compared to controls, whereas priming with higher Al_2O_3 NPs (0.05–0.5%) exhibited adverse effect on above-mentioned parameters (Latef et al., 2020).

Priming of *Zea mays* seed with 60 ppm TiO_2 NPs exposed to 200 mM NaCl was able to alleviate detrimental impact of salinity stress on maize plants grown in sand, which was reflected in improved germination, growth characteristics of seedlings, K^+ levels, RWC, TPC and proline concentration, and considerably enhanced activities of antioxidant enzymes (SOD, CAT, and phenylalanine ammonia-lyase (PAL)). On the other hand, priming with TiO_2 NPs reduced Na^+ concentration, electrolyte leakage, and MDA content compared to control plants under salinity stress (Shah et al., 2021).

Nanopriming with MgO NPs of 12 nm prepared using marine brown alga, *Turbinaria ornate,* considerably enhanced seed germination (%) and seedling vigor of *Vigna radiata* compared to control, exceeding that observed with the use of hydropriming (Anand et al., 2020).

Priming of seven-year-old *Vicia faba* seeds with AgNPs pronouncedly increased length of radicles, enhanced CAT activity, especially at a dose of 100 ppm AgNPs, and affected APX, which decreased in the radicles but increased in the plumules. Exposure to AgNPs considerably reduced percentages of micronuclei and chromosomal abnormalities in both interphasic and mitotic cells compared to control resulting in lower number of genotoxic and mutagenic aberrations, and with increasing AgNPs concentrations an increase in mitotic cell cycle and *V. faba* growth was observed compared to control (Younis et al., 2019). Investigation of the impact of priming of seeds of *Pennisetum glaucum* L. with AgNPs (50–100 nm) on pearl millet plants exposed to saline stress (120 and 150 mM NaCl) showed that using a dose

20 mM AgNPs the plant growth characteristics, RWC, and proline content as well as fresh and dry biomass of plant organs increased compared to control plants. Nanopriming with AgNPs reduced oxidative stress in pearl millet salt-stressed plants due to enhanced activities of antioxidant enzymes. Moreover, in AgNPs-treated plants Na^+ and Na^+/K^+ ratio showed a decrease in contrast to K^+, which increased, suggesting enhanced salinity tolerance of plants (Khan et al., 2020). Priming of diploid (Riverside) and triploid (Maxima) watermelon seeds with AgNPs for 96 h resulted in enhanced glucose and fructose levels during germination and 14 days after sowing considerably higher seedling emergence rate was observed with triploid seeds. The yields of AgNP-treated Riverside and Maxima watermelons grown in greenhouse exceeded those of control watermelons by 31.6 and 35.6%, respectively. On the other hand, TPC, radical-scavenging activities, and macro- and microelements in treated watermelon fruits were comparable with those of control suggesting that fruit quality was maintained (Acharya et al. (2020). Priming of winged bean seeds with 50 mg/mL of AgNPs (15.47–20.98 nm) biosynthesized using *Psophocarpus tetragonolobus* leaf extract improved germination percentage by 88.33% compared to hydroprimed and unprimed control, enhanced activities of POD, CAT, APX, and SOD as well as soluble sugar, soluble protein, sucrose, and Chl levels resulting in improved seedling growth (Kumar et al., 2020). AgNPs and AuNPs green synthesized using onion extract, which were used for priming of aged onion seeds were found to be internalized into onion seeds and improved seed germination, emergence, growth, and yield compared with unprimed and hydro primed seeds. The results of both year experiments showed that priming with AuNPs resulted in pronounced increase in emergence percentage compared to control (63.2% vs 37.4%) and an average yield increase of 23.9% (Acharya et al., 2019). Priming of aged maize seeds with 5 ppm AuNPs green synthesized using rhizome extract of galanga plant enhanced emergence percentage observed with unprimed control (43%) and hydroprimed seeds (56%) to 83%, whereas priming with 10 ppm AuNPs was found to be optimal for improvement of physiological and biochemical properties of *Zea mays* seedlings. AgNPs remained internalized in seeds, did not translocate to roots and shoots, and were less phytotoxic than chemically synthesized AuNPs (Mahakham et al., 2016).

CeO_2 NPs phytosynthesized using aqueous seed extract of *Cassia angustifolia* and Se-doped CeO_2 NPs (Se-CeO_2 NPs) prepared using $NaSeO_3$ as a dopant compound applied for nanopriming of *Macrotyloma uniflorum* (horse gram) seeds were found to penetrate seeds and stimulated their germination as well as seedling vigor (Antony et al., 2021). Priming of cotton seeds with poly(acrylic acid)-coated CeO_2 NPs (500 mg/L; 24 h), which subsequently germinated under salinity stress, resulted in pronounced increase of growth characteristics compared to control, reduced ROS accumulation in roots, mitigated morphological and physiological changes caused by excess salinity, modified the levels of essential metals in roots and it was found that for improved tolerance against salinity ROS and conserved Ca^{2+} plant signaling pathways could be responsible (An et al., 2020).

Priming with SiNPs protected rice seedlings against adverse impact of fluoride-induced stress, which was reflected in improved plant growth and yield as well as increased levels of nonenzymatic antioxidants, activation of glutathione reductase resulting in glutathione (GSH) synthesis, which was inhibited by fluoride stress, and suppressed F^- accumulation in grains. Moreover, seedling health during fluoride stress was improved by the uptake of nutrients, whereby SiNPs acted as nanozyme since high concentrations of Cu, Zn, and Fe promoted the activities of antioxidant enzymes (SOD, CAT, APX, and glutathione peroxidase (GPX)), which together with non-enzymatic antioxidants scavenged ROS and stimulated fluoride tolerance (Banerjee et al., 2021). Priming of wheat seeds with SiNPs (300–1200 mg/L) for 24 h showed beneficial impact on growth characteristics and Chl content of plants exposed to stress induced by Cd; SiNPs reduced oxidative stress in stressed plants, stimulated activities of antioxidant enzymes, and reduced Cd concentrations in roots (by 11–60%), shoots (by 10–52%) and grains (by 12–75%) compared to control (Hussain et al., 2019).

Priming of *Helianthus annuus* seeds with sulfur NPs (SNPs; 12.5–200 μM) for 18 h pronouncedly diminished oxidative stress in plants irrigated with 100 mM $MnSO_4$ via stimulating activities of CAT and SOD and enhancing the levels of non-enzymatic antioxidants such as flavonoids and TPC resulting in considerable decrease of $O_2^{\bullet-}$ and lipid peroxidation in Mn-stressed plants. Great decline in GSH levels observed at exposure to SNPs was supposed to be due to its consumption and incorporation into biosynthesis of other chelating ligands (Ragab & Saad-Allah, 2021). Similarly, priming of wheat seeds for 12 h with 100 μM SNPs improved growth characteristics, contents of pigments, and non-enzymatic antioxidants and rebalanced the declined N, P, and K contents and decreased Na uptake in salt-stressed (100 or 200 mM NaCl) plants (Saad-Allah & Ragab, 2020).

2.2 Essential Metal-Based Nanofertilizers

Essential metals such as Cu, Zn, Fe, Mg, and Mn are indispensable micronutrients for development and growth of plants because they are catalytic and structural cofactors in many enzymes or can be included also in the constituents of photosynthetic apparatus, and therefore are frequently used as nanofertilizers whether alone or in combination, in the form of nanocomposites or controlled release nanoformulations with biodegradable polymers (Masarovičová et al., 2014; Jampílek & Kráľová, 2017a, 2019a, 2019b; Kráľová et al., 2019, 2021; Kráľová & Jampílek, 2021a, 2021b).

2.2.1 Cu-Based NPs

CuNPs phytosynthesized using *Azadirachta indica* leaf extract (41 ± 21 nm; zeta potential of −18.2 mV) stimulated germination of *Vigna radiata* L seeds and increased Cu content in treated seedlings; a dose of 100 ppm was found to be the most effective (Jahagirdar et al., 2020). Exposure of *Cajanus cajan* L. seedlings to

20 ppm CuNPs (20 nm; zeta potential of −16.7 mV) considerably enhanced height, root length, fresh and dry biomass, which increased up to 82.35% when seedlings were harvested after 4 weeks (Shende et al., 2017). Exposure of chick-pea seeds to 500–700 ppm bioengineered copper quantum dots (Cu QDs) for 72 h under dark stress pronouncedly improved seed germination, enhanced the levels of photosynthetic pigments of chick-pea plants over control, and suppressed antioxidant responses of plants suggesting that Cu QDs were able to scavenge ROS and reduce oxidative stress (Humaira et al., 2020). Exposure to *Fortunella margarita* Swingle seeds to spherical CuO NPs with the size ca. 300 nm coated with biodegradable chitosan (CS)-sodium alginate (ALG) (CS-Na-ALG) ensuring slow release of the nutrient resulted in improved germination and seedling growth. In contrast to uncoated CuO NPs, at treatment with coated CuO NPs root elongation with a greater number of secondary roots was observed, which also positively affected the development of the shoots. The best development of plant organs was achieved with CuO NPs-CS-Na-ALG nanohybrid containing 10 and 50 ppm CuO NPs. Up to 80% Cu release from nanohybrid was observed after 22 days compared to 1 day recorded for bare CuO NPs (Leonardi et al., 2021).

Comparison of the impact of CuO NPs (10–100 nm; zeta potential of −34.4 ± 0.5 mV) and CuO microparticles (MPs) (100–10,000 nm; zeta potential of −42.7 ± 0.2 mV) applied at doses 200 and 400 mg Cu/kg for 60 days on *Lactuca sativa* plant grown in soil showed that at harvest CuO NPs released pronouncedly more Cu^{2+} ions and diethylenetriamine pentaacetate (DTPA)-extractable Cu than CuO MPs. At exposure to CuO NPs and CuO MPs, copper accumulated more in roots. CuO NPs increased shoot biomass by 16.3–19.1% in contrast to CuO MPs, which did not affect plant biomass. Moreover, treatment with CuO NPs resulted in increased transpiration rate and considerably higher stomatal conductance compared to control and plants exposed to CuO MPs (Wang et al., 2019a). Exposure of soil-cultivated sweet potato cultivar showing high lignin content to 25 mg/kg CuO NPs resulted in increased root length, while treatment of a cultivar showing low lignin content with 125 mg/kg CuO NPs increased Mg content in periderm by 232% suggesting potential of CuO NPs to be used as nanofertilizer for sweet potato storage root production (Bonilla-Bird et al., 2020). CuO NPs phytosynthesized using *Sesbania aculeata* leaf extract applied at doses 25 and 30 mg/100 mL stimulated the growth of *Brassica nigra* plants (Elakkiya et al., 2021).

Cucumis sativus plants hydroponically cultivated in the presence of $CuFe_2O_4$ NPs (30.7 nm; 0.04–5 ppm) showed improved fresh weight, increased protein content, and considerably increased activities of SOD and POD as well as Fe and Cu levels in plant tissues (Abu-Elsaad & Hameed, 2019). Investigation of Cu distribution and speciation in roots of hydroponically cultivated wheat plants exposed to nanosized CuO, $Cu(OH)_2$, and CuS showed that CuO NPs and CuS NPs showing lower solubility than $Cu(OH)_2$ NPs were more persistent on the roots and delivered Cu to leaves over the 48-h depuration period suggesting that by tuning of NPs solubility slow delivery of micronutrients for long period can be achieved (Spielman-Sun et al., 2018).

Sulfur fertilization was found to reduce Cu concentration in soil pore water in the rice rhizosphere region, change the morphology and elementary composition of colloids in soil pore water, and affect the migration of CuO NPs in the soil column through soil colloids, whereby speciation transformation of CuO NPs was observed during the process of migration (Sun et al., 2020).

2.2.2 Zn-Based NPs

Lactuca sativa L. and *Daucus carota* subsp. *sativus* plants grown in soil fertilized with ZnO NPs (1–100 mg/kg soil) showed pronouncedly higher biomass as well as higher levels of Zn, Mg, and K than the control, except for the Mg content of *D. carota* roots cultivated in 20 mg/kg ZnO NPs, while highest concentration of nitrogen in both species was observed with application of 5 and 20 mg/kg ZnO NPs (Song & Kim, 2020). ZnO NPs improved growth and yield of *Zea mays* plant and increased grain Zn content by 82% compared to control suggesting successful biofortification with this essential metal (Umar et al., 2021). Nanocomposites of ZnO NPs and ALG, which were tested as fertilizer for *Zea mays* plants cultivated in poor Zn acidic soil (LUFA 2.1, pH 5.2), exhibited constant Zn release, maintained steadier Zn concentration in soil pore water over time, and avoided early-stage Zn toxicity observed at the application of conventional Zn fertilizer suggesting that the Zn nanocomposite can provide sustained Zn delivery to plants also in acidic soils (Martins et al., 2020). In sorghum pants exposed to drought stress ZnO NPs accelerated development of plants, stimulated yield, fortified grains with Zn, and improved N acquisition. Such treatments can be favorable not only for increasing cropping systems resilience to ensure food and nutrition security but also for reduced environmental pollution caused by nutrient losses (Dimkpa et al., 2019).

Zhu et al. (2020) investigated the mechanism of ZnO NPs entry into leaves of wheat applied via foliar spraying and found that ZnO NPs crossed the leaf epidermis via stomata, accumulated, and released Zn ions in the apoplast, which together with ZnO NPs were subsequently transported to mesophyll cells. Reduction of stomatal aperture diameter resulted in reduced Zn concentrations in wheat leaf apoplast and cytoplasm, with greater decrease in the cytoplasm. Although foliarly applied mostly spherical ZnO NPs (<20 nm) on *Setaria italica* L. plants did not pronouncedly affect plant height, 1000 grain weight, and grain yield quantitative characteristics, they considerably increased contents of oil and total nitrogen and markedly reduced crop water stress index (Kolencik et al., 2019). ZnO NPs (31.4 nm) applied using foliar treatment at a dose 40 ppm in the mixture with $ZnSO_4$ improved the agronomic and physiological features of rice plants resulting in higher yield and nutrient (N, K, and Zn)-enriched rice grains compared to fertilization with $ZnSO_4$ alone, although ZnO NPs exhibited negative impact on P uptake (Elshayb et al., 2021). Foliar application of fertilizer containing 2% w/v of urea and 40 mg/L of Zn in the form of complexes with CS NPs to wheat plants enhanced Zn grain content by ca. 36%, whereby the applied dose was ten-fold lower than the recommended dose of $ZnSO_4$ with 400 mg Zn/L, which achieved ca. 50% enrichment in grain Zn content suggesting that Zn content in grains following treatment with NPs showed eight-fold higher Zn use efficiency (Dapkekar et al., 2018). ZnO NPs showing hexagonal wurtzite structure and mean size of 45 nm tested as foliar nanofertilizer in combination with boric acid showed beneficial impact on dry matter yield of tomato plant cultivated in pots, along with considerable amelioration of fruit quality showing higher concentrations of total soluble solids, % titratable acidity, and ascorbic acid content (Ybanez et al., 2020). Foliar application of 1000 mg/L ZnO NPs on habanero pepper plants (*Capsicum chinense* Jacq.) performed during the main stages of phenological development showed beneficial impact on height, stem diameter, Ch content, fruit yield, and biomass of plants compared to control. On the other hand, treatments with double ZnO NPs concentration adversely affected plant growth but pronouncedly improved fruit quality, and increased capsaicin content by 19.3%, and TPC and total flavonoids content (TFC) in fruits by 14.50% and 26.9%, respectively, which contributed to increased antioxidant capacity (Garcia-Lopez et al., 2019).

Foliar treatment of *Oryza sativa* plants cultivated in Zn-deficient soil with ZnO NP increased growth and yield as well as Zn content in rice plants (Bala et al., 2019). Considerable increase of *Melissa officinalis* biomass along with ameliorated development of lateral roots, and increased levels of K, Fe, and Zn in plants was achieved via irrigation of plants with nutrient solution containing both ZnO NPs and SeNPs (Babajani et al., 2019). The beneficial as well as adverse effects of ZnO NPs in plants were comprehensively discussed by Kumar et al. (2021).

ZnNPs and CuNPs phytosynthesized using basil extract applied at a dose 4000 ppm ZnNPs +2000 ppm CuNPs to *Ocimum basilicum* plants considerably improved most morphological parameters, enhanced Chl*a*, Chl*b*, and carotenoid levels in the leaves as well as TPC and TFC content, and increased antioxidant activity of plants (Abbasifar et al., 2020). Fertilizer containing AgNPs or CuNPs, which was sprayed on winter wheat or maize leaves twice at a dose of 1%, increased the grain yield of *T. aestivum* and *Zea mays*, while application of such fertilizer at the dose of twice 2 L/ha resulted in improved yield of sugar beetroots (Jaskulska & Jaskulski, 2020). Combined application of nano zinc-iron oxide with *Azotobacter* biofertilizer at a dose of 1.5 g/L increased the grain yield of wheat by 88% as compared to control under severe drought stress (Sharifi et al., 2020).

2.2.3 Fe-Based NPs

Nano-iron applied to *Mentha piperita* plants in foliar application (0.5–1.5 g/L; three times of the interval of 15 days up to flowering stages) showed considerably enhanced Chl content, stem number, and essential oil (EO) content, whereby using a dose of 0.5 g/L the EO content and oil production increased by 60% and 50%, respectively, with pronounced increases in secondary metabolites such as menthone and menthol (Lafmejani et al., 2018). Treatment of *Capsicum annuum* plants with FeNPs (52.4 ± 5.1 nm; zeta potential of −23.3 ± 1.2 mV) applied at low doses stimulated plant growth via altering the leaf organization, increasing the chloroplast number and grana stacking and regulating the development of vascular bundles, whereby FeNPs absorbed in the roots were transported to the central cylinder in bioavailable forms, where they were translocated and utilized by the leaves and stems, suggesting the suitability of FeNPs to be used in appropriate doses as fertilizers to alleviate Fe deficiency in plants (Yuan et al., 2018). The beneficial impact of Fe/SiO_2 NPs applied as fertilizer on the growth of barley and maize was reported by Disfani et al. (2017). Iron-humic nanofertilizers (^{57}Fe NFs) containing ferrihydrite in their structures were synthesized from leonardite potassium humate and applied as fertilizers for soybean (*Glycine max*) grown in calcareous soil. These ^{57}Fe NFs were able to supply ^{57}Fe to the plants and ^{57}Fe was translocated from roots up to pods. Moreover, this nanoformulation showed slow and sustained release of Fe ensuring its long-term supply at required amounts to Fe-deficient plants cultivated in calcareous soil (Cieschi et al., 2019). Treatment of *Hordeum vulgare* plants with 500 mg/L of $Ni_{0.4}Cu_{0.2}Zn_{0.4}Nd_{0.05}Y_{0.05}Fe_{1.9}O_4$ NPs enhanced the levels of K, Ca, Mg, and P in roots, while pronouncedly decreased their content in leaves (except for Ca), and micronutrients Zn, Ni, Cu, and Fe were found to be incorporated into the plant body by the inclusion of NPs suggesting that treatment with NPs of essential minerals can be used to cope single or multiple nutrient deficiencies in plants (Tombuloglu et al., 2020).

