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Review Article

Nanobiosensors and nanoformulations in agriculture: new advances and challenges for sustainable agriculture

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In the current scenario of climate change, global agricultural systems are facing remarkable challenges in order to increase production, while reducing the negative environmental impact. Nano-enabled technologies have the potential to revolutionise farming practices by increasing the efficiency of inputs and minimising losses, as well as contributing to sustainable agriculture. Two promising applications of nanotechnology in agriculture are nanobiosensors and nanoformulations (NFs). Nanobiosensors can help detect biotic and abiotic stresses in plants before they affect plant production, while NFs can make agrochemicals, more efficient and less polluting. NFs are becoming new-age materials with a wide variety of nanoparticle-based formulations such as fertilisers, herbicides, insecticides, and fungicides. They facilitate the site-targeted controlled delivery of agrochemicals enhancing their efficiency and reducing dosages. Smart farming aims to monitor and detect parameters related to plant health and environmental conditions in order to help sustainable agriculture. Nanobiosensors can provide real-time analytical data, including detection of nutrient levels, metabolites, pesticides, presence of pathogens, soil moisture, and temperature, aiding in precision farming practices, and optimising resource usage. In this review, we summarise recent innovative uses of NFs and nanobiosensors in agriculture that may boost crop protection and production, as well as reducing the negative environmental impact of agricultural activities. However, successful implementation of these smart technologies would require two special considerations: (i) educating farmers about appropriate use of nanotechnology, (ii) conducting field trials to ensure effectiveness under real conditions.

Introduction

Agriculture can greatly benefit from practical applications of nanotechnology. For example, the development of more efficient and less polluting agrochemicals (nanoformulations) or the design of devices that helps to detect biotic and abiotic stresses in plants before they affect plant production (nanobiosensors). Advancements in these fields will assist in mitigating some of the serious problems and challenges that agriculture faces in the coming years. These include reducing the negative environmental impact that agricultural activities have on the environment, dealing with issues related to climate change (such as altered precipitation patterns, temperature changes, and the emergence of new plant pathogens), and overcoming the plateau in crop yields [1]. The number of nanotechnological applications being tested in agriculture is continually increasing and expanding to various areas, including soil and water management, pathogen detection, and plant production amongst others [1–4] (Figure 1). However, in this mini-review, we will focus on the two most important applications: nanobiosensors and nanoformulations (NFs).

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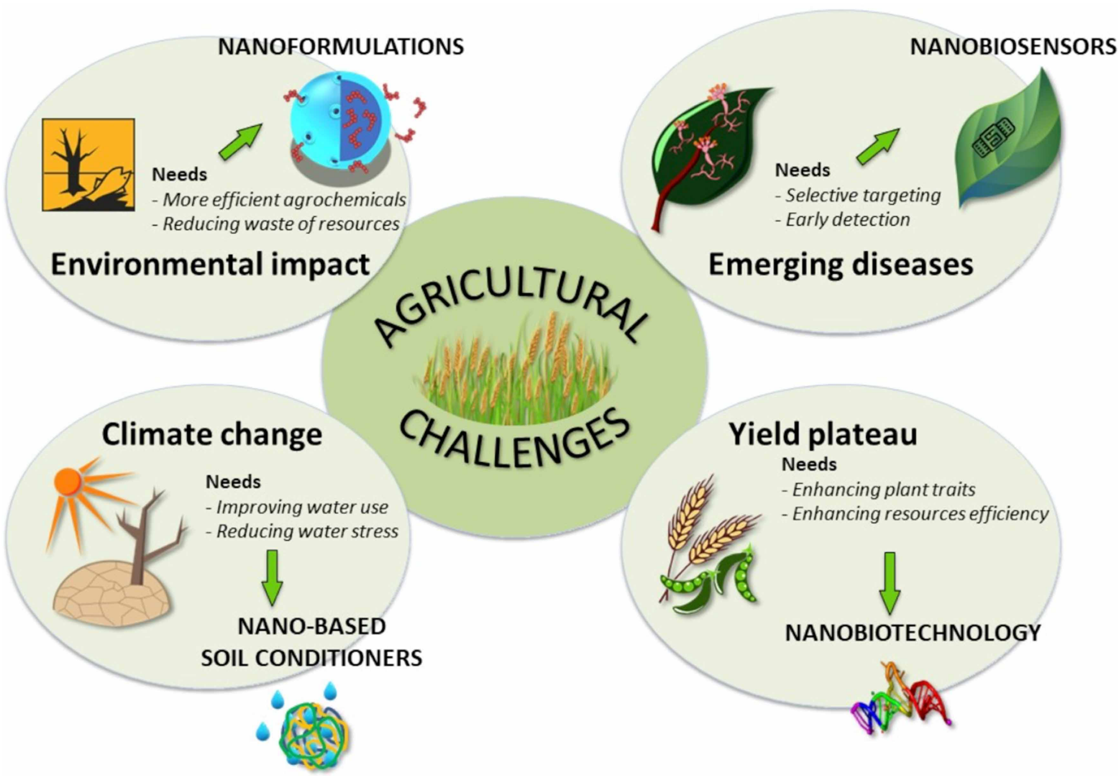