Treatment of muskmelon (*Cucumis melo*) plants with 100 mg/L of γ-Fe_2O_3 and Fe_3O_4 showing size of 20 nm NPs stimulated fruit weight by 9.1% and 9.4%, respectively, and due to treatment with 100 mg/L Fe_3O_4 NPs vitamin C content increased by 46.95% suggesting improvement of fruit quality of melon, although treatment with NPs did not increase Fe content in plant organs. Exposure to iron oxides also increased Chl content at a certain stage of exposure; for example, in the second week plants treated with 400 mg/L Fe_3O_4 NPs the contents of soluble proteins were higher by 42.7% compared to control (Wang et al., 2019b). Yttrium doped γ-Fe_2O_3 NPs delivered by irrigation in a nutrient solution to *Brassica napus* plants cultivated in soil strongly reduced H_2O_2 levels and MDA formation in plants and enhanced growth rate of leaves, dry matter yield, and Chl content resulting in improved agronomic properties of plants (Palmqvist et al., 2017). Bare and CS-coated Fe_3O_4 NPs with sizes 3–22 nm applied at a dose 200 and 400 mg/kg had beneficial impact on seed germination and growth of *Capsicum annuum* L., although the effects of CS-coated Fe_3O_4 NPs were more pronounced. On the other hand, higher concentrations (800 and 1600 mg/kg) of CS-coated Fe_3O_4 NPs were phytotoxic (Bahrami et al., 2018).

2.2.4 Mg-Based NPs

Foliar treatment of bean plants with 50 ppm MgNPs was found to be optimal to achieve highest biomass as well as highest levels of assimilation pigments in plants, while application of a dose of 100 ppm ameliorated pods yield and increased activity of the nitrate reductase. On the other hand, decreasing levels of carotenes were observed when MgNPs dose increased (Salcido-Martinez et al., 2020). Cotton plants, which were foliar sprayed at vegetative and boll formation stages of cotton with 60 ppm MgO NPs (50 nm) considerably enhanced the number of opened bolls per plant, single plant yield, and seed cotton yield. Seed cotton yield of plants treated with MgO NPs achieved 42.2% over control compared to 39.9% and 24.8% observed with bulk MgO and $MgSO_4$. In addition, foliar fertilization with MgO NPs showed beneficial impact on macronutrient (N, P, K) levels and Mg content in plants (Kanjana, 2020). Increased Mg levels in leaves compared to control (12.93 mg/g vs 9.30 mg/g) in *Nicotiana tabacum* L. plants treated with MgO NPs (50–250 μg/mL) were responsible for enhanced Chl content and improved plant growth (Cai et al., 2018a). Application of 100 mg/kg of nanosized $Mg(OH)_2$ increased biomass of Chinese cabbage cultivated in pots and reduced Cd concentration in plants exposed to Cd stress more effectively than the same dose of bulk $Mg(OH)_2$ (Luo et al., 2020). Stimulation of seed germination and improved growth characteristics of maize plants was achieved using 500 ppm $Mg(OH)_2$ NPs phytosynthesized using filtrate from *Aspergillus niger* (Shinde et al., 2020). Phytosynthesized MgO NPs (5–25 nm) improved germination and growth of maize along with increasing Chl levels, a dose of 100 mg/L being most effective (Jayarambabu et al., 2016).

2.2.5 Mn-Based NPs

Comparison of the impact of soil and foliar exposure of *T. aestivum* plants to Mn_2O_3 NPs (30 nm) showed that application of foliar exposure resulted in greater shoot and grain Mn contents by 37% and 12%, respectively, reduced levels of soil nitrate nitrogen by 40%, and increased P levels in soil and shoot by 17 and 43%, respectively. Although differences in yield increases observed at treatments with $MnCl_2$ and bulk and nanosized Mn_2O_3 (9%, 13%, and 16%) at soil exposure were statistically insignificant, foliar application of Mn_2O_3 NPs increased grain yield by 22%, and compared to soil application greater grain yield by 5% was achieved (Dimkpa et al., 2018).

The beneficial impact of bimetallic MnO_x/FeO_x NPs green synthesized using bacteria supernatant containing indole-3-acetic acid complex on germination rates, root growth, and fresh weight in maize plantlets was reported by Bettencourt et al. (2020). An increase in the growth of *Lactuca sativa* plants by 12–54% was observed at application of 50 ppm MnO_x NPs and FeO_x NPs applied at low concentrations (Liu et al., 2016). Manganese zinc ferrite ($Mn_{0.5}Zn_{0.5}Fe_2O_4$) NPs fabricated at 160 °C applied to growing *Cucurbita pepo* plants at a dose 10 ppm increased the yield by 49.3% and 52.9%, respectively, compared to the untreated squash for the two consecutive seasons, achieving fruit yield of 54.8 and 55.2 t/ha. It was shown that the synthesis temperature of NPs affected surface, pore structure, particles size, and shape of these fertilizers, which had influence on plant growth (Shebl et al., 2020). Enhanced plant germination, growth, and biomass of *Hordeum vulgar*e seedlings was observed due to treatment with $MnFe_2O_4$ NPs (14 nm), particularly using a dose 250 mg/L, whereby the leaves of treated plants showed 4–seven-fold higher levels of Fe and 7–nine-fold higher levels of Mn than the control suggesting translocation of NPs from roots to leaves (Tombuloglu et al., 2018).

2.3 Other Plant Growth-Stimulating Inorganic Nanoparticles

Besides nanoscale essential micronutrients used as nanofertilizers and discussed in previous section also some other metal/metalloid-based NPs/NCs were found to have beneficial impact on plant growth. In this section, we focused attention on NPs/NCs of Ag, Ca, Se, Si, SiO_2, and TiO_2, which can be used as plant growth-promoting agents in agricultural practice.

2.3.1 AgNPs

Low ROS levels, reduced lipid peroxidation, and H_2O_2 content compared to the control along with increased levels of some antioxidant enzymes was observed in AgNPs-treated *Oryza sativa* plants showing increased biomass and improved root branching suggesting that AgNPs were involved in regulating ROS generation and their scavenging (Gupta et al., 2018). Increased activities of antioxidant enzymes APX, POD, and CAT were also observed in *Cicer arietinum* seedlings exposed to 0.1%, w/v Ag-CS NPs (20–50 nm) showing improved growth characteristics (Anusuya and Banu 2016). Stimulation of early growth of wheat seedlings at treatment with 10 mg/L AgNPs phytosynthesized using *Phyllanthus emblica* L. fruit extract was explained by reduced ROS levels, whereby lower Ag accumulation in roots compared to chemically synthesized AgNPs resulted in higher root cell viability (Kannaujia et al., 2019). Markedly increased morphological characteristics including seeds number per pod, number of pods per plant, green pod yield, etc., compared to the control plants showed *Pisum sativum* plants following treatment of seeds and foliar spraying with 60 ppm AgNPs (10–100 nm) (Mehmood & Murtaza, 2017). Foliar treatment of two *Phaseolus vulgaris* cultivars with 10 ppm *Gum acacia*-capped AgNPs (16.7 nm) exhibited considerable increase of morphological attributes, especially of seed yield, whereby the stimulating impact was associated with altered protein patterns in the two varieties and increased levels of growth-regulating substances in plants (El-Batal et al., 2016). In greenhouse experiments, treatment with 15 mg/kg AgNPs (10 nm) stabilized with polyhexamethylene biguanide hydrochloride promoted the growth of fodder beet (*Beta vulgaris* L.), likely due to the modified activity of oxidases and subsequent changes of volume of auxins in plant tissues (Gusev et al., 2016). Razzaq et al. (2016) observed improved growth characteristics and higher number of grains per spike and 100-grain weight compared to control of *Triticum aestivum* plants exposed 25 ppm AgNPs (10–20 nm), while stimulation of growth and yield of wheat plants by chemo-blended AgNPs prepared by mixing AgNPs, nicotinic acid and KNO_3 can be explained by regulation of energy metabolism via suppression of glycolysis, whereby in the next generational plants toxicity symptoms were not observed (Jhanzab et al., 2019).

2.3.2 Ca-Based NPs

Preharvest fertilization of apple (*Malus domestica* Borkh. "Red Delicious") by spraying with 2.0% suspension of nanosized Ca increased titratable acidity, TPC, total antioxidant activity as well as fiber and starch content to greater extent than conventional $CaCl_2$, while reduced total sugars, and anthocyanin levels, suggesting that this nanosized fertilizer can improve the overall characteristics of apple fruit (Ranjbar et al., 2020). Suspensions of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) NPs (HpNPs; 35 and 45 nm) stabilized with carboxymethylcellulose (CMC) showed dose-dependent stimulating effect on root elongation of tomato seedlings and enhanced root elongation by 64% and 97%, respectively, at treatment with 200 and 500 mg/L CMC-HpNPs. In hydroponically cultivated tomato plants CMC-HpNPs doses of 200 and 500 mg/L pronouncedly reduced the ATP amounts in roots and shoots compared to the control. Treatment with CMC-HpNPs did not affect significantly P content in plant organs. On the other hand, Ca levels in shoots of treated plants were lower than those in control plants and plants treated with 500 mg/L CMC-HpNPs showed even four-fold lower Ca concentration than the control plants, although with further increasing of CMC-HpNPs concentrations up to 2000 mg/L the Ca shoot concentrations showed a slight increase (Marchiol et al., 2019).

2.3.3 TiO_2 NPs

Beneficial effects of titanium on plants reflected by improved growth and photosynthesis, increased activity of enzymes, and improved nutrient uptake contributing to higher crop yield and quality were summarized by Lyu et al. (2017), and applications of TiO_2-based nanomaterials as antimicrobial, growth-regulating, and fertilizer-like agents in sustainable agriculture were overviewed by Rodriguez-Gonzalez et al. (2019). Stimulation of the shoot and seedling lengths of *T. aestivum* plants by 2 and 10 ppm TiO_2 NPs exceeded that observed with bulk TiO_2 (Feizi et al., 2012), and greatly increased growth characteristics of maize plants were recorded at treatment 25 mg/L TiO_2 (2–6 nm) (Yaqoob et al., 2018). Treatment with TiO_2 NPs (40 nm) at doses <10 μg/L positively affected seed germination and root elongation of plants and partially suppressed metal root translocation (Rodriguez-Gonzalez et al., 2019), and ameliorated germination also showed *Pennisetum glaucum* seeds exposed to spherical TiO_2 NPs with sizes 50–71 nm (Rafique et al., 2019). Foliar treatment of mung bean plants with 10 mg dm^{-3} TiO_2 NPs stimulated growth of plant organs, increased the contents of Chl and total soluble leaf protein as well as activities of some enzymes such as acid phosphatase, alkaline phosphatase, phytase, and dehydrogenase over the control (Raliya et al., 2015), while TiO_2 NPs (0.5–2 g/L) considerably promoted the growth of tomato plants grown in hydroponium and increased glutathione synthase and glutathione *S*-transferase expressions in both roots and leaves, suggesting that in detoxification of TiO_2 NPs in tomato plants thiol groups are involved (Tiwari et al., 2017). Moreover, application of 100 mg/L TiO_2 NPs alleviated adverse impact of salinity stress on *Dracocephalum moldavica* L. plants reflected in ameliorated agronomic traits, increased antioxidant enzyme activity, and reduced H_2O_2 levels compared to untreated plants exposed to salinity (Gohari et al., 2020).

2.3.4 Si and SiO_2 NPs

For nanofertilizer formulations also the metalloid silicon NPs and SiO_2 NPs could be used. Ameliorated seed germination and enhanced biomass as well as increased total protein and Chl contents showed *T. aestivum* and *Lupinus angustifolius* plants treated with 500 and 1000 mg/L of mesoporous SiO_2 NPs (20 nm; zeta potential of and −22.5 mV; pore diameter of ca. 2.78 nm) (Sun et al., 2016) and 400 mg/L SiO_2 NPs improved morphological, physiological, and biochemical characteristics of *Zea mays* L., *Phaseolus vulgaris* L., *Hyssopus officinalis* L., and *Nigella sativa* L. plants (Sharifi-Rad et al., 2016). SiO_2 was reported to facilitate SiO_2 uptake, growth, and stress tolerance in plants (Mathur & Roy, 2020). In field experiment, exposure of rice plants to SiNPs and ZnNPs via foliar or soil application resulted in markedly increased yields and by combined treatment with both NPs improved grain and straw yields with higher Si, Zn, and N levels were achieved (Kheyri et al., 2018).

2.3.5 SeNPs

El-Ramady et al. (2014) presented a review paper dealing with the production, biological effects, and use of SeNPs in agroecosystems. Findings related to the impact of ionic selenium and SeNPs on plant metabolism and the synthesis of primary and secondary metabolites increasing stress tolerance as well as the current achievements related to the biofortification of horticultural crops with these Se forms were overviewed by Marquez et al. (2020). Positive impact of SeNPs (20–30 nm) on growth, biochemical characteristics, and yield of cluster bean (*Cyamopsis tetragonoloba*) cultivated in pots for 60 days was reported by Ragavan et al. (2017). Foliar application of Cs–Se NPs showing a size ca. 50 nm applied at doses 10 and 20 mg/L increased root dry weight, RWC, and number of fruits per plants in bitter melon and mitigated adverse impact of salt stress on growth and some biochemical parameters of *Momordica charantia* via increased antioxidant enzyme activity, proline concentration, RWC, and K^+, and reduction of MDA and H_2O_2 levels and Na aggregation in plant tissues (Sheikhalipour et al., 2021). Alleviation of saline stress by SeNPs was also reported for groundnut (Hussein et al., 2019), eggplant (Abul-Soud & Abd-Elrahman, 2016), strawberry (Zahedi et al., 2019), or tomato plants (Mozafariyan et al., 2016; Morales-Espinoza et al., 2019).

2.4 Slow-Release Mineral Fertilizers with Microporous Structure

Excessive fertilization resulted in contamination of environmental matrices and therefore, it is desirable to decrease high fertilization rates. In general, at application of salt- and macrosized NPK fertilizers low nutrient use efficiency is observed, however their entry in aqueous system results in eutrophication (Queiros et al., 2015; Li et al., 2020a; Barcala et al., 2021). On the other hand, accurately used mineral fertilizers containing primarily macronutrients N, P, and K in desirable amounts applied at the right time and in the right place can significantly contribute to the improvement of fertilizer efficiency (Bindraban et al., 2015). Therefore, attention is focused on carriers suitable to ensure slow release of these macronutrients and deliver them with high efficiency to plants as such aluminosilicates such as zeolites (ZEO), nanoclays or montmorillonite are frequently used (Yuan, 2014; Messa et al., 2016; Jampílek & Kráľová, 2017a; Maghsoodi et al., 2020a; Naseem et al., 2020; Soltys et al., 2020; Mondal et al., 2021; Rudmin et al., 2021).

Zeolites, frequently also used as ion-exchangers or catalysts, are crystalline aluminosilicates showing 3-D microporous structures with general empirical formula of $M_{2/n} \bullet Al_2O_3 \bullet xSiO_2 \bullet yH_2O$, where M is alkaline or alkaline earth metal; n is the degree of its oxidation; x is the number of SiO_2 molecules (from 2 to 10); y is the number of H_2O molecules (from 2 to 7) (Pavelic et al., 2018). Their structure is characterized with SiO_4 (some of them being replaced by AlO_4) tetrahedra rings containing open cavities in the form of channels with certain size, enabling adsorption of compounds and penetration of molecules with smaller diameter than that of the channel. For example, zeolite A contains sodalite cages connected by four-membered rings forming a three-dimensional (3D) network, whereby central cavities of cages of 1.14 nm are interconnected by eight-ring openings with a 0.41 nm aperture creating a framework with a void volume fraction of 47% (McCusker & Baerlocher, 2001). Inner surface area of these channels achieving several hundred square meters per gram of zeolite is responsible for superb ion exchanging properties of ZEO. Strong affinity of natural zeolites for NH_4^+ and K^+ is utilized for optimization of N use efficiency in agriculture (Eslami et al., 2020). Moreover, application of ZEO can reduce soil acidity and improve soil ability to retain water (Hasbullah et al., 2020; Ibrahim & Alghamdi, 2021). Structure of zeolites is shown in Fig. 2. Montmorillonite (MMT) is a phyllosilicate mineral with nanolayered structure (ca. 1 nm in thickness) consisting of stacked layers, whereby each layer is composed of two O-Si-O tetrahedral sheets sandwiching one O-Al(Mg)-O octahedral sheet (approx. 100 nm × 100 nm) (Zhu et al., 2020). Structure of MMT is shown in Fig. 3.

Application of nanoclays, nanozeolites, and nanominerals can enhance water retention, and they can be used as nutrient carriers and for stimulation of seed germination, plant growth as well as P and N fixation (Pulimi & Subramanian, 2016; Jampílek & Kráľová, 2017a). Due to cation exchange ability and porosity, ZEO can be used as slow-release fertilizers releasing nutrient for longer period and

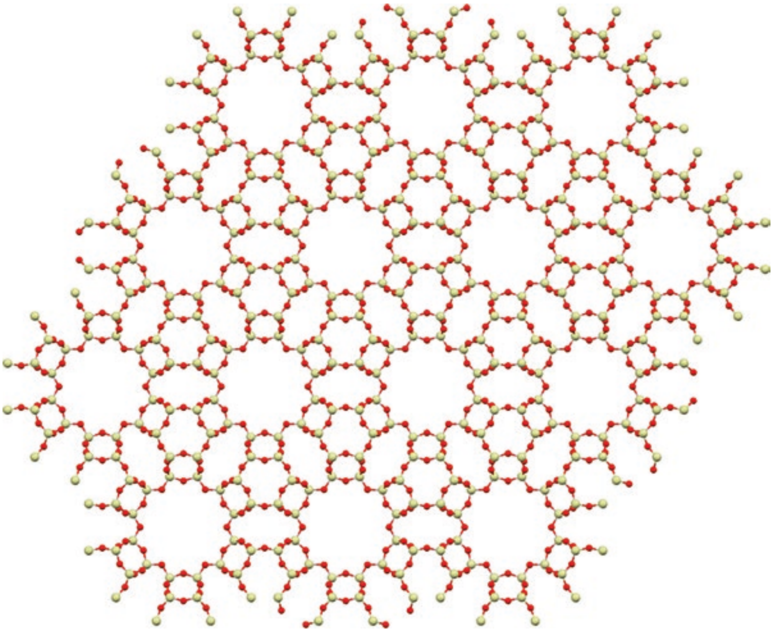

Fig. 2 Structure of zeolites. (Structural formula based on crystallographic study of Barrer & Villiger, 1969)

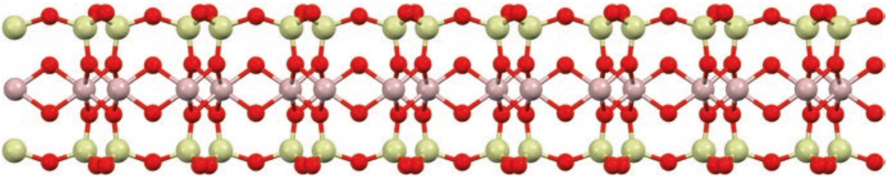

Fig. 3 Structure of montmorillonite (Structural formula based on crystallographic study of Viani et al., 2002)

preventing nutrient leaching. Soltys et al. (2020) summarized the recent findings related to the use of ZEO-based composites as fertilizers and their impact on nutrient retention and release into the soil. Nanozeolite composite slow-release fertilizer, in which macronutrients were incorporated in nanozeolite carrier and were released for prolonged period, stimulated plant growth, pronouncedly improved the quality and the water retention capacity of the soil, and can serve as an environment friendly source of nutrients for plants (Khan et al., 2021). ZEO application resulted in enhanced root biomass as well as pronouncedly higher K content in soil and K and Ca concentrations in leaves of chestnut plants compared to application of vermiculite and the soil application of a controlled release fertilizer (CRF) (Chatzistathis et al., 2021). In another experiment it was found that co-application of ZEO and manure resulted in 16.5–37.5-fold increase of exchangeable K^+ and potassium concentration of *Solanum lycopersicon* leaves, which was considerably higher compared to treatment with CRF (Chatzistathis et al., 2020). ZEO/Fe_2O_3 NCs, in which Fe_2O_3 NPs with average particle sizes of 1.45, 2.19, and 2.20 nm were situated on the ZEO surface and Fe_2O_3 NPs constituted 4, 7, and 12 wt% in the NCs, have potential to be used as an iron smart nanofertilizer for the slow-release of iron ions resulting in improved crop yield and soil productivity (Jahangirian et al., 2020).

Investigation of nitrogen (N) release pattern of ZEO as carrier of urea and urea-hydroxyapatite nanohybrids in water and in calcareous waterlogged soil showed that 20 days after their application in soil 75.0% and 58.1% of urea was converted to NH_4^+, respectively, whereas using urea alone >85% was converted to NH_4^+ within 12 days suggesting that due to slow urea release the N loss in soil can be reduced along with enhanced nitrogen use efficiency in calcareous paddy soils (Maghsoodi et al., 2020a). At one-time application of urea-ZEO fertilizer (157.5 kg N/ha), after initial burst N release from ZEO, slow release of nitrogen for 20 days was observed resulting in stabilizing of the grain-filling process and increased grain yield of rice and improved taste value was observed as well (Wu et al., 2020). Ammonium-enriched ZEO used as slow-release fertilizer showed beneficial impact on strawberry plants as well as bacterial nitrification (Costamagna et al., 2020). Investigation of nutrient uptake, and N use efficiency in *Brassica napus* and *Triticum aestivum* plants for 2 years using two crop rotations of "canola-soybean-wheat" and "canola-wheat" showed that co-application of ZEO with urea and composted manure or ZEO with urea and azocompost was able to preserve higher levels of nutrients in the rhizosphere compared to other treatments (Akbari et al., 2020). Zheng et al. (2019) reported that the combined application of ZEO and P under improved alternate wetting and drying irrigation regime reduced water use and grain yield in rice due to increased P uptake in aboveground plant part, which resulted in alleviation of the environmental pollution due to excessive P. Moreover, ZEO application increased NH_4^+-N retention in the topsoil and blocked NO_3^--N from leaching into deeper soil layers. Besides ZEO also vermiculite and nanoclay amendment to sandy loam soil can effectively decrease NH_4^+-N transport and improve the efficiency of N fertilizer (Mazloomi & Jalali, 2019).

Combined treatment of nanozeolite and bio-inoculants (promotory *Bacillus* spp.) stimulated growth characteristics as well as contents of assimilation pigments, total sugar, protein, and phenols in maize plants and enhanced the levels of antioxidant enzymes and non-enzymatic antioxidants compared to control plants, resulting in great increase (29.80%) in productivity of *Zea mays* plants (Chaudhary et al., 2021). Also using plant growth-promoting rhizobacteria, PS2-KX650178 and PS10-KX650179, combined with nanozeolite was found to improve the growth of *Trigonella foenum-graecum* plants and soil (Kumari et al., 2020). *Bacillus* spp. (accession number KX650178 and KX650179) with nanozeolite (50 ppm) applied to maize seeds besides beneficial impact on growth and performance of *Zea mays* plants also pronouncedly enhanced dehydrogenase, fluorescein diacetate hydrolysis, and alkaline phosphatase activity (up to three-fold) (Khati et al., 2018).

Multilayer films of carboxymethylcellulose/ZEO enriched with macro and micronutrients and containing macro in the inner and micronutrients in the outer layer functioned as enhanced efficiency fertilizers, showed similar release of nutrients than commercial Basacote® and were able to release the nutrients for a long period (Pereira et al., 2020). Treatment with mesoporous $ZnAl_2Si_{10}O_{24}$ NC with surface area of 193.07 m^2/g and particle size of 64 nm loaded with urea suitable for simultaneous slow delivery of both Zn and urea resulted in pronouncedly higher yield of rice compared to commercial urea preparation (Naseem et al., 2020).

Clinoptilolite is a natural ZEO composed of a microporous arrangement of silica and alumina tetrahedra $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_6{\cdot}12H_2O$. Combination of nanoclinoptilolite ZEO with nanohydroxyapatite can function as powerful P fertilizer in calcareous soil (Mikhak et al., 2018). Clinoptilolite ZEO coated with $Fe_2H_2O_4$ pre-loaded with 255 mg N/kg and 224 mg P/kg applied to sand-based root zone at 5–10% as water-soluble fertilizer reduced the quantity of leached P by 96.2% and 91.3%, respectively, and the quantity of leached N by 88.6% and 82.7%, respectively, and was able to maintain the growth of creeping bentgrass (Sloan et al., 2019). Evaluation of the pore-size distribution of natural and modified mesoporous clinoptilolites showed the presence of the pores of fracture-type from 25–50 to 100 nm between clinoptilolite grains, whereby the pores between crystal aggregates achieved the size up to 500 nm (Kowalczyk et al., 2006). Using clinoptilolite co-loaded with NH_4^+ and K^+, which can potentially adsorb both NH_4^+ and K^+ up to 25.00 mg NH_4^+/g and 47.61 mg K^+/kg, respectively, as a binary fertilizer considerably increased nitrogen uptake by *Zea mays* plants; uptake of K (2.05 g/pot) observed at application of clinoptilolite was comparable with that of controlled release fertilizers (Eslami et al., 2020).

Methods used for synthesis of hierarchical ZEO (containing two or more types of pores of different size, whereby additional larger pores can overwhelm the intrinsic limitations of conventional ZEO) and nanozeolites and their enhanced properties were discussed by Koohsaryan and Anbia (2016). Synthesis of zeolites with nano-sized crystals was discussed by Knyazeva and Ivanova (2019). Investigation of the fertilizing effect of synthetic nanozeolite saturated with $(NH_4)SO_4$ (nCp-NH_4^+), nanohydroxyapatite (nHA) with particles showing diameters of 25–50 nm and triple superphosphate $[Ca(H_2PO_4).H_2O]$ as well their combinations on agro-morphological characteristics of *Matricaria recutita* plants showed that best impact on growth characteristics, chamazulene content and root and shoot P content was achieved using combined application of nCp-NH_4^+ with nHA or nCp-NH_4^+ with $Ca(H_2PO_4).H_2O$, suggesting that co-application of Cp-NH_4^+ with nHA can be used as effective P fertilizer ensuring improved agronomical yield along with reduction of risks of water eutrophication (Mikhak et al., 2017).

Microhydroxyapatite, nanohydroxyapatite, and normal hydroxyapatite were found to increase soil pH and reduce soil exchangeable acid and exchangeable Al, although the changes in the composition of soil microbial community depended on the size of the used amendment (Cui et al., 2018). Urea-hydroxyapatite nanohybrids for slow release of N were prepared by incorporating urea molecules into a matrix of hydroxyapatite NPs, which resulted in its reduced solubility and binding of a large amount of urea molecules to NPs characterized with large surface area. Nanohybrid with 40 wt.% of N exhibited slow release enabling to reduce the amount of applied urea without reducing crop yield (Kottegoda et al., 2017). Hybrid nanofertilizer (HNF) consisting of urea-modified hydroxyapatite with incorporated Cu, Fe, and Zn NPs showed availability of Ca^{2+}, PO_4^{3-}, NO_2^-, NO_3^-, Cu^{2+}, Fe^{2+}, and Zn^{2+} during leaching studies and improved swelling ratio, water absorption, and retention capacities. Moreover, compared to commercial fertilizer, which was applied to *Abelmoschus esculentus* at a dose of 5 g/week, a dose of 50 mg HNF/week was sufficient to ensure pronounced increase in the uptake of Cu^{2+}, Fe^{2+}, and Zn^{2+} in plants due to their slow release (Tarafder et al., 2020). Also, hydroxyapatite NPs maintaining longer P availability for plants are suitable for P nutrition of plants; in contrast to their beneficial impact on sorghum and pea plants, they showed adverse effects on growth of some other plants (e.g., mung bean sprouts, tomato, and Pakchoi plants), likely due to increased Ca^{2+} levels in cells suggesting that their impact on plants depends on the plant type and applied NPs concentration (Maghsoodi et al., 2020b). Self-assembling of natural or synthetic humic substances and hydroxyapatite was used to develop a novel biocompatible and multifunctional P nanofertilizer characterized with self-assembling natural or synthetic humic substances and hydroxyapatite, which was shown to cause considerable amelioration of early growth and productivity of maize plants and had positive impact on rhizobacteria (Yoon et al., 2020). Environment-friendly biosynthesis of nanohydroxyapatite using *Bacillus licheniformis* and K_2HPO_4 concentrations ranging from 2% to 20% w/v of K_2HPO_4 was described by Priyam et al. (2019). The nanohydroxyapatite prepared with 2% P source can be recommended to be used as nanofertilizer.

Zincated nanoclay polymer composite (ZNCPC) was found to be a promising fertilizer able to improve Zn use efficiency in the rhizosphere of *Oryza sativa* plants. In pot experiments, in Zn-deficient soil showing diethylenetriaminepentaacetic acid (DTPA)-extractable Zn of 0.48 mg/kg, its use resulted in DTPA-extractable Zn content in soil at harvesting stage of 3.50 mg/kg, higher dehydrogenase activity at maximum tillering stage, maximum acid and alkaline phosphatase activities at panicle initiation stage and maximum Zn uptake of 303.42 mg/kg (Dubey et al., 2021). Similar results were reported by Adhikary et al. (2020) who observed that application of 100% ZNCPC resulted in considerable increase of water soluble, exchangeable, and organically bound Zn and grain Zn content compared to application of ZnO NPs (40.57 mg/kg vs 34.71 mg/kg); maximum apparent Zn recovery achieved 26.35% and 18.73% at treatment with 100% ZNCPC and ZnO NPs, respectively. Novel ZNCPC applied in wheat rhizosphere showed favorable properties as fertilizer formulation able to increase DTPA extractable Zn, Olsen-P, and soil enzyme activities (Mandal et al., 2019). Investigation of various PVA/nanoclay hydrogel NCs with different weight fractions of nanoclay (0.25–1.0) loaded with a potassium phosphate fertilizer showed that increasing nanoclay content reduced porosity of the hydrogel and made it denser, decreased the swelling of the hydrogels, and improved its controlled release properties (Hakim et al., 2019). Using batch and column experiments, Mazloomi and Jalali (2019) showed that amending sandy loam soil with vermiculite, nanoclay, and ZEO can reduce NH_4-N transport and thus improve the efficiency of N fertilizer.

Bortolin et al. (2016) developed hydrogel-based NCs suitable for slow/controlled release of macro- and micronutrients achieving up to 5000-fold higher absorbing water contents than their weight. The presence of calcium MMT increasing swelling degree ameliorated nutrient (sodium octaborate and urea) loading capacity. The NC containing approx. 50.0% wt MMT showing in water 2000-fold higher swelling and loading capacity of 74.2 g of urea and 7.29 g of boron per gram exhibited simultaneous slow release of both nutrients suggesting potential to be used as carrier for nutrient release in agricultural practice. CS and MMT clay hybrid microspheres encapsulating KNO_3 fertilizer achieving swelling of 200% showed fast KNO_3 release at pH 4 and 5.5; in soil tests, after higher release for first 10 days, they exhibited slow and sustained release until 60 days (Messa et al., 2016). Fertilizer fabricated by intercalation of urea in MMT showed initially high release from the outer urea film, followed by slow and sustained release of exchangeable N from the interlayer space of MMT ensuring prolonged nutrition of plants (Rudmin et al., 2021). CS-bentonite nanoclay film composite suitable for effective removing NH_4^+-N from aqueous solution can be reused as a fertilizer for agricultural purposes (Haseena et al., 2016).

From nanoclay polymer composites fabricated using partially neutralized acrylic acid and bentonites and loaded with urea and nitrification inhibitors (Schiff base, dicyandiamide, and neem oil) the most effective inhibition of nitrification (30–87%) was observed with NC containing Schiff base, which was able to reduce nitrate movement by 78.5% at the depth of 5 cm in soil column (Saurabh et al., 2019). Nanostructured hydrogels based on poly(methacrylic acid)/Cloisite-Na^+ showed an increase of the porous diameter and thermal stability with increasing nanoclay content, which also contributed to amelioration of controlled release (release time and quantity) of potassium fertilizer (Ferreira et al., 2018). By encapsulation of NPK fertilizer into NC hydrogels fabricated using graft copolymerization of acrylic acid and copolymer acrylamide onto sodium carboxymethyl cellulose and MMT slow-release fertilizer formulation was prepared suitable to be used for sustainable agricultural applications (Ahuja et al., 2020). As prospective slow-release fertilizer also composites of Na-ALG-g-poly(acrylic acid-co-2-hydroxyethyl methacrylate)/MMT (Kenawy et al., 2019) and carboxymethyl cellulose-g-poly(acrylamide)/MMT (Kenawy et al., 2018) were reported.

Hybrid materials based on halloysite (HAL) and ALG or MTT and ALG polymers, which were used to encapsulate microbial fertilizers *Pseudomonas fluorescens* Ms-01 and *Azosprillum brasilense* DSM1690, showed swelling ratios of 61.5 ± 1.35% and 36.5 ± 5% for the MMT and HAL formulations, respectively, and preserved bacterial survival. Hal-ALG formulation provided considerable release of bacterial cells after 15 days of incubation in saline water (15.24 log CFU/mL) and treatment of wheat plants with these capsules pronouncedly enhanced root and shoot biomasses and nitrogen content in the roots (Kadmiri et al., 2021).

3 Herbicidal Effects of Metal-Based NPs

Metal-based NPs applied at higher doses show herbicidal impact on plants reflected in reduced growth, inhibition of photosynthetic processes, decline in the levels of assimilation pigments (Chl, carotenoids), increased generation of ROS resulting in higher lipid peroxidation, membrane injury and electrolyte leakage, decreased activity of antioxidant enzymes, reduced levels of non-enzymatic antioxidants such as GSH and genotoxic effects as well. This adverse impact of metal-based NPs on plants is due to excess levels of metal ions, which reached already phytotoxic concentrations as well as nanospecific toxicity of NPs, which is affected by their small size, shape, and high surface to volume ratio. The negative effects of metal-based NPs on plants were comprehensively reviewed by several researchers (Masarovičová & Kráľová, 2013; Masarovičová et al., 2014; Rastogi et al., 2017; Jampílek & Kráľová, 2019b; Kráľová et al., 2019, 2021; Kráľová & Jampílek, 2021b; Ameen et al., 2021; García-Sánchez et al., 2021). However, in the agricultural practice, the metal-based NPs are not used as herbicides because they do not act especially against unwanted vegetation and when applied at higher concentrations needed for herbicidal effect, they could threaten the growth and development of crops. However, agricultural soils can be contaminated with metal-based NPs originating from anthropogenic activities and can adversely affect agricultural production. The main adverse effects of metal-based NPs on plants are shown in Fig. 4.

4 Insecticidal Formulations of Inorganic NPs

At present ca. 5–20% of major grain crops are consumed by insects and based on the analysis of Deutsch et al. (2018) the yield loss of wheat, rice, and maize caused by insects due to changing climate conditions will increase by 10–25% per degree

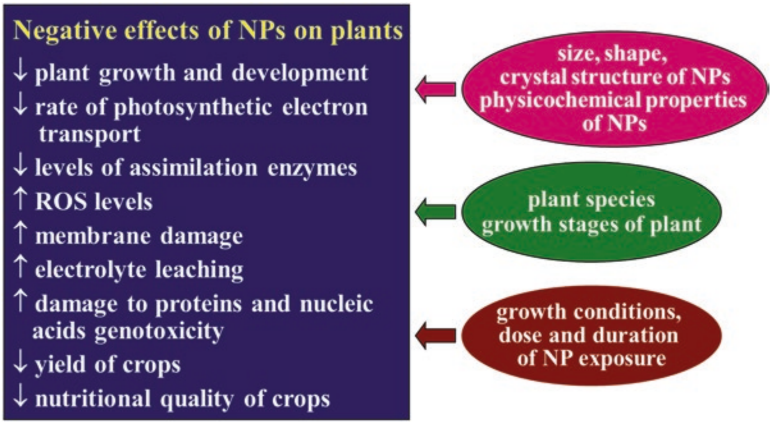

Fig. 4 Main adverse effects of metal-based nanoparticles on plants

Celsius of warming, whereby the highest impact will be observed in the temperate zone. There are a great variety of synthetic compounds showing insecticidal activity; however, their use is frequently accompanied with the development of resistance in the insects, adverse impact on non-target organisms, including pollinators, and contamination of environmental matrices (Iyaniwura, 1991; Katagi, 2010; Jampílek & Kráľová, 2015, 2017b, 2019c; Jampílek et al., 2020; Thompson et al., 2020; Zhao et al., 2020a). Therefore, increasing attention is devoted to the use of nanoscale formulations containing bioactive compounds showing insecticidal activity such as nanoemulsions of essential oils (Jampílek & Kráľová, 2017b, 2018, 2019c; Hashem et al., 2018; Jampílek et al., 2019; Echeverría & de Albuquerque, 2019; Pavoni et al., 2020; Kavallieratos et al., 2021), metal-based NPs (Chen, 2018; Jampílek et al., 2020; Yaqoob et al., 2020), SiO_2 NPs (e.g., Debnath et al., 2011; Shoaib et al., 2018; Caceres et al., 2019) as well as diatomaceous earth (Gao et al., 2018; Van den Noortgate et al., 2018) or zeolites (Van den Noortgate et al., 2018; Ilhami et al., 2020). Currently, use of phytosynthesized and mycosynthesized NPs is preferred because capping with bioactive compounds contained in plant extracts or fungal filtrates acting as reductants is beneficial from the aspect of improved biological efficiency of NPs (Masarovičová et al., 2014; Kráľová & Jampílek, 2021b, 2021c; Kráľová et al., 2021).

Mode of action of different types of NPs on insects was comprehensively reviewed by Benelli (2018). The most important effects of metal-based NPs and SiO_2 NPs are presented in Fig. 5. Insecticidal inorganic NPs can be used alone, in the form of nanocomposites or in nanoformulations with degradable polymers, ensuring their controlled release and can also serve as carriers for synthetic insecticides (Jampílek et al., 2020).

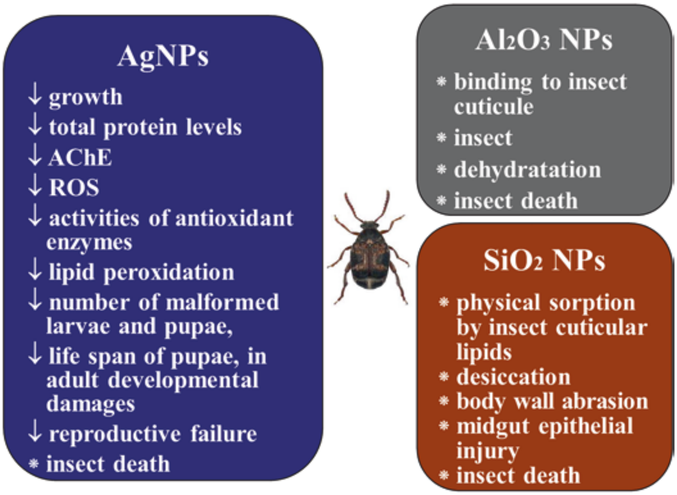

Fig. 5 Most important effects of metal-based and SiO_2 nanoparticles on insects

4.1 AgNPs

AgNPs fabricated using *Acacia catechu* extract showed phytopesticidal activity against agronomically important polyphagous insect pests *Spodoptera litura* and *Helicoverpa armigera* exceeding that of leaf ethanol extract of *A. catechu.* The LC_{50}/LC_{90} (in µg/mL) values related to the larval toxicity of phytosynthesized AgNPs against *S. litura* and *H. armigera* were 22.32/43.51 and 26/48.16, respectively, and those observed for *A. catechu* were 64.47/47/129.27 and 77.35/149.43, whereas the LC_{50}/LC_{90} (in µg/mL) values related to the pupal toxicity of phytosynthesized AgNPs against *S. litura* and *H. armigera* were 35.9/68.24 and 41.14/78.85, respectively, and those observed for *A. catechu* were 91.28/173.15 and 107.84/206.64 (Baranitharan et al., 2021). AgNPs phytofabricated using leaf extract of *Borago officinalis* as reducing and capping agent showed considerably higher toxicity against *Spodoptera littoralis* with LC_{50} and LC_{90} values of 0.33 mg/g and 0.33 mg/g, respectively, while the crude extract showed LC_{50}/LC_{90} values of 22.6/969.0 mg/g. Although both AgNPs and plant extract did not pronouncedly prolong the pupal period in both males and females compared to control treatment, elongation in larval period at treatment with AgNPs and leaf extract achieved 18.02 and 18.82 days, respectively, compared to 15.78 days observed in control treatment (Hazaa et al., 2021). By loading of λ-cyhalothrin onto the surface of AgNPs a nanocomposite was fabricated showing 37-fold higher effectiveness against second instar larvae of cotton leafworm under laboratory and field condition as well, suggesting that this NC can considerably reduce the required insecticide dose and thus, reduce not only development of the resistance against this pesticide but also reduce environmental pollution (Ahmed et al., 2019).

In *Bombyx mori* fed with AgNPs (100 or 400 mg/L) differentially expressed genes involved in the digestion process, various metabolic pathways, transmembrane transport, and energy synthesis were observed. Increasing AgNPs concentration resulted in downregulation of the expression of digestive enzymes damaging *B. mori* tissue, and inhibited activity of SOD. Increased ROS due to oxidative stress caused by AgNPs had adverse impact on the digestive system of the insect and a dose 400 mg/L AgNPs destroyed the basal lamina and the columnar cells (Chen et al., 2019a). A review paper dealing with the toxicity of AgNPs on insects, and especially on *Bombyx mori,* was presented by Pandiarajan and Krishnan (2017). Benelli (2018) reported that AgNPs can cause developmental damages and reproductive failure in insects by reducing acetylcholinesterase (ACHE) activity, modification of key insect genes as well as via negative influence on protein synthesis, and gonadotrophin release.

Spherical AgNPs of 17.33 nm phytosynthesized using leaf extract of *Annona reticulata* showed high repellency against *Sitophilus oryzae* and feeding deterrence (Malathi et al., 2019). AgNPs phytosynthesized using *Ziziphus jujuba* extract applied at a dose of 3000 ppm to whitefly infested eggplant hybrid grown in a greenhouse effectively decreased population density of *Bemisia tabaci* nymphs reaching 100, 90, and 80% effectiveness 7, 12, and 21 days after treatment (Al Shammari et al., 2018). The insecticidal effectiveness of biogenic AgNPs green synthesized using *Murraya koenigii* leaf extract (B-AgNPs) with standard AgNPs (S-AgNPs) against *Callosobruchus maculates* was tested using both types of AgNPs as priming agents of chickpea seeds at doses 25–30 and 65–70 ppm, respectively. Whereas at treatment with 65–70 ppm S-AgNPs 100% mortality of cowpea weevil was observed after one week, at exposure to B-AgNPs this period doubled to 2 weeks. On the other hand, two weeks after treatment with 65–70 ppm the minimum seed damage and minimum seed weight loss achieved at exposure to S-AgNPs was 41.63% and 1.24%, respectively, while at exposure to B-AgNPs the respective values were higher, 45% and 1.68%, respectively, suggesting improved entomological parameters of B-AgNPs compared to S-AgNPs (Abid et al., 2020). Feeding the second instar larvae of khapra beetle, *Trogoderma granarium* (Everts) (Coleoptera: *Dermestidae*) with grains treated with sublethal concentrations of AgNPs (22.5–66.2 nm) biosynthesized using alkaloids of *Peganum harmala* L. seeds resulted in pronounced reduction in the growth and development of insects accompanied with high ratio of malformed larvae and pupae, prolonged life span of pupae, and in considerable decline in adult emergence. Moreover, the biosynthesized AgNPs showed improved insecticidal activity compared to pure alkaloids (Almadiy et al., 2018).

Insecticidal effect of AgNPs mycosynthesized using entomopathogenic fungus *Beauveria bassiana* against mustard aphid (*Lipaphis erysimi* Kalt.) was described by Kamil et al. (2017). The LC_{50} values of AgNPs and Ag-Zn NPs, which were tested against the oleander aphid, *Aphis nerii* Boyer de Fonscolombe, were assessed as 424.67 and 539.46 mg/mL, respectively, and using a dose 700 mg/mL highest insect mortality was achieved (Rouhani et al., 2012).

4.2 Fe-Based NPs

Spherical shaped Fe^0NPs mycosynthesized using *Beauveria brongniartii* with sizes 0.41–0.80 μm showed LC_{50} values of 59 ppm against second instar of *S. litura* after 7 days and median survival time (LT_{50}) at exposure to 500 ppm Fe^0NPs of 2.93 days. Considerable decrease in feeding and growth parameters such as relative growth rate, relative consumption rate, and efficiency of conversion of ingested food along with reduced glutathione-*S*-transferase activities during treatment with Fe^0NPs and diminished activities of antioxidant enzymes in *S. litura* at the end of the experimental period was observed (Xu et al., 2020). Fe_2O_3 NPs (3.8–11.95 nm) phytosynthesized using *Trigonella foenum-graecum* leaf extract, insecticidal effectiveness of which was tested against *Tuta absoluta*, an important lepidopteron pest of tomato, when applied at a dose 100 μg/mL showed 50% mortality at 48 h and 72% mortality at 96 h and respective LC_{50} and LC_{90} values were 147.32 and 198.0 μL/mL, respectively, suggesting strong insecticidal activity of Fe_2O_3 NPs against *T. absoluta* pest (Ramkumar et al., 2020).

Insecticidal activity of biogenic FeS NPs (40 nm) prepared using *Artemisia herba-alba* leaves against the early and late nymphal instars of green peach aphid was reflected in LC_{50} values of 251 and 302 ppm, respectively, and these NPs considerably affected insect longevity and fecundity for three generations as well (Asoufi et al., 2018a, 2018b).

4.3 Cu-Based NPs

Ammar and Abd-ElAzeem (2021) mycosynthesized CuNPs and gelatin-CuNPs using fungal filtrates of *Aspergillus wentii*, *Aspergillus mottae*, and *Penecillium expansum*, which showed powerful activity against spiny bollworm, *Earias insulana*, causing immense damages in cotton crop. Gelatin-CuNPs showed smaller size and those biosynthesized using *A. wentii* caused highest larval and pupal mortality reflected in the lowest values of LC_{50} and LC_{90}, respectively, and they were most efficient also in reduction of the percentage of hatchability and egg numbers. Biogenic CuNPs synthesized using cell-free culture extract of Cu-resistant bacteria *Pseudomonas fluorescens* MAL2 with mean size of 48.07 nm and zeta potential of −26.00 mV displayed toxicity against the stored grain pest (*Tribolium castaneum*) with LC_{50} value of 37 ppm after 5 days of treatment (El-Saadony et al., 2020). Cu-NPs phytosynthesized using aqueous leaf extract of *Prosopis juliflora* (33.8 nm; zeta potential of −69.7 mV) and *Pluchea sericea* (68.10 nm; zeta potential of −53.9 mV) showed pronounced toxicity to *Phenacoccus solenopsis* Tinsley (Hemiptera: *Pseudococcidae*) after 96 hours, achieving mortality rates of *P. solenopsis* of 20 and 14% as well as reduction of cell viability by 38 and 30% at treatment with Cu-NPs phytosynthesized using *P. juliflora* and *P. sericea,* respectively (Leon-Jimenez et al., 2019). Insecticidal activity of phytosynthesized CuO NPs against *Myzus persicae* Sulzer (Homoptera: *Aphididae*) was reported by Ghidan et al. (2018). Spherical bimetallic Cu/ZnNPs (74.33–59.46 nm) phytosynthesized using aqueous leaf extract of *P. juliflora* applied at a dose 100 ppm caused >30% mortality of cotton mealybug, *Phenacoccus solenopsis* (Hemiptera: *Pseudococcidae*) at 96 h after treatment, while at exposure to *P. juliflora* extract and Cu/Zn solution the observed insect mortality was negligible. Exposure to biogenic AgNPs also considerably reduced the cell viability in insects (Mendez-Trujillo et al., 2019).

4.4 ZnO NPs

Investigation of the impact of nonlethal concentration of ZnO NPs (10–30 nm) on the larval stages of *S. littoralis* applied to insects via feeding of 10 mg/mL ZnO NPs dipped castor leaves for 6 days showed that ZnO NPs ingestion interfered with the digestive and immunological physiology as well as the development of *S. littoralis* (Ibrahim & Ali, 2018). Lethal concentrations LC_{50} and LC_{90} of ZnO NPs on *Galleria* *mellonella* L. 1758 (Lepidoptera: *Pyralidae*) larvae after 24 h treatment estimated by force feeding method were 6.03 μg/10 μL and 12.86 μg/10 μL, respectively, and the NPs did not significantly affect the total hemocytes counts at doses $<LC_{50}$ value after 24 h treatment. On the other hand, at exposure of larvae to 5 μg/10 μL, 10.01% dead cells were observed compared to 3.03% recorded in the control group (Eskin et al., 2019).

ZnO NPs phytosynthesized using extract of brown macroalga *Sargassum wightii* Greville ex J. Agardh showed insecticidal activity against *Helicoverpa armigera* Hubner with LC_{50} ranging from 12.278 (larva I) to 20.798 ppm (pupa), whereby greatly reduced longevity and fecundity as well as food consumption of the insects was observed (Murugan et al., 2018). *Bacillus thuringiensis*-coated ZnO NPs (20 nm; zeta potential of −12.7 mV) was found to reduce the fecundity (eggs laid) and hatchability of *Callosobruchus maculates* and decrease mid-gut α-amylase, cysteine protease, α-glucosidase, and glutathione *S*-transferase (GST) activities in treated insects; 100% mortality of the insect was achieved using a dose of 25 μg/mL, while the respective LC_{50} value was 10.71 μg/mL (Malaikozhundan et al., 2017). Similar results were obtained at exposure of *C. maculates* to ZnO NPs (21.3 nm; zeta potential of −12.45 mV) phytosynthesized using *Pongamia pinnata* leaf extract, which pronouncedly delayed the larval, pupal, and total development period (Malaikozhundan & Vinodhini, 2018).

Based on evaluation of entomotoxic efficacy of ZnO NPs, Al_2O_3 NPs, and TiO_2 NPs on *Sitophilus oryzae*, Al_2O_3 NPs were found to be the most efficient insecticide causing 90% mortality of *S. oryzae* after 4 days using a dose of 1 g/kg, whereas the same effect was observed with a dose of 2 g/kg of ZnO NPs or TiO_2 NPs after 14 days. On the other hand, ZnO NPs or TiO_2 NPs show also antimicrobial activity and thus, can ensure protection against microbial infections, whereas Al_2O_3 NPs are phytotoxic, what limits their application in agriculture (Das et al., 2019).

The fourth instar larvae of *S. litura* fed with leaves, which were impregnated with a nanocomposite of ZnO NPs and thiamethoxam with mean particle size of 30 nm at doses 10–90 mg/L, showed increased larval mortality, malformation in pupae and adults, overdue emergence, and reduced fecundity and fertility compared to control. At higher doses strong reduction in SOD and GST activity by 72.42 and 33.82%, respectively, along with increased levels of thiobarbituric acid reactive substances (TBARS) was observed compared to the control, suggesting that ZnO NPs generated oxidative stress in larvae (Jameel et al., 2020). Exposure of *Eisenia andrei* for 28 days period to ZnO NPs and chlorpyrifos (CPF) in natural soil resulted in considerable reduction of fecundity and fertility with EC_{50} values of 278 and 179 mg Zn/kg for ZnO NPs, and of 50.75 and 38.24 mg/kg for CPF, respectively. However, when *E. andrei* was exposed to the binary mixture, impact on fertility was stronger than that of ZnO NPs and CPF applied alone and caused fertility inhibition close 100%, regardless of the ZnO NPs and CPF concentrations in the mixture (Garcia-Gomez et al., 2019).

4.5 NiO NPs

NiO NPs biosynthesized using aqueous *Rauvolfia serpentine* leaf extract showing foamy interconnected particles with a wide distribution of irregular voids in their porous structures were tested against *Callosobruchus maculatus*. Using *Vigna mungo* L. seeds treated with 5–40 ppm NiO NPs it was found that the fecundity of insects reared on these seeds decreased with increasing NiO NPs in a dose-dependent manner and the lowest fecundity, highest duration of immature stages, and lowest adult emergence were observed in insects reared on seeds treated with 40 ppm NiO NPs. On the other hand, the longevity of both males and females reared on seeds treated with NiO NPs did not differ pronouncedly from insects reared on control seeds. On the other hand, germination of NiO NPs-treated black gram seeds slightly decreased with increasing NiO NPs concentration (Rahman et al., 2021). NiO NPs (24.49 ± 3.88 nm) applied at sublethal dose of 0.03 mg/g caused DNA damage and ovarian ultrastructural lesions induced in *Blaps polycresta* (Coleoptera: *Tenebrionidae*) reflected in considerable higher frequency of micronucleus formation and pronounced increase in the tail length of comets compared to control. Moreover, exposure to NiO NPs resulted in strong increase in chromatin condensation of the ovarian nurse and follicular cells, and accumulation of lysosomes and endo-lysosomes in cytoplasm was observed suggesting their genotoxic potential (Kheirallah et al., 2021).

4.6 TiNPs and TiO_2 NPs

TiNPs biosynthesized using banana peels extract with mean diameter of 88.45 nm exhibited strong insecticidal activity against *Musca domestica* and caused high mortality percentage of three larval stages of house fly, whereby the highest mortality was observed for first stage and the lowest one in third larval stage (Hameed et al., 2019). Protection of wool carpets and other fabric made proteinaceous fibers against *Anthrenocerus australis* and *Tineola bisselliella* by TiO_2 NPs was evaluated and it was found that it was more difficult to reduce the feeding of *T. bisselliella* on carpet, than on fabric (Sunderland & McNeil, 2017). Feeding with TiO_2 NPs stimulated 20-hydroxyecdysone biosynthesis, shortened developmental progression, and reduced duration of molting in *Bombyx mori* (Li et al., 2014a). On the other hand, several researchers described beneficial impact of TiO_2 NPs on body size and weight of *B. mori*, attenuation of oxidative stress and phoxim-induced midgut injury in silkworm and increasing insect tolerance to abiotic stress (Wang et al., 2015; Li et al., 2016, 2018; Shi et al., 2017). The ectopic exposure to 1 mg/cm^2 TiO_2 NPs and 0.5 mg/cm^2 Al_2O_3 NPs did not induce lethal toxicity in *Oncopeltus fasciatus* and did not modify any of the reproductive parameters. However, TiO_2 NPs and Al_2O_3 NPs produced an increase in nymphal life span. In the parental generation TiO_2 NPs increased protein content, whereas Al_2O_3 NPs decreased it. As a consequence of parental exposure in the filial generation, trans-generational effects of both NP types were observed (Lopez-Munoz et al., 2019).

4.7 Other Metal-Based NPs

Ingestion of AuNPs (15 and 30 nm)-containing food (87.44 μg/g) reduced ootheca viability of *Blattella germanica* females and the number of hatched nymphs by 32.8% compared to control; reduction of the number of *B. germanica* nymphs that molted to second and third instars by 35.8% as well as of the life span at exposure to AuNPs was observed as well (Small et al., 2016). Green synthesized $Mg(OH)_2$ NPs were reported as more efficient insecticidal agents against *Myzus persicae* Sulzer (Homoptera: *Aphididae*) than CuO NPs or ZnO NPs (Ghidan et al., 2018). Evaluation of the insecticidal activity of nanostructured Al_2O_3 on *Sitophilus oryzae* (L.) (Coleoptera: *Curculionidae*) showed that treatment with 250 and 500 ppm Al_2O_3 dust caused higher morality of insects than treatment with DiatomitD®, and Protect-It® (commercial diatomaceous earth), along with considerable reduction of grain weight loss and frass production in wheat infested by *S. oryzae* (Lopez-Garcia et al., 2018). Insecticidal impact of Al_2O_3 NPs against *Acanthoscelides obtectus* (Say) was described by Lazarevic et al. (2018).

Pd NPs (16–73 nm) green synthesized using aqueous extract of *Lagenaria siceraria* peel were reported to exhibit pronounced insecticidal activity against *Sitophilus oryzae* (Kalpana & Rajeswari, 2018). MoS_2 NPs showed insecticidal activity against Asian weaver ant, *Oecophylla smaragdina*, showing LC_{50} value of 50 μg/mL. Moreover, ants fed with MoS_2 NPs showed altered grooming behavior, strong reduction in hemocyte count, and higher ROS level compared to control. Thus, exposure to MoS_2 NPs resulted in enhanced oxidative stress reflected in increased lipid peroxidation and SOD activity, whereas activities of CAT and GST and GSH level showed a decrease, and the transcript levels of SOD, CAT, and GST were upregulated (Sheeja et al., 2020). In green peach aphids (*Myzus persicae*) fed with leaves of *Nicandra physaloides* (L.) Gaertn. (*Solanaceae*), which were previously sprayed with aqueous suspension of CeO_2 NPs (1–1000 mg Ce/L), Ce was detected in the oral cavity and digestive system, although the NPs did not reduce survival and fecundity of aphids (Marucci et al., 2019).

4.8 SiNPs and SiO_2 NPs

Encapsulation of sea fennel (*Crithmum maritimum*) seed essential oil in SiO_2 NPs showed considerable toxicity against larvae and pupae of cotton leafworm *S. litura* with LC_{50} values ranging from 24.610 (I instar larvae) to 64.546 μL/L (pupa) and reduced adult longevity and fecundity (Suresh et al., 2020). The insecticidal effect of SiO_2 NPs against *Tenebrio molitor* larvae was reported by Rankic et al. (2019).

SiNPs of 20 and 100 nm functionalized with (3-aminopropyl)triethoxysilane, suitable to be taken up by plants via roots as well as leaf surfaces, were conjugated with soybean trypsin inhibitor (STI). Loading of 0.4 mg of STI per 0.8 mg of NPs was found to be optimal and exposure to 25 °C or pH 8.0 contributed to STI release. The STI-SiO_2 NPs were able to inhibit bovine trypsin by 80% and *Helicoverpa armigera* gut proteinase (HGP) activity by 50%; and their ingestion by second instar *H. armigera* larvae (whether incorporated in artificial diet or leaves) resulted in considerable growth retardation. Moreover, in choice assays the insect larvae circumvent leaf disks treated with these NPs (Bapat et al., 2020). Nanoenzyme conjugate of SiO_2 NPs surface-modified by 3-aminopropyltriethoxysilane with chitinase produced by *Serratia marcescens* SU05 showed effective insecticidal activity against armyworm *S. litura*. Moreover, when it was loaded with plant extracts showing insecticidal activity (*Azadirachta indica, Adhatoda vasica, Leucas aspera,* and *Curcuma longa*) synergistic insecticidal effect resulting in high mortality rates of third and fourth instars larvae of *S. litura* was observed. In addition, toxicity lethal study against brine shrimp (*Artemia salina*) showed that the median lethal concentration (LD_{50}) estimated for nanoenzyme conjugate was by ca. 40% lower than that for SiO_2 NPs (Narendrakumar & Namasivayam, 2021).

Caceres et al. (2019) in a review paper overviewed the findings related to the potential of SiO_2 NPs used in pest insect management for delivery of bioactive compounds, improvement of release control as well their toxicity and mode of action as insecticide along with toxic impact of SiO_2 NPs on non-target organisms and environment.

Avermectin-loaded starch functionalized with biodegradable disulfide-bond-bridged mesoporous SiO_2 NPs with loading capacity of 9.3% effectively protected avermectin from photodegradation and premature release and showed redox and α-amylase dual stimuli-responsive behavior. After decomposition of the coated starch and disulfide-bridged structure of NPs, avermectin can be released on demand when NPs were metabolized by GSH and α-amylase in insects. These avermectin-loaded NPs were able to control *Plutella xylostella* larvae for longer period than avermectin emulsifiable concentrate (Liang et al., 2020). Nanocapsules showing a size of 800 nm encapsulating λ-cyhalothrin with 31% (w/w) loading efficiency, which were fabricated using SiO_2 covalently bonded with dopamine, showed sustainable release properties and exhibited pronouncedly improved insecticidal activity compared to emulsifiable concentrate of the synthetic insecticide along with considerably reduced genotoxicity to non-target organisms (Zhang et al., 2019). Abamectin (Aba)-loaded mesoporous SiO_2 NPs showing spherical shape, rough surface and loading efficiency of 44.8% showed controlled-release properties and protected Aba, from photodegradation showed superb insecticidal activity against *Plutella xylostella* larvae and maintained it until the 15th day causing 70% mortality of the target insect (Feng et al., 2020).

Also in another experiment, using Aba-loaded mesoporous SiO_2 NPs with sizes 142–712 nm depending on the used hexadecyl-trimethylammonium bromide (CTAB) concentration, and Aba loading of 46.3%, Aba insecticide was protected from the damage caused by natural light and at alkaline conditions its release was stimulated due to destruction of mesoporous structures. Following exposure of third instar larvae of *Plutella xylostella* to this nanoformulation the survival rate at day 15 was 30% compared to that of Abamectin EW, which achieved 93.3%. The nanoformulation showed sustained Aba release with prolonged impact on third instar larvae of *P. xylostella* and exhibited lower cytotoxicity than traditional formulation (Feng et al., 2021). The insecticidal activity of mesoporous SiO_2 NPs, which were functionalized with octadecyltrimethoxysilane loaded with imidacloprid (IMI), showed diameters of ca. 100 nm and were coated with a 6 nm thin paraffin wax outer layer. They showed sustained release property and considerable increase of insecticidal activity with temperature (LC_{50} values of 13.66 ppm and 6.20 ppm at 25 and 40 °C, respectively), suggesting that this nanoformulation could be successfully applied in high-temperature areas (Yao et al., 2021). A temperature-responsive release formulation consisting of hollow mesoporous SiO_2 creating the core and thermoresponsive copolymer, poly(*N*-isopropylacrylamide-co-methacrylic acid) used as the outer shell, which encapsulated positive temperature coefficient insecticide, thiamethoxam, was able to protect its degradation under UV irradiation, ensured good adhesion to rice leaves, exhibited temperature-responsive release and insecticidal activity against *Nilaparvata lugens* (Stal) (Hemiptera: *Delphacidae*) for 14 days, whereby the mortality of insects correlated with temperature (Gao et al., 2020).

Carbon dots-embedded fluorescent mesoporous SiO_2 NPs, which were loaded with indoxacarb (loading content of 24%) exhibited pH-sensitive release of insecticide and higher insecticidal activity against *P. xylostella* than technical indoxacarb applied at the same doses, inhibited the activities of detoxification enzymes of *P. xylostella* such as GST, carboxylesterase, and P450 and were able to reach the midgut of *P. xylostella*. Higher mortality of *P. xylostella* observed under exposure to these NPs along with diminished activities of enzymes in treated *P. xylostella* suggested that this nanoformulation could have potential to be applied in insecticide resistance management (Bilal et al., 2020).

4.9 Zeolites

Encapsulation of spores of *Metarhizium anisopliae*, a fungus able to infect more than 200 insect pests, with zeolite NPs coating agent resulted in 92.5% mortality rate of third instar of *Crocidolomia pavonana* larvae and lethal time up to 1.075 days compared to 27.5% and 2.235 days observed when the spores were applied alone. By encapsulation of *M. anisopliae* spores with magnesium silicate NPs the mortality increased to 85.0% and the larval lethal time achieved up to 1.150 days. Hence, both inorganic coatings can be used for encapsulation of *M. anisopliae* spores to fabricate a nanoscale bioinsecticide for the control of *C. pavonana* larvae (Ilhami et al., 2020).

5 Plant Protection by Inorganic Nanosized Bactericides, Fungicides, and Antiviral Agents

Besides weeds, i.e., unwanted vegetation and harmful insects having adverse impact on agricultural production, there are plant diseases caused by viruses, bacteria, fungi, and nematodes which cost the global economy ca. $220 billion (FAO, 2019) and significantly contribute to yield loss of crops (e.g., Blank et al., 2016; Adhikari et al., 2017; FAO, 2019; Kolomiiets et al., 2019; Perveen et al., 2020), whereby for approximately 50% of the emerging plant diseases viruses are responsible (Bernardo et al., 2018). Therefore, developing effective management strategies to cope with devastating plant diseases is inevitable (FAO, 2020), whereby cooperation with researchers designing effective environment-friendly pesticides is necessary. Only such an approach can ensure production of sufficient healthy food for increasingly growing human population.

Plant diseases are mostly caused by fungi, viruses, bacteria, and nematodes (Agrios, 2005). For plant disease outbreaks the presence of a virulent pathogen, a susceptible host, and a disease-friendly conductive environment and their interactions are necessary (Francl, 2001; Agrios, 2005; Islam, 2018) and disease onset and intensity also depend on the duration of the above factors on plants (Francl, 2001; Slippers, 2020). High humidity or free moisture on the leaf and moderate temperatures facilitate disease outbreak (Chen et al., 2014; Garrett et al., 2016; Hoffmeister et al., 2020), whereby susceptible plant cultivars with missing resistance genes are particularly vulnerable (Ekroth et al., 2019; Gibson & Nguyen, 2021).

Nanosized metal/metalloids can be used as powerful weapons against plant devastating diseases caused by viruses, bacteria, and fungi, because in addition to killing these pathogens, they have a beneficial effect on plant growth and performance (Abd-Elsalam & Prasad, 2018; Elmer & White, 2018; Rai et al., 2018; Fu et al., 2020; Rajwade et al., 2020; Varympopi et al., 2020; Zhao et al., 2020b; Alghuthaymi et al., 2021; Farooq et al., 2021). Adverse effects of inorganic NPs on bacterial and fungal phytopathogens along with their beneficial impact on plants are shown in Fig. 6.

At application of nanoscale metal/metalloid pesticides the NPs situated on the surface of phytopathogens generate ROS causing oxidative stress and exhibit nanospecific toxicity resulting in mechanical penetration and destruction of cell wall membrane of the pathogen and causing apoptosis of pathogen cells (Elmer & White, 2018; Ali et al., 2020; Chen et al., 2020).

Considering the ongoing climate change manifested as great changes in temperature, prolonged periods of severe drought, rainstorms, flooding, and enhanced frequency of extreme events, it is evident that not only geographic distribution of crops and their associated pathogens will be affected but also changes in pathogen incidence and severity can be expected, whereby the extension of phytopathogens due to insect migration and increasing world trade in goods will occur as well (Burdon & Zhan, 2020; Jindo et al., 2021). Nanoparticles provide a valuable tool to restrain phytopathogen spreading and suppress plant diseases, whereby they also can

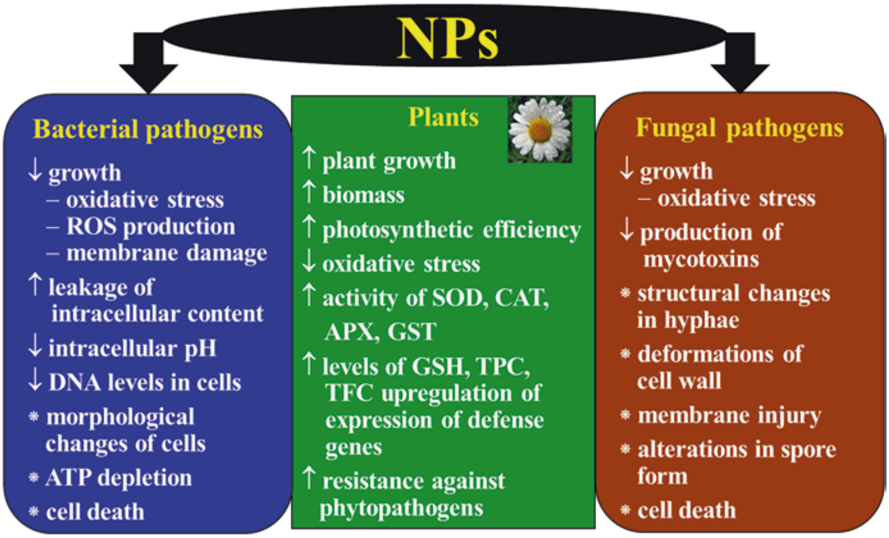

Fig. 6 Adverse effects of inorganic nanoparticles on bacterial and fungal phytopathogens along with their beneficial impact on plants

pronouncedly reduce post-harvest losses, and enhance plant resistance against phytopathogens, which is important for securing sufficient food for world human population, which according to United Nations report is expected to reach 8.6 billion in 2030, 9.8 billion in 2050, and 11.2 billion in 2100 (UN, 2019; Santo Pereira et al., 2021; Shahzad et al., 2021).

5.1 Antiviral Nanoparticles for Plant Protection

Phytoviruses are particularly destructive plant pathogens causing virus diseases in crops, which cause enormous qualitative and/or quantitative losses of crops yield. Many of them can pass from one generation to the next via seeds, whereby abiotic and biotic stresses affect the infection cycle. Therefore, strategies focused on the elimination of virus sources and avoiding spatiotemporal coincidences between viruses, vectors, and crops could be designed (Navas-Castillo & Fiallo-Olivé, 2017; Farooq et al., 2021). The epidemiology of plant virus diseases was discussed by Jeger (2020), while Jones and Naidu (2019) focused attention on global dimensions of plant virus diseases and future perspectives, while global plant virus diseases threatening the 6 most important staple food crops were analyzed by Jones (2021).

Green synthesized AgNPs sprayed on leaves of *Nicotiana glutinosa* 24 h before inoculation with *Tobacco mosaic virus* (TMV) pronouncedly inhibited the virus caused lesions and effectively reduced TMV growth also if they were applied 24 h after inoculation of plants with TMV (Ahsan, 2020). Pre-treatment of tomato plants by spraying with 50 ppm AgNPs, which were subsequently inoculated with *Tomato mosaic virus* (ToMV) and *Potato virus Y* (PVY) greatly reduced disease severity and concentration of both viruses, induced a systemic acquired resistance against these viruses and increased the contents of assimilation pigments and total soluble protein as well as antioxidant enzymes in infected plants (El-Dougdoug et al., 2018). Powerful reduction of *Tomato spotted wilt virus* (TSWV) infection on *Chenopodium amaranticolor* and potato plants by AgNPs applied 24 h after virus inoculation was reported by Shafie et al. (2018) and excellent antiviral activity against *Bean yellow mosaic virus* (BYMV) was also exhibited by biogenic AgNPs (Elbeshehy et al., 2015).

Systemic resistance of cucumber plants against *Cucumber mosaic virus* (CMV) was developed using NiO nanostructures showing antiviral activity, which increased expression of regulatory and defense-related genes in salicylic acid (SA) and jasmonic acid (JA)/ethylene signaling pathways (Derbalaha & Elsharkawy, 2019), and foliar treatment of *Nicotiana benthamiana* plants with Fe_3O_4 NPs resulted in improved plant growth characteristics and plant resistance against TMV as well (Cai et al., 2020). Inhibition of proliferation of *Turnip mosaic virus* on *N. benthamiana* plants by Fe_2O_3 NPs and TiO_2 NPs was reported by Hao et al. (2018). Spraying the mixture of 150 μm TiO_2 nanostructures onto faba bean plants infected with *Broad bean strain virus* (BBSV) reduced the disease severity and induced considerable expression of regulatory and defense gene involved in the SA signaling pathway; foliar treatment was found to be more effective than soil drenching (Elsharkawy & Derbalah, 2019). On the other hand, chitosan (CS)-TiO_2 nanobiocomposites effectively reduced disease severity in faba bean plants infected with *Bean yellow mosaic virus* (BYMV) and showed favorable impact on growth, photosynthesis, and levels of antioxidants resulting in reduced oxidative stress and electrolyte leakage in treated plants (Sofy et al., 2020).

Biogenic ZnO NPs applied as pre-treatment or 24 h after inoculation of tomato plants with TMV markedly reduced viral accumulation level and disease severity; treatment with 100 μg/mL ZnO NPs induced systemic acquired resistance in plants and improved plant growth characteristics (Abdelkhalek & Al-Askar, 2020). Antiviral impact against CMV in eggplant along with increasing growth and yield characteristics showed ZnO NPs (El-Sawy et al. (2017). Daily spraying of tobacco leaves with ZnO NPs and SiO_2 NPs for 12 days considerably inhibited TMV replication by activation of the plant defense and growth responses and showed beneficial impact on growth characteristics of treated plants (Cai et al., 2019). Inoculation of CMV-infected tobacco and cucumber plants with *Phoma* sp. GS8–3 and treatment with SiO_2 NPs pronouncedly improved growth characteristics of plants not only in pot experiments but also in field conditions, and upregulation of defense-related genes expression contributed to the resistance against CMV (Elsharkawy et al., 2020b). SiO_2 nanopowder applied to cucumber plants induced systemic resistance against *Papaya ring spot virus* (PRSV) and its vector *Myzus persicae* and expression of most various pathogen-related genes contributing to ameliorated defense mechanism against PRSV infection (Elsharkawy & Mousa, 2015).

5.2 Antibacterial Nanoparticles for Plant Protection

Metal and metalloid-based NPs exhibit effective antimicrobial activity due to destruction of bacterial cell integrity via direct contact of NPs with bacterial cell wall, release of antimicrobial metal ions from NPs, generation of excess ROS, resulting in damage of cellular membranes resulting in leakage of intracellular content, ATP depletion, decline of intracellular pH and DNA levels in cells and can downregulate genes involved in pathogenesis resulting ultimately in bacterial cell death (Vanti et al., 2020) (Fig. 6). Using metal-based NPs development of bacteria resistance observed against synthetic antimicrobials such as antibiotics can be overcome (Nan-Yao et al., 2019; Ruddaraju et al., 2020; Amaro et al., 2021). Therefore, metal-based NPs are frequently used as antimicrobial agents not only in agriculture but also in medicine (e.g., Jampílek & Kráľová, 2017c; Boroumand et al., 2018; Crane, 2020; Teirumnieks et al., 2021), whereby biogenic NPs fabricated using plant extracts or fungal filtrates as reducing and capping agents are preferred (e.g., Hossain et al., 2019; Gogoi et al., 2020; Vanti et al., 2020; Ahmed et al., 2021). For foliar application of metal NPs their improved adherence to the leaves preventing runoff loss and rolling down of the NPs can be achieved using their hybrids with biopolymers (Alonso-Diaz et al., 2019), and improvement of antibacterial activity against phytopathogens can be achieved, for example, using their nanocomposites with chitosan showing superb antimicrobial activity (Shahryari et al., 2020). However, treatment of plants infected with bacterial or fungal phytopathogens with metal and metalloid-based NPs results not only in strong decline of disease severity but had beneficial impact on plant performance reflected in improved plant growth, increased biomass production, higher photosynthetic efficiency, suppression of oxidative stress along with increasing activities of antioxidant enzymes and enhanced levels of non-enzymatic antioxidants as well as upregulation of expression of defense genes resulting in the development of resistance against phytopathogens (Egusa et al., 2015; Alonso-Diaz et al., 2019; Cumplido-Najera et al., 2019; Quiterio-Gutierrez et al., 2019; Ahmed et al., 2020; Elsharkawy et al., 2020a, 2020b; Li et al., 2020b; Sofy et al., 2020; Tauseef et al., 2021) (Fig.6).

Green synthesized AgNPs were reported to show effective antibacterial activity against numerous phytopathogens such as *Pseudomonas syringae* pv. *syringae* (Khan et al., 2019; Gogoi et al., 2020), *Xanthomonas axonopodis* pv. *punicae* (Vanti et al., 2020), *Clavibacter michiganensis* subsp. *michiganensis (*Noshad et al., 2019a, 2019b), *Xanthomonas campestris* pv. *campestris* (Dzimitrowicz et al., 2018), *Xanthomonas oryzae*, *X. campestris* pv. *vesicatoria*, *Pectobacterium carotovorum*, and *Ralstonia solanacearum* (Javed et al., 2020).

Strong antibacterial activity of CuO NPs was reported against *C. michiganensis* subsp. *sepedonicus, R. solanacearum, Dickeya solani* (El-Batal et al., 2020), *E. amylovora* (Varympopi et al., 2020), *Xanthomonas oryzae* pv. *oryzae* (Li et al., 2020b) and *R. solanacearum* (Chen et al., 2019b), while hybrid Cu/Zn (50:50%) NPs showed antibacterial activity against *X. perforans* (Carvalho et al., 2019) and

CS-Cu NCs applied at a dose of 100 μg/mL killed the Cu-tolerant *X. perforans* strain within 1 h of exposure (Strayer-Scherer et al., 2018).

Biofabricated Fe_2O_3 NPs (56–350 nm) inhibited the growth of *R. solanacearum* on infected tomato plants (Alam et al., 2019), while MgO NPs showed antimicrobial activity against *X.* pv. *oryzae* (Abdallah et al., 2019), *Acidovorax oryzae* (Ahmed et al., 2021), *R. solanacearum* (Cai et al., 2018b), and even induced systemic resistance in tomato plants against *R. solanacearum* (Imada et al., 2016).

ZnO NPs exhibited strong antibacterial activity against *P. syringae* pv. *tomato* DC3000 and induced systemic resistance in treated tomato plants via enhanced expression of the defense-related gene (Elsharkawy et al., 2020a). Foliarly applied ZnO NPs on *Daucus carota* plants infected by *P. carotovorum* and *X. campestris* pv. *carotae* was found to decrease disease severity (Siddiqui et al., 2019), while biosynthesized ZnO NPs showed antibacterial against *C. michiganensis* subsp. *michiganensis*, *Pseudomonas cichorii*, *P. syringae* pv. *phaseolicola*, and *Pseudomonas* subsp. *carotovorum* (Sahin et al., 2021). Kalia et al. (2020) in their review paper focused on Zn-based nanomaterials used for diagnosis and management of plant diseases.

TiO_2 NPs as affective antimicrobial agent against *Allorhizobium vitis* were reported by Korosi et al. (2020). Treatment with TiO_2 NPs caused morphological changes of *Dickeya dadantii* and was able to disintegrate the cell envelopes after 4 h exposure in nutrient broth resulting in cell death (Hossain et al., 2019), while bactericidal activity of TiO_2 NPs against *Agrobacterium tumefaciens* under UV irradiation was described by Aminedi et al. (2013).

Antibacterial nanocomposites of SeNPs encapsulated in biopolymer matrices against *Clavibacter michiganensis* subsp. *sepedonicus* (Nozhkina et al., 2019; Perfileva et al., 2020) was reported as well.

Volatile biocides such as essential oil or their constituents encapsulated into SiO_2 NPs can be used for effective prevention of microbial diseases in crops as well (Cadena et al., 2018a, 2018b), and melittin-conjugated SiO_2 NPs showed antibacterial activity against *A. tumefaciens* (Li et al., 2014b).

5.3 Antifungal Nanoparticles for Plant Protection

Utilization of nanobiotechnology in fungal diseases management is currently increasing (Alvarez et al., 2016), whereby metal and metalloid-based NPs and their nanocomposites are particularly suitable to be used as effective antifungal agents against fungal phytopathogens. In contrast to synthetic pesticides, extensive use of which often results in development of resistant fungal strains, the effectiveness of metal-based nanoparticulate fungicides is usually not affected. Metal-based NPs adhered to fungal cells after penetration into fungal cells induce oxidative stress by generating excess ROS, which results in damaged cell membranes and they also can cause structural changes in hyphae and alterations in spore form, which is reflected in strong growth decline or even in fungal cell death (Ali et al., 2015; Ammar et al., 2019; Chen et al., 2020; Lakshmeesha et al., 2020; Marathe et al., 2021) (Fig. 6). In addition, in toxigenic fungi they can suppress production of mycotoxins (e.g., El-Naggar et al., 2018; El-Naggar et al., 2018; Jampílek & Kráľová, 2020a, 2020b). Along with effective reduction of the severity of fungal diseases in infected plants, treatment with metal-based NPs exhibits beneficial impact on plants, similarly to that observed at treatment of plants infected with bacterial phytopathogen (Fig. 6).

AgNPs effectively controlled spore viability and growth rate of 8 major toxigenic *Fusarium* spp. with effective lethal doses (ED_{50}, ED_{90}, and ED_{100}) 1–>45 μg/mL (Tarazona et al., 2019), caused complete inhibition of *Phytophthora parasitica* and *P. capsici* at several developmental stages (Ali et al., 2015). Biogenic mycosynthesized AgNPs exhibited excellent fungicidal activity against *Cladosporium fulvum* (Elgorban et al., 2017), *Fusarium verticillioides* (Elamawi et al., 2018; Marathe et al., 2021), *Helminthosporium oryzae*, *Pyricularia grisea*, *Penicillium brevicompactum,* and *Fusarium moniliforme* (Elamawi et al., 2018), *Alternaria* sp. (Win et al., 2020; Mahawar et al., 2020a), and *Sclerotinia sclerotiorum* (Guilger-Casagrande et al., 2021). Exposure to 50, 75, and 100 ppm AgNPs was able to eliminate the mycotoxin deoxynivalenol to 34.44%, 34.60%, and 34.89%, respectively (El-Naggar et al., 2018), whereas treatment with AgNPs reduced ergosterol biosynthesis by *Fusarium verticillioides* (Marathe et al., 2021).

CuNPs were reported to show fungicidal activity against *F. oxysporum* and *Phytophthora capsici* (Ammar et al., 2019; Pham et al., 2019), *Colletotrichum capsici* (Iliger et al., 2021), and *Aspergillus niger* (Vanathi et al., 2016), while SeNPs and CuNPs were able to decrease the severity of *Alternaria solani* (Quiterio-Gutierrez et al., 2019).

ZnO NPs effectively inhibited *Colletotrichum* sp. (Mosquera-Sanchez et al., 2020). *Pyricularia grisea* and *Helminthosporium oryzae* (Kalboush et al., 2016), *Cladosporium cladosporioides* (Lakshmeesha et al., 2020; Suryadi et al., 2020), and *F. oxysporum* (Lakshmeesha et al., 2020). TiO_2 NPs applied at a dose 100 ppm decreased mycelial growth of *A. alternata* by 90% in vitro and decreased the severity of leaf blight disease of tomato more than SeNPs and AgNPs (El-Gazzar & Ismail, 2020). As effective antifungal agents against *Bipolaris sorokiniana* TiO_2 NPs (Satti et al., 2021) and AgNPs (Mishra et al., 2014) were reported. MgO NPs suppressed the growth and spore germination and impede sporangium development of *Phytophthora nicotianae* and *Thielaviopsis basicola* (Chen et al., 2020).

Mesoporous SiO_2 NPs (20 nm; pore sizes of ca. 3.0 nm), which were functionalized on the surface with decanethiol gatekeepers and loaded with salicylic acid, pronouncedly ameliorated pineapple resistance to *Phytophthora cinnamomi* (Lu et al., 2019).

It is important to note that the treatments with antifungal metal NPs resulted, for example, in the increase in Chl levels in infected plants (Kalboush et al., 2016; Mahawar et al., 2020a, 2020b) or improved quality and yield of infected plants (Satti et al., 2021).

6 Conclusion

Based on ongoing climate change and human population growth scenarios in the twenty-first century, one of the most important challenges is to ensure higher productivity of agricultural production while reducing the use of harmful chemicals that contaminate the environment. The use of nanotechnologies, which make it possible to achieve the same or even higher efficiencies than their bulk counterparts using lower doses of bioactive agents, can make a significant contribution to this. Unlike synthetic agrochemicals, metal- and metalloid-based nanoparticles used as fertilizers or to protect plants from insects and various other phytopathogens have the advantage not only in preventing the development of pest resistance, but also in favor of the development, growth, and increased resistance of crops to abiotic and biotic stresses, as well as higher production of valuable secondary metabolites that improve crop nutritional value. In addition, the application of nanoscale essential mineral formulations, such as Fe and Zn, can increase the levels of these micronutrients in crops and thus improve their nutritional quality, which provides public health benefits. On the other hand, minerals such as zeolites, montmorillonite, and nanoclays exhibiting 3-D microporous structures cannot only improve soil quality and ability to retain water but can also serve as macronutrient carriers in slow-release fertilizers. Therefore, the use of metal- and metalloid-based nanoparticles in agriculture can significantly contribute to the control of harmful insect populations, reduce the severity of plant diseases, and significantly improve plant performance resulting in higher crop yields. However, for the widespread implementation of predominantly green synthesized metal- and metalloid-based nanoparticles in agricultural practice, it is essential to design nanoformulations that show high stability, that can be easily applied by farmers, are safe for crops even in transgenerational exposure, are not harmful to non-target organisms and are also, if possible, cheaper than conventional synthetic agrochemicals. Therefore, it is desirable to focus the increased attention of researchers on providing field experiments with appropriate metal- and metalloid-based nanoformulations to verify their efficacy even under environmental conditions, which is a prerequisite for the widespread use of these nanoformulations in advanced agriculture.

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Inorganic Porous Nanoparticles as Pesticide or Nutrient Carriers

Vinicius Bueno and Subhasis Ghoshal

Abstract Nano-enabled agriculture has been gaining interest recently as a pathway to improve crop yield and protection while reducing fertilizer and pesticide application rates compared to traditional agricultural practices. Inorganic, porous nanoparticles can have a pivotal role in the successful deployment of nanotechnology. Inorganic porous nanoparticles can provide a structurally stable framework to encapsulate and transport active ingredients, such as pesticides and fertilizers. Herein, we provide a review of promising features that these porous nanocarriers possess that may be of interest in agriculture. For instance, porous nanocarriers can increase the apparent solubility and mobility of poorly soluble pesticides and control the release of these over time. Commonly studied inorganic nanomaterials include silica, iron oxide, zinc oxide, copper oxide, clays, and hydroxyapatites, each of which has its own attributes and characteristics that can be relevant to crop growth and protection in the field. This chapter also includes explanations of the uptake of these nanocarriers through roots and leaves, and their further translocation within the plants. The important role of particle physicochemical characteristics, e.g., zeta potential and size in uptake and translocation are reviewed along with emerging approaches for rational design of nanoparticles to provide them with stimuli-responsive characteristics that can be triggered by changes in pH, temperature, ionic strength, light, enzymes, and redox agents.

Keywords Inorganic nanocarriers · Nano-enabled agriculture · Nanopesticides · Nanofertilizers · Nanocarrier · Nanoencapsulation · Mesoporous silica nanoparticles

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1 Introduction

Inorganic porous nanoparticles (NPs) are versatile, because of their wide range of mechanical and physicochemical properties. They can be chemically stable over long periods of time and are promising candidates for nanocarriers for pesticide agriculture. As a nanocarrier, they can provide the matrix to carry the active ingredient (AI), which includes a vast spectrum of organic and inorganic molecules (Fernandez-Fernandez et al., 2011; Pérez-De-Luque & Rubiales, 2009), and/or they can be used as an AI itself. Several metallic NPs have been reported to have antimicrobial properties (Rai et al., 2009; Zhang & Chen, 2009; Richter et al., 2015), thus can act as a nanopesticide. Furthermore, some metals are essential micronutrients to plants, such as zinc (Zn) (Tarafdar et al., 2014), and therefore, the respective metallic NPs can be directly used as a nanofertilizer. Inorganic NPs are in general more easily manufactured with consistent properties when it comes to size distribution, shape, and batch-to-batch reproducibility, compared to organic NPs (Mostafa et al., 2021). Furthermore, inorganic NPs are currently easier to analytically track in plant matrices and are more chemically stable in the field with respect to temperature, photo- and biodegradation over time (Lino et al., 2018; Jesus & Grazu, 2012).

A wide range of inorganic porous nanomaterials have potential applications in agriculture, such as those composed of SiO_2 (Rastogi et al., 2019), Zn (Sabir et al., 2014), Fe (Shan et al., 2020), hydroxyapatite (Marchiol et al., 2019), Cu (Kasana et al., 2016), and clay (Manjunatha et al., 2016). These inorganic nanoparticles can be tailored to specific sizes (Lin & Haynes, 2009), porosity (Parra-Nieto et al., 2021), intraparticle pore sizes (Zhang et al., 2011), and functionalized with molecules to manipulate surface charge or functional groups (Mishra et al., 2014; Subbiah et al., 2010). Generally, surface modifications of nanocarriers are made to facilitate uptake and translocation, target the delivery, and to provide controlled stimuli-responsive capabilities to the NPs. Figure 1 summarizes the most commonly studied nanomaterials and their morphologies, potential active ingredients to be encapsulated, and application methods.

2 Nanoparticles as Active Ingredients and Carriers of Active Ingredients

Typically, metal oxide NPs (ZnO, Fe_2O_3, Fe_3O_4, CuO) and nHAP are themselves molecules of interest to be taken up by plants, because they are essential elements for plant development and nutrition. Thus, these NPs are nanocarriers delivering the essential nutrients in their structural matrix, and a different AI is embedded in the matrix. These NPs can be applied bare and as synthesized, without further modifications to the NP surface. This is generally the case when plants have dedicated internalization pathways for the elements delivered by the nanocarrier, e.g., Si, and thus no modifications are required to facilitate the internalization of the NPs.

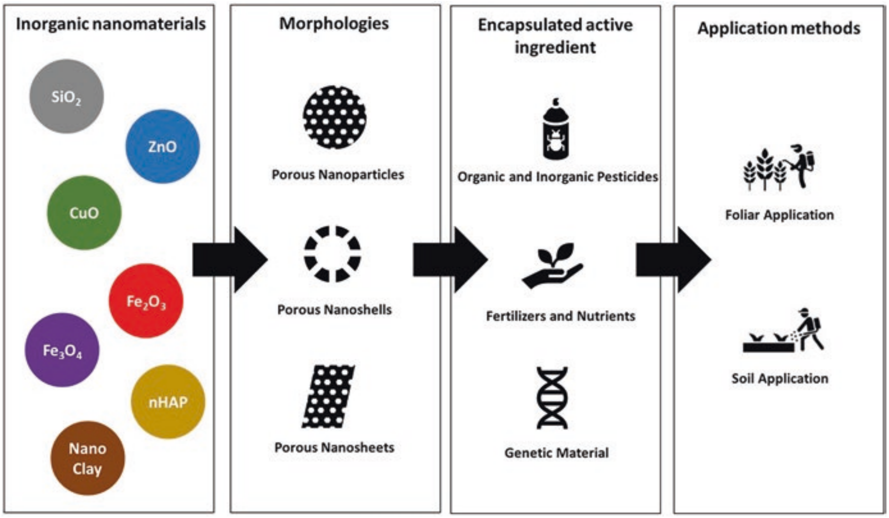

Fig. 1 Commonly studied nanomaterials, morphologies, encapsulated active ingredients, and application methods for nano-enabled agriculture

2.1 *Silica Nanoparticles*

The use of silica NPs has been proposed for nano-enabled agriculture, primarily for two reasons: (1) Si is considered a *quasi*-essential nutrient for plants (Epstein, 1972) and the use of SiO_2 NPs as a source of Si has been shown to result in beneficial effects on plant health (Luyckx et al., 2017; Abdel-Haliem et al., 2017; Abdelrahman et al., 2021; El-Shetehy et al., 2020). (2) Synthesis and functionalization of SiO_2 NPs of varied forms with a wide range of pore structures and particle characteristics are feasible. Currently, there are established procedures for synthesis of SiO_2 NPs of various structures, such as solid spherical nanoparticles (Stöber et al., 1968), mesoporous nanoparticles (Slowing et al., 2006), and porous hollow nanoparticles (Bueno & Ghoshal, 2020). Furthermore, certain characteristics can be controlled during synthesis, including particle size distribution (Fernandes et al., 2019; Pack et al., 2021), pore size (Nandiyanto et al., 2009; Ren et al., 2021), shell thickness (Tsou et al., 2014), and even functionalization of the surfaces with bioactive molecules (Wang et al., 2015b). Potential applications of SiO_2 NPs in agriculture include acting as nanocarriers for pesticides and fertilizers (Plohl et al., 2021; Gao et al., 2021) as well as the AI itself, delivering Si to plants (Attia & Elhawat, 2021).

Si is considered a *quasi*-essential nutrient, that is Si is not essential for plant development but it is beneficial to plants when present (Siddiqui et al., 2020). For this reason, Si also has dedicated transport pathways for uptake in plants. Si is generally internalized as $Si(OH)_4$ through aquaporin-like channels (Luyckx et al., 2017). Foliar application of SiO_2 NPs has been demonstrated to be beneficial for plant growth (Attia & Elhawat, 2021; Suriyaprabha et al., 2014). Porous hollow

SiO_2 NPs are promising candidates to carry a wide spectrum of organic and inorganic molecules. SiO_2 NP structure is highly malleable during the synthesis, as one can tune characteristics such as the particle size, the size of the pores, the overall porosity, and the presence and size of a hollow core. The facile synthesis of different SiO_2 NP structures and biocompatibility makes them exceptional candidates as nanocarriers. Although most research have been done on solid spherical nanoparticles first synthesized by Stöber et al. (1968), most agricultural applications involve the use of mesoporous nanoparticles, such as the MCM-41, and porous hollow SiO_2 NPs (PHSNs). MCM-41 is a popular choice for medical and agricultural applications because of the enhanced surface area providing the potential for the high-density loading of molecules of interest through sorption. The synthesis procedure is a modification of the Stöber method with the addition of a surfactant called cetrimonium bromide (CTAB), which provides a highly uniform distribution of pores etched in the SiO_2 matrix and an enhanced specific surface area that could reach over 1000 $m^2\ g^{-1}$ (Chen et al., 1993). Several studies have reported having encapsulated pesticides such as prochloraz (Zhao et al., 2018), abamectin (Feng et al., 2021), and herbicides in general (Shan et al., 2019) within mesoporous SiO_2 NPs for targeted delivery. PHSNs have a more complex structure because of the presence of a hollow core within a porous SiO_2 shell. This structure can be achieved either through hard templating using materials such as polystyrene (Vu et al., 2021) or soft-templating using surfactants (Bueno & Ghoshal, 2020; Bueno et al., 2022). While hard-templating methods require the functionalization of the hard template to allow for the anchoring of the soon-to-be nanoshell and the post-synthesis removal of the template by either calcination of solvent extraction, soft-templating methods involve the use of surfactants and/or oil phase as template, which could be part of the final nanoformulation or removed through means of heating or acid wash (Bueno & Ghoshal, 2020; Yang et al., 2021). The hollow core of PHSNs provides a cargo space for the high-density loading of biomolecules or even other nanoparticles. Bueno and Ghoshal (2020) used the hollow core as a nanoreactor to synthesize Fe NPs within the porous SiO_2 shell through the successive addition of Fe ions and sodium borohydride. Some studies reported the encapsulation of biomolecules, such as avermectin (Li et al., 2006), fipronil (Wibowo et al., 2014), and even DNA strands (Hai et al., 2018). The PHSN shell also provides physical protection to the cargo molecules and avoid premature degradation (Li et al., 2007).

2.2 *Hydroxyapatite Nanoparticles*

Hydroxyapatite (HAP) is one of the most commonly occurring forms of calcium phosphate in nature, with well-defined crystalline structures (Marchiol et al., 2019). Most P-based fertilizers in current use are derived from phosphoric acid, such as triple superphosphate and ammonium dihydrogen phosphate, which rapidly chelate with Al^{3+}, Fe^{2+}/Fe^{3+}, and Ca^{2+} in soil thus becoming unavailable for plants (Szameitat et al., 2021). Therefore, there is increasing interest in HAP as a fertilizer because it is a highly stable, naturally occurring material, which will not chelate with earth-abundant metal ions nor precipitate as easily as phosphoric acid-based fertilizers. Moreover, it is a naturally occurring compound in the environment instead of emerging contaminants from the transformation of phosphoric acid-based fertilizers, which carry in their commercial formulation, particularly triple superphosphate, a certain amount of heavy metals, such as, Cd, Cr, Pb, Hg, Ni, and V that are released into the environment once the phosphorous fertilizer is metabolized (Mortvedt, 1996; Molina et al., 2009). HAP is biocompatible, naturally porous, and can be found in bones and teeth of vertebrates, and for this reason, it has been the target of study for biomedical applications (Sadat-Shojai et al., 2013; Verma et al., 2013; Ansari et al., 2020). Due to the reduced size when compared to the bulk counterpart, nanosized HAP (nHAP) can be internalized through the roots and leaves. To date, although promising, few studies used nHAP as nanofertilizer to provide P to plants. However, Szameitat et al. (2021) recently reported the foliar and root application of nHAP in phosphorous deficient barley restored the plant metabolism and functionalities that were previously limited due to the lack of the element. These promising results may pave the way to more research on nHAP applications in nano-enabled agriculture in the near future.

Conventional phosphorous fertilizers, consisting mostly of soluble phosphates, are estimated to have an overall efficiency of 20% because of their high mobility in soil and susceptibility to being transported with runoff (Taşkin et al., 2018). In this context, nHAP can be a promising candidate to replace conventional phosphorous fertilizers due to its properties of slow but pH-dependent dissolution, and hindered mobility in soil when compared to soluble phosphates (Maghsoodi et al., 2020; Taşkin et al., 2018). Generally, nHAP surfaces are functionalized to maintain their colloidal stability in suspension, and enhance uptake, for instance with carboxymethyl cellulose (CMC) as reported by Liu and Lal (2014) and with urea as reported by Kottegoda et al. (2011).

2.3 Iron Oxide Nanoparticles

Fe is among the essential nutrients for plant health because it participates in several metabolic processes such as photosynthesis, nitrogen cycling, and biomolecules synthesis, as it is involved in the reaction mechanisms of the formation of chlorophyll, chloroplasts, and cytochromes (Tiwari et al., 2016). The lack of Fe in plant nutrition hinders plant chlorophyll production and respiration, thus leading to chlorosis (Jeyasubramanian et al., 2016). In fact, the impacts of Fe deficiency go beyond the agriculture, as over 25% of the human population suffer from anemia (Lopez et al., 2016), a condition directly correlated with the insufficient amount of Fe in the blood. Some studies have reported that increasing the amount of Fe in food crops, particularly rice, has a direct positive impact on human health (WHO, 2009; Meng et al., 2005). Current methods for Fe fertilization have very low efficiencies, because Fe rapidly complexes with organic matter and becomes biologically unavailable to plants and microorganisms (Lucena et al., 2010). The nano-sized forms of Fe minerals, however, are more stable and take longer to release Fe ions compared to the salt-based formulations. The synthesis of porous and hollow-porous Fe NPs can involve different synthesis mechanisms, such as sol-gel (Wang et al., 2015a; Yadav et al., 2015), micelle-assisted (Gavrilović et al., 2014), co-precipitation method (Nikumbh et al., 2014; Safi et al., 2016), radiation-assisted (Li et al., 2015; Raut et al., 2016), and hydrothermal-assisted (Ozel et al., 2015; Tadic et al., 2014). There are conflicting results in the agriculture about the use of Fe NPs in nano-enabled agriculture. Depending on the oxidation state of Fe and concentration of these NPs, they can lead to positive and negative impacts on the plant growth. Rui et al. (2016) reported that ppm levels of Fe_2O_3 NPs had a positive impact in the production of chlorophyll and increased the Fe stock in the *Arachis hypogeae*. Nonetheless, a higher concentration of Fe_2O_3 NPs (50 mg L^{-1}) led to decreased photosynthesis activity in another study (Li et al., 2018). At 30 mg L^{-1}, Fe_3O_4 NPs have been reported to cause oxidative stress to ryegrass and pumpkin grown hydroponically (Wang et al., 2011). However, in another study, at 50 mg L^{-1}, the treatment with Fe_3O_4 NPs resulted in higher chlorophyll activity and attenuated oxidative stress (Li et al., 2021).

There are two pathways for uptake of Fe in plants, particularly rice. The first pathway is through the adsorption of insoluble Fe(III) on the roots, followed by its chelation and reduction to Fe^{2+} ions catalyzed by the ferric-chelate reductase, and lastly the transport of the ions from the cell wall to cytosol mediated by iron-regulated transporters (IRT) (Robinson et al., 1999; Eide et al., 1996). Liu et al. (2021) recently reported that nZVI promoted the formation of an iron plate on rice root surface which resulted in further increase in biomass, chlorophyll content, and grain yield up to 55%, while it simultaneously induced the removal of pentachlorophenol (PCP) from contaminated soil used for rice cultivation. The second pathway consists in excreting mugineic acid (MA) that complexes with insoluble Fe(III), forming MA-Fe(III) that are internalized to the cytosol mediated by YSL transporters (Kobayashi & Nishizawa, 2012). Fe translocation from the cytosol to the other parts of the plants is then mostly mediated by protein members of the YSL family (Curie et al., 2001).

2.4 Zinc Oxide Nanoparticles

Zn is an essential micronutrient for plant health that plays a critical role in maintaining key metabolic activities (Sturikova et al., 2018). It is also a cofactor for several metalloenzymes involved in antioxidant reactions as well as in the synthesis of biomolecules such as nucleic acids, proteins, carbohydrates, and lipids (Palmer & Guerinot, 2009). Furthermore, it participates in the control of cell proliferation, and chloroplast formation, thus being directly involved in the photosynthesis activity (Hänsch & Mendel, 2009). In terms of uptake and translocation within plants, Zn is internalized mostly by the roots in the form of Zn^{2+} or complexed with organic chelators (Palmgren et al., 2008) and is distributed through the xylem by transporters known as zinc regulatory transporters (Milner et al., 2013). Zn uptake could take place through the leaf surface or the roots. The latter is aided by dedicated protein transporters referred to as zinc-regulated, iron-regulated transporter-like proteins, as known as ZIP protein family (Ajeesh Krishna et al., 2020). These proteins are located in the cell wall and mediate the internalization of Zn to the cell plasma and vacuoles (Milner et al., 2013). The internalized Zn is then transferred to the xylem with the aid of another group of transport proteins called heavy metal ATPase, particularly HMA2 and HMA4 (Hussain et al., 2004). Then, from the xylem, the Zn is distributed throughout the plant. There are reports of translocation of Zn through the phloem with the aid of yellow stripe-like (YSL) proteins, but the mechanism is not yet well elucidated (Curie et al., 2009). Foliar uptake of ZnO NPs has been reported to take place through the stomata, which then migrate to the apoplast to be dissolved into Zn^{2+} (Zhu et al., 2020). The cations and some undissolved ZnO NPs are then transferred to mesophyll cells before they finally reach the xylem, leading to the further translocation of Zn inside the plant (Zhu et al., 2020). Porous Zn NPs can be synthesized by a variety of different methodologies, including microemulsion-based synthesis (Zhu et al., 2008), co-precipitation (Akhtar et al., 2017), hydrothermal synthesis (Ramimoghadam et al., 2013), sol-gel (Kim & Tai, 2007), and self-assembly synthesis (Bo et al., 2020).

ZnO NPs have been suggested as a fertilizer alternative to increase the availability of Zn ions to plants. In practice, both positive and negative effects have been reported followed by the application of ZnO NPs to plants. Khan and Siddiqui (2021) reported that ZnO NP application promoted pathogen resistant of beetroot crops against *Pectobacterium betavasculorum*, *Meloidogyne incognita,* and *Rhizoctonia solani*. Semida et al. (2021) reported that ZnO NPs promoted drought stress resistance in eggplants. Dutta et al. (2019) synthesized ZnO NPs functionalized with humic acid and citrate, which promoted smart, sustained release of Zn when photoinduced, and enhanced the growth of wheat. In contrast, other studies listed toxic effects from the application of ZnO NPs such as inhibition of root and shoot growth, cell wall damage, and chlorophyll synthesis impairment (Ma et al., 2015; Torabian et al., 2016; Sturikova et al., 2018). In summary, the factors influencing whether the application will result in positive or negative effects were mostly nanoparticle concentration, method of application, and plant species.

2.5 Copper Oxide Nanoparticles

Cu is not only an essential nutrient for plant health, but also has antimicrobial properties. This allows the use of Cu-based products for both fertilization and pesticidal activity. Cu NPs have been tested to a variety of food crops leading to contrasting results depending on the dose concentration. At low doses (up to 20 mg per plant), CuO NPs have been reported to increase Cu accumulation inside the plant leading to beneficial metabolic activities, such as the oxidative stress tolerance and increased sulfur metabolization, due to the ROS generation from the internalized Cu (Keller et al., 2017; Nair & Chung, 2014). Further increases in dosage, however, leads to increased ROS generation and damaging oxidative stress, which have been reported to impact seed germination (Zafar et al., 2017), promote phytotoxicity (Xiong et al., 2017), and inhibit photosynthesis (Da Costa & Sharma, 2016). The synthesis of porous Cu NPs has been systematically reported in the literature (Ashok et al., 2015; Zhao et al., 2019; Zhang et al., 2014; Jiang et al., 2017; O'Mara et al., 2019).

Both excess Cu and a deficiency in Cu can lead to an increase in the formation of ROS leading to oxidative stress that can harm the plant (Ravet & Pilon, 2013). Therefore, plants have developed a mechanism that closely control the level of Cu inside the cells. Cu uptake takes place mostly through the rhizosphere with the aid of Cu-specific high-affinity protein transporters, as known as the COPT family, which mediate the internalization from the external media to the cell cytoplasm and further facilitate the transfer from the root cells to the xylem (Sanz et al., 2019; Ogunkunle et al., 2018).

2.6 Clay Nanoparticles

Clays are naturally occurring minerals with varying shapes, sizes, and chemical compositions. They are generally referred to as nanoclays when at least one external dimension of these minerals is in the nano-sized range. These nanoclays are usually formed by stratified sheets of aluminosilicates, such as silicon tetrahedra and aluminum octahedra, stacked above one another (Nazir et al., 2016; Uddin, 2008). Due to the porosity, elevated surface area, and ionic charge, nanoclays have been suggested as a promising nanocarrier for the delivery of AIs, such as fertilizers and pesticides (Chen et al., 2018b; Merino et al., 2020). For instance, aluminosilicate nanoclays are generally negatively charged, allowing the complexation with charged or polar organic and inorganic chemicals that are essential for plant nutrition, such as zinc (Shafigh et al., 2019; Songkhum et al., 2018), copper (Yuan, 2014), ammonium (Mazloomi & Jalali, 2019), nitrate (Bhardwaj et al., 2012), urea (Madusanka et al., 2017), and potassium (Said et al., 2018). The elevated surface area and ionic charge of nanoclays facilitates the loading of molecules of interest through sorption and ionic interactions. Some examples include diammonium phosphate (DAP) (Verma et al., 2016), Zn^{2+} (Mandal et al., 2018), urea (Wei et al., 2019), potassium phosphate (Hakim et al., 2019), and potassium nitrate (Ganguly & Das, 2017). The high porosity of nanoclays allows for the loading of these AI through extended surface area of the structure followed by their subsequent slow and/or controlled release, which is one of the advantages of using porous inorganic nanocarriers to deliver AI. Although most studies with nanoclays involved the loading of small molecules and ions, these nanocomposites have also been tested, at a lesser extent, to analyze the sorption efficiency of larger molecule pesticides, such as atrazine, imidacloprid, and thiamethoxam, on nano-montmorillonite and its potential to be used as a delivery system for larger agrochemical molecules (Narayanan et al., 2017). A more sophisticated application involved the topical delivery of RNA interference, loaded on layered double hydroxide clay nanosheets, to *Arabidopsis thaliana*, providing these plants with sustained protection against viruses (Mitter et al., 2017).

Nanoclays, however, are not as tunable and controlled during synthesis as SiO_2 NPs. The size distribution is less uniform, and one can have a population of nanoclay with different size and morphology, and thus unpredictable loading capacity. On the other hand, MCM-41 and PHSN are engineered NPs whereas most nanoclays occur naturally, reducing the energy and materials footprint of chemicals applied in the agriculture and in the environment as a whole.

3 Impact of Size and Surface Properties for Efficient Uptake in Foliar and Root Systems

Nanocarriers must possess very specific properties to overcome several chemical and physical barriers in plants, as shown in Fig. 2. The NPs are primarily taken up through plant tissues in the roots and in the foliar region, particularly through cuticles, stomata, and specialized pores, such as lenticels and hydathodes (Wang et al., 2016). To achieve significant uptake, NPs are required to have the right size and surface properties to cross cellular membranes until they successfully reach the vascular systems and translocate within the plant. The first barriers for foliar entry are the size exclusion limits (SELs) of each pore structure. The stomata are minute orifices on foliar surface to control gas exchange, with sizes ranging from 10 to 100 μm (Eichert et al., 2008; Uzu et al., 2010). However, there is evidence that NPs

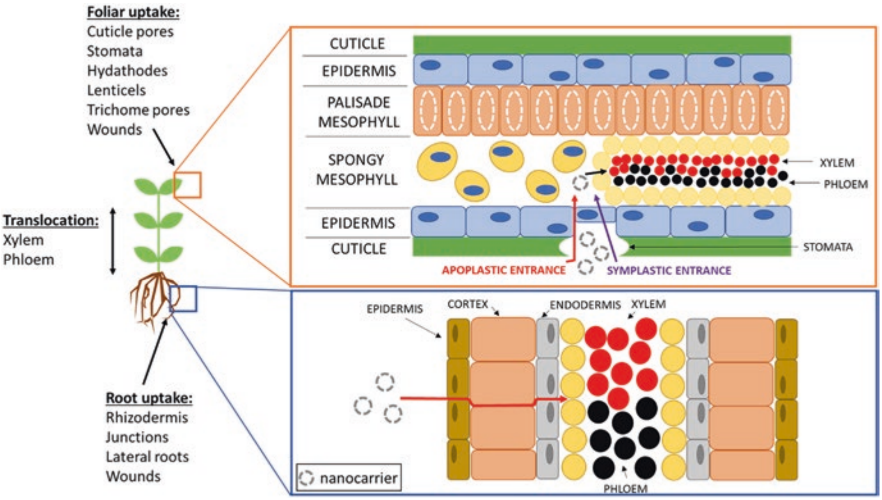

Fig. 2 Schematic representation of possible nanocarrier pathways for uptake through the roots or the leaves followed by translocation through the vascular systems (xylem and phloem)

can be internalized through stomatal uptake for particles up to 50 nm in diameter (Avellan et al., 2019). A second route for foliar uptake would be through the cuticles, which is a protective waxy and porous layer for the leaves and stem. There are significantly more cuticular areas than stomatal areas on leaves; however, the SELs for cuticles are remarkably smaller, ranging from 0.1 to 10 nm (Wang et al., 2016). However, Larue et al. (2014) estimated that NPs up to 100 nm can traverse the cuticle region under certain conditions, such as a temporary disruptions of the waxy layer.

Once the NPs cross the first barrier, they must navigate across cellular membranes and organelles before reaching the vascular systems. One important route to cross from one cell to another is the apoplastic transport, which is a channel where materials can diffuse freely between adjacent cells. The apoplastic pathway is restricted by the opening of the space which can vary from 5 to 20 nm (Eichert et al., 2008; Ma et al., 2010; Dietz & Herth, 2011). The apoplast, however, can be interrupted by Casparian strips which have a SEL below 1 nm limiting the diffusion of compounds (Aubert et al., 2012). Following the apoplastic pathway, the symplastic pathway plays a crucial role in transporting low-density molecules through an interconnected network of protoplast plasmodesmata, which opening size varies from 3 to 50 nm and limits the transport of larger particles (Zhai et al., 2014; Lucas & Lee, 2004).

A priori, one would not expect uptake of NPs exceeding the upper size limit of the SELs. However, some studies reported the uptake and translocation of larger particles, such as gold NPs of 50 nm (Avellan et al., 2019), which clearly exceeds the size barrier for apoplastic and Casparian strip transport. It is speculated that the SEL can be influenced by the particle's surface charge, the presence of some elements such as Ca and Si, (a)biotic stress, which can induce structural changes in these openings (Dietz & Herth, 2011; Schwab et al., 2016; Larue et al., 2014; Larue et al., 2012).

Surface characteristics also play a crucial role in the uptake and translocation of NPs. Surface charge, for instance, can enhance adsorption to rhizodermis, facilitate the chelation process of specialized protein transporters within the cells and vascular systems that further distribute the NPs across the organism, and allow the passage of molecules through cellular ionic channels in plants. It has been reported that positively charged NPs easily attach to the commonly negatively charged rhizodermis of wheat and tomato roots (Spielman-Sun et al., 2017; Li et al., 2019), whereas negatively charged particles have enhanced translocation to aerial parts (Zhu et al., 2012; Li et al., 2016; Spielman-Sun et al., 2019). Both positively and negatively charged NPs are more likely to be internalized when their absolute surface charge surpass 30 mV, while NPs with surface charge close to zero have difficulties in crossing the cellular lipidic bilayer (Lew et al., 2018; Wong et al., 2016). Furthermore, the combination of size and surface properties may facilitate or exclude the uptake of NPs. It has been suggested that smaller-sized NPs require a greater absolute surface charge than larger particles of comparable chemical composition and surface structure (Hu et al., 2020; Lew et al., 2018; Wong et al., 2016).

Overall, it is known that surface charge plays a crucial role in the interaction of the NPs with different biological structures and the subsequent capability to cross the cuticular, stomatal, or rhizodermis barriers, diffuse between adjacent cells, and be carried in the vascular system to distant organelles (Lew et al., 2018; Albanese et al., 2012); therefore, it is important to produce a nanocarrier with specific size and surface properties that has the ability to enter the plant and target the delivery to the specific regions of interest.

4 Surface Functionalization to Facilitate Uptake and to Target Delivery

Surface properties play an important role in the uptake of NPs in plants. Surface charge and charge intensity influence the ability of NP to be internalized and its further translocation (Zhu et al., 2012; Li et al., 2016; Spielman-Sun et al., 2019; Lew et al., 2018). Therefore, although the size is an important factor when designing nanocarriers, surface properties may dictate whether the NP will indeed be internalized and distributed to the organelles of interest. As synthesized NPs might not always fit in all the criteria and thus, surface modifications are a popular pathway to transform bare NPs into a versatile nanocarrier. Santana et al. (2020) functionalized quantum dots (QD) with peptide recognition motifs to target the delivery of these NPs to chloroplasts in *Arabidopsis thaliana*. In this study, the authors used specific guiding peptides on the surface of the QD to mimic chloroplast-biorecognition mechanisms and to target its delivery to the organelle. Although QD are not relevant to plant growth or protection, this approach has the potential to be used for different porous materials as peptide-functionalization has been reported in MSN (Hu et al., 2016).

Future applications might rely on this mechanism to target the delivery of an AI-encapsulated nanocarrier to specific organelles and tissues. Different plant compartments require specific molecules to ensure proper functioning. To obtain these molecules of interest, the cells forming the outer surfaces of these organelles and tissues developed mechanisms to selectively identify the essential biomolecules and facilitate their uptake. In the case of chloroplasts, the redox status controls the diffusion of molecules in and out of the organelle. Santana et al. (2020) took advantage of this mechanism to introduce a chain of polypeptides capable of imitating the redox conditions specific to this organelle and thus being identified by the chloroplast-biorecognition system in the cell membrane leading to the nanocarrier internalization. Another example was the use of citrate to enhance the adhesion of Au NPs to the leaf and the α-1,5-arabinan antibody to target stomata on the leaf surfaces, thus guiding and facilitating the internalization of the NPs (Spielman-Sun et al., 2020). Similar rationale can be used to design nanoformulations to target other organelles and tissues. These rationally designed surface modifications are crucial to further nano-enabled agriculture applications and thus are necessary for the next-generation porous inorganic nanopesticides and nanofertilizers. Nano-enabled agriculture can also benefit from the advances in nanomedicine, where a vast spectrum of molecules have been tested to target the delivery, including antibodies, peptides, aptamers, saccharides, and proteins (Baeza et al., 2015), and porous SiO_2 nanocarriers, in particular, are promising candidates because they can transport and deliver AI in plants and can be easily functionalized their surfaces (Trewyn et al., 2007).

Functionalization can also enhance NP stability and improve the apparent solubility of hydrophobic compounds in aqueous media. For example, it has been reported that functionalizing nHAP with citric acid (Montalvo et al., 2015; Samavini et al., 2018) and CMC (Liu & Lal, 2014) improved overall NP stability in suspension and thus increased P delivery to plants. Carboxylic acid ligands have been reported to enhance the apparent solubility of carbon nanotubes in water by providing a hydrophilic surface coverage (Tripathi et al., 2011; Sonkar et al., 2012). Other advantages of surface modifications include aiding the loading and release of AI in porous nanocarriers and provide different functionalities to the nanoformulation. MSN surfaces were functionalized with nontoxic trimethylammonium to enhance loading and promote the slow-release of 2,4-dichlorophenoxy acetic acid (Cao et al., 2017) and pyraclostrobin (Cao et al., 2016). Functionalizing CuO NPs with biocompatible polymers provided fungicidal properties to the nanoformulation (Cao et al., 2014).

More sophisticated surface modifications can use the surface ligands to trigger a reaction involving a second molecule of interest loaded within the NP. Torney et al. (2007) loaded mesoporous SiO_2 NPs (MSN) with β-oestradiol, capped the pores with small gold NPs to prevent the cargo from leaching out, and functionalized the MSN surface with a double-stranded DNA plasmid containing a green fluorescent protein (GFP) gene. Then, immature maize embryos were bombarded with the transformed MSN to assess whether these NPs could deliver not only the genetic material but also the β-oestradiol, which is responsible to trigger the GFP gene expression. This work successfully reported that the MSN system simultaneously delivered the plasmid as well as β-oestradiol, the chemical responsible to trigger the gene expression to targeted plant cells. Porous nanocarriers are particularly ideal to carry two or more biomolecules that complement each other activities because they can be stored in different areas of the nanoparticle, for example, inside the pores, hollow core, or on the surface of PHSN. Ultimately, these particles can be designed in a way that the multiple molecules of interest loaded in them will only interact with one another at the destination site, usually controlled by gatekeeper molecules, which control the release of AIs after chemical or physical stimuli.

5 Stimuli-Responsive Porous Nanocarriers

Porous nanoparticles are not only able to carry a wide variety of organic and inorganic compounds, protect them from premature degradation, and target their delivery, but they can also provide controlled release of molecules of interest upon triggered on-demand responses. That is, the AIs are loaded into the nanocarrier pores, which are further capped with another type of compound, referred to as gatekeepers, that prevent the AI from leaching out prematurely. These gatekeepers are designed to block the AIs from leaving the pores and unwanted molecules from entering the pores, and to enable the release of the cargo when triggered by a stimulus, as shown in Fig. 3. Triggering factors include pH change (Yang et al., 2010; Liu et al., 2010; Muhammad et al., 2011; Yuan et al., 2011; Gao et al., 2020; Gao et al., 2019; Chen et al., 2019; Baldi et al., 2018), light stimulus (Niu et al., 2014; Li et al., 2014; Zhang et al., 2012; Fomina et al., 2012; Chen et al., 2018a; Xu et al., 2018), ionic strength (Zhang et al., 2018; Bernardo et al., 2018; Cao et al., 2017), redox agents (Koo et al., 2013; Cui et al., 2012; Kim et al., 2010; Hou et al., 2018; Yi et al., 2015), enzymes (Kaziem et al., 2017; Liang et al., 2017; Guo et al., 2015), and temperature (Ye et al., 2011; Wei et al., 2017; Zhang et al., 2019) as summarized in Table 1.

For pH-triggered nanocarriers, the gatekeeper compound capping the pores is sensitive to pH. Compounds containing amines, hydroxyl, and carboxylic acid functional groups are susceptible to protonation and deprotonation depending on the pH of the medium. This can affect the charge of the gatekeeper compound, and thus the interactions with the nanocarrier and AI. Mattos et al. (2018) functionalized thymol-loaded SiO_2 NPs with amino functional group (-NH_2), which at neutral pH is protonated (-NH_3^+), thus strongly interacting with the electronegative group O^- in thymol and preventing the AI from being released. At acidic pH, however, thymol undergoes protonation, weakening the interaction with the gatekeeper, which then leads to a greater release of the AI. Complex structures, such as polymers (i.e., hydrogels), denature and undergo structural changes depending on the pH of the medium. Sarkar and Singh (2017) reported that at alkaline pH, a hydrogel coating comprised of CMC and citric acid undergo hydrolysis, liberating the release of chlorpyrifos pesticide from a nanoclay matrix.

Photo-responsive gatekeepers can undergo structural change when exposed to the light of a certain wavelength. Some structural changes include oxidation, isomerization, and fragmentation of the interaction with the carrier (Grillo et al., 2021). Chen et al. (2018a) functionalized a glyphosate-loaded porous nano-sized biochar with amino-silicon oil, which undergoes isomerization when exposed to light at 420 nm wavelength. This process, then, releases the loaded glyphosate. Interestingly, when this nanoformulation ceases to be exposed to the specific wavelength of light, the gatekeeper returns to cap the pores of the nanocarrier and block the AI to be released. That is, one can turn on and off the release of the molecule of interest by simply exposing or not the nanoformulation to light.

Ionic strength-responsive gatekeepers generally rely on the electrostatic interactions among the medium, nanocarrier, AI, and the gatekeeper itself. Cao et al. (2017) functionalized 2,4-dichlorophenoxy acetic acid (2,4-D)-loaded MSNs with trimethylammonium (TA) to avoid premature release of the pesticide. Because 2,4-D is extremely soluble in aqueous media, leaching is generally a threat when it is applied in agricultural soils. The TA acts as a binding agent for the 2,4-D, increasing the loading by 21.7% and as a capping agent to avoid leaching. The change in ionic strength, however, can affect the interaction between TA and 2,4-D, leading to either

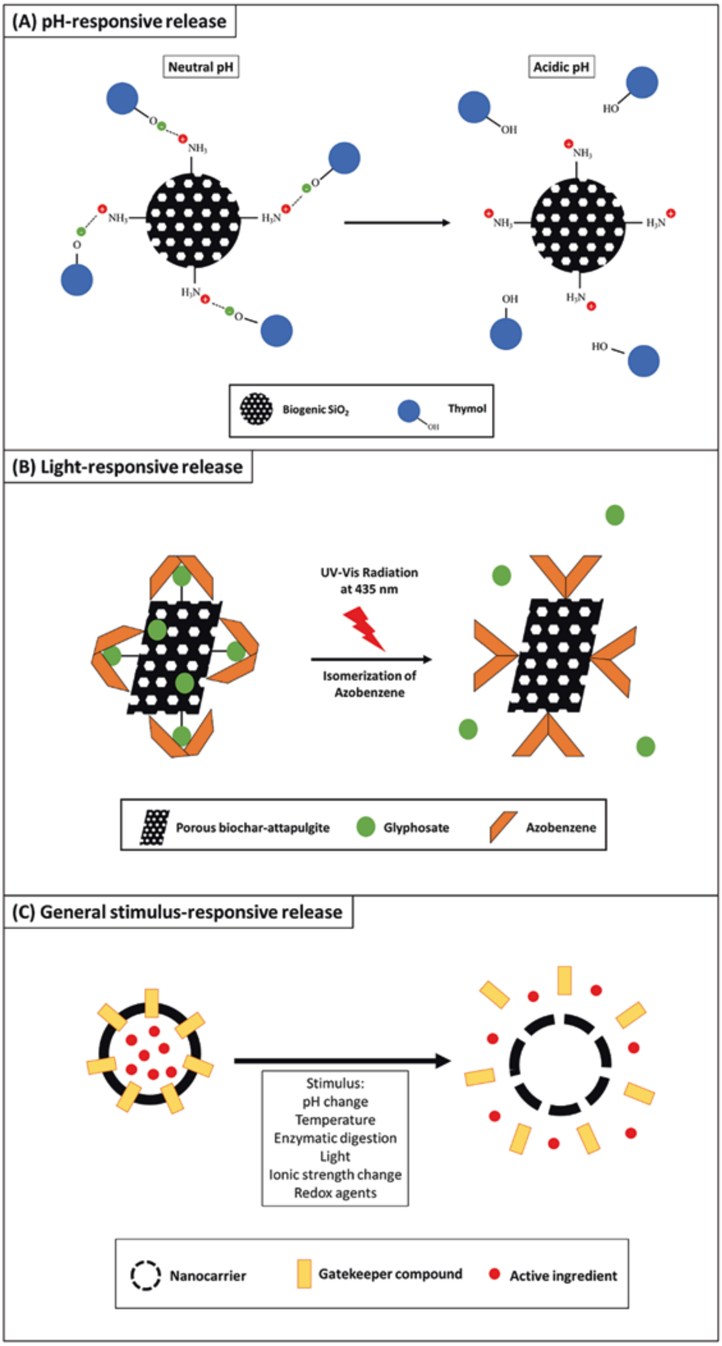

Fig. 3 Conceptual schematic of a (**a**) pH-responsive nanocarrier suggested by Mattos et al. (2018): at neutral pH there is a strong interaction between the negatively charged hydroxyl group in thymol and the positively charged amino group in the functionalized biogenic nano-SiO_2 and when the pH becomes more acidic, this interaction is weakened due to the protonation of the hydroxyl group in thymol; (**b**) light-responsive nanocarrier suggested by Chen et al. (2018a): under UV-Vis light radiation at 435 nm, azobenzene undergoes isomerization releasing the encapsulated glyphosate from the porous biochar-attapulgite framework; (**c**) general stimulus-responsive nanocarrier: the AI is trapped within the nanocarrier until a stimulus disrupts the structure of the gatekeeper compound, thus liberating the pores and allowing the AI to be released

Table 1 List of stimuli-responsive nanocarriers with their respective gatekeepers and active ingredients

Stimulus	Nanocarrier material	Gatekeeper(s)	Active ingredient	Reference
pH	Mesoporous silica	Poly(allylamine hydrochloride)	Doxorubicin	Yang et al. (2010)
	Mesoporous silica	Gold NPs and acid-labile acetal linker	2,2′-bipyridine	Liu et al. (2010)
	Mesoporous silica	ZnO QDs	Doxorubicin	Muhammad et al. (2011)
	Mesoporous silica	Poly(acrylic acid)	Doxorubicin	Yuan et al. (2011)
	Mesoporous silica	Calcium carbonate	Prochloraz	Gao et al. (2020)
	Mesoporous silica	Pluronic F127	Chlorpyrifos	Chen et al. (2019)
	Clay	Hydrogel	Chlorpyrifos	Sarkar and Singh (2017)
	Biogenic silica	Functionalized amino group	Thymol	Mattos et al. (2018)
Light	Mesoporous silica	Gold NPs	Doxorubicin	Niu et al. (2014)
	Mesoporous silica	Sulfonatocalix(4)arene	Gold nanorods	Li et al. (2014)
	Mesoporous silica	Gold NPs	Doxorubicin	Zhang et al. (2012)
	Porous biochar-attapulgite	Azobenzene	Glyphosate	Chen et al. (2018a)
Ionic strength	Porous hollow carbon	Cationic polymer PEI	Selenate	Zhang et al. (2018)
	Hydrotalcite	Mg and Al	Phosphate	Bernardo et al. (2018)
	Mesoporous silica	Trimethylammonium	2,4-dichlorophenoxy acetic acid	Cao et al. (2017)
Redox agents	Mesoporous silica	Glutathione	N-acetyl-L-cysteine	Koo et al. (2013)
	Mesoporous silica	Glutathione	Fluorescein	Cui et al. (2012)
	Mesoporous silica	Glutathione	Cyclodextrin	Kim et al. (2010)
	Mesoporous silica	Glutathione	Salicylic acid	Yi et al. (2015)
Enzymes	Hollow porous silica	α-Cyclodextrin	Chlorantraniliprole	Kaziem et al. (2017)
	Mesoporous silica	Isocyanate and poly(ethylenimine)	Pendimethalin	Liang et al. (2017)
	Mesoporous silica	Carboxymethylcellulose	Emamectin benzoate	Guo et al. (2015)
Temperature	Hollow porous silica	Poly(N-isopropylacrylamide)	Fe_3O_4	Ye et al. (2011)

more release of the AI, or a stronger interaction thus preventing the discharge of the pesticide in the soil.

An example of redox-responsive release is when disulfide bonds between the nanocarriers and the capping agent are undone, liberating the loaded molecules to be released. The most common gatekeepers for redox-sensitive response are β-cyclodextrins, sulfidated polyethylene glycol (S-PEG), and cadmium sulfide. Yi et al. (2015) designed MSN functionalized with decanethiol, through disulfide conjugation. The disulfide bonds between the MSN and decanethiol could be easily cleaved by glutathione (GSH). In this study, the release of salicylic acid was directly controlled by the concentration of GSH in the medium.

Enzyme-triggered response involves using enzymes to degrade the gatekeepers associated with the loaded nanocarrier. Kaziem et al. (2017) synthesized PHSN, loaded these nanocarriers with chlorantraniliprole, and functionalized their surface with α-cyclodextrin. The α-cyclodextrin-PHSN successfully retained the AI under thermal stress and UV radiation; however, the release was triggered when α-amylase was introduced, leading to the degradation of the capping agent, and unblocking the pathway for the AI to be discharged.

AI release can also be triggered by thermal stress. This happens when the gatekeepers are thermosensitive, particularly compounds that are sensitive to temperatures in the environmental range. Because high temperatures can lead to the degradation of the AI and nanocarrier as well, the gatekeeper must be able to undergo transformation with light variations of ambient temperatures. Ye et al. (2011) used a thermosensitive polymer, poly(N-isopropylacrylamide-co-acrylamide), to cover MSN-coated Fe_3O_4 NPs. The subtle difference in temperature from 34 to 42 °C led to changes in structure and magnetic properties of the nanocarrier, that can be used in conjunction with molecules of interest to modulate their release.

In the future, sophisticated applications of nanotechnology in agriculture will take advantage of the ability to functionalize porous nanocarriers, particularly SiO_2 and clay NPs, to target the delivery of the formulation to specific plant organelles and tissues, and to promote stimuli-responsive release of molecules of interest, all at once while carrying several molecules of interest that will only interact with one another at the destination. Two or more compounds will play a role in capping the pores to prevent AI premature release, mimicking biorecognition mechanisms in the different parts of the plants, and in some cases, activating the AI. More research should be focused on the functionalization of porous nanocarriers with biomolecules and how their interaction can modulate the uptake and release of pesticides, fertilizers, and genetic material to plants.

6 Conclusions

Inorganic porous nanoparticles play a pivotal role in nano-enabled agriculture and toward making agricultural practices more sustainable. A variety of methodologies for synthesis and structure modifications of inorganic nanomaterials have been extensively studied, providing us with the expertise to fabricate nanocarriers with specific features to encapsulate, transport, and release agrochemicals in a way that avoids wastage by targeting specific sites in the plant. For instance, the shape, diameter, and porosity can be tuned to optimize the loading of AI but keep it in the range for uptake through roots or leaves, and translocation through the xylem and phloem. Further modifications can be done to improve uptake and translocation as well as target specific organelles, such as changing the zeta potential or functionalizing the nanocarrier surfaces with biomolecules to mimic biorecognition mechanisms.

Given the immense possibilities for inorganic porous nanomaterials to increase crop yields and to offer crop protection many new nanotechnology solutions will be proposed in the near future, with the objective to make agricultural practices more efficient. However, to ensure these developments are sustainable, nanomaterials should be formulated with safe and/or earth-abundant chemicals and using green chemistry principles. However, given that in some instances materials at the nanorange may be toxic compared to their bulk counterparts, the environmental and human health exposures and risks of new nanomaterials used in agriculture need to be evaluated. Although the goal of the use of nanomaterials and nanocarriers is to ensure that AI delivered is utilized efficiently, without wastage, some losses to the environment are expected. For example, the nanomaterials can be washed off leaves and deposit on the ground during precipitation events, and along with nanomaterials applied in soils, may be mobilized in the soil and groundwater. As well nanomaterials dosed in plants may lead to exposures to insects, including those involved in pollination, as well as birds. Thus, their ecological safety needs to be verified. Various silica and other inorganic porous nanomaterials are being used in medicine, which suggest that their safety to human health may already be verified (Mamaeva et al., 2013; Lohse & Murphy, 2012).

It is also important to assess the scalability of production of inorganic porous NPs for field applications, and as well field studies need to perform to verify if the efficacy determined in lab studies are translated adequately to the field. In a recent assessment of technology efficacy and readiness level for commercial applications, nanocarriers for fertilization and pesticide delivery ranked high on both counts, suggesting that their commercial applications are likely to grow rapidly (Hofmann et al., 2020).

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