Figure 1. Applications of nano-enabled technologies in agriculture.
Nano-based soil conditioner helps mitigate the effects of climate change. Nanobiosensors can be used for efficient crop protection contributing to precision farming. Nanoformulations contribute to sustainable agriculture by reducing the enviromental impact of the agrochemicals. Nanobiotechnology improves yield plateaus.

Biosensors incorporating nanoparticles (NPs) are defined as nanobiosensors. The properties at the nanoscale of NPs result on a more organised and efficient material (enhanced optical and mechanical properties, and high chemical customisation among others) in comparison with conventional biosensors. Nanobiosensors can play a crucial role in agriculture by detecting and monitoring various parameters related to plant health and environmental conditions [5,6]. These small devices can detect the presence of pathogens, pests, and diseases at an early stage, allowing for timely intervention and minimising crop losses [7]. Nanobiosensors can also provide real-time analytical data, including the detection of nutrient levels, metabolites, pesticides, soil moisture, and temperature, aiding in precision farming practices and optimising resource usage [5,8].

NFs refer to the development of agrochemicals, such as pesticides and fertilisers, in nano-sized formulations. By reducing the particle size, these formulations offer several advantages. They enhance the efficiency of the active ingredients, allowing for lower doses while maintaining effectiveness [9], which reduces environmental pollution and minimises the potential negative impacts on beneficial organisms. NFs also improve the targeted delivery of agrochemicals, ensuring that they reach the intended plant tissues or pests more effectively [10], and decrease damage to non-targeted sites of plants, controlling the detrimental effects of chemicals on the environment.

Overall, nanotechnology offers promising solutions to address agricultural challenges and enhance productivity while minimising environmental impact. Continued research and development in this field has the potential to revolutionise farming practices and contribute to sustainable and efficient agriculture. However, the use of nanotechnology in agriculture requires educating farmers to ensure appropriate use of this technology, which is still a worldwide challenge for governments.

Nanobiosensors: crop detection problems

One of the major challenges in crop production is monitoring their health status. Acting quickly against incipient diseases or compensating for nutritional or water deficiencies can result in significant savings, not only

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economically but also environmentally, especially if such interventions are localised only where and when they are needed. Smart farming aims to address this need by employing advanced technologies such as drones, remote operations, real-time information, etc. Within these technologies, the development of nanobiosensors plays a crucial role. These devices can monitor markers for specific stresses (drought, disease, etc.) and detect them in advance, even at the level of individual plants.

Nanobiosensors are found either in the field or in the laboratory for analysis. The combination of nanoscience, computer, biology, and electronics is allowing researchers to develop nanobiosensors with powerful sensing abilities. Ray et al. [11] listed the ideal characteristics of nanobiosensors. Briefly, (i) nanobiosensors should be cheap, biocompatible, non-toxic, and portable; (ii) they should be stable when stored at regular conditions; (iii) the interaction with the analytes to be determined should be extremely specific, so that minimum reactivity is required; (iv) received signals from nanobiosensors should be precise, accurate, and reproducible.

A nanobiosensor needs to be able to convert the chemical signals from plants into digital information that can be measured and monitored by external electronic devices. Tipically, a nanobiosensor has three components: (i) bioreceptor; (ii) transducer; and (iii) detector (Figure 2). The bioreceptors are generally biological materials (antibodies, enzymes, microorganisms, nucleic acids, and etc.) that interact and accept the chemical signal from the analyte to be detected, and then transfer it to the transducer. Next, the transducer works as an interface which measures the signal from the bioreceptor and transforms it into a quantifiable electrical signal in the detector. Finally, the detector processes the signals to amplify and analyse them (Figure 2). A list of representative nanobiosensors used for crop detection problems, their targets, and their detection mechanism is presented in Table 1.

There are several ways to achieve the conversion from the presence of a specific chemical compound to an electrical or luminous signal correlated with the amount of compound to be detected. For example, there are nanobiosensors with a receptor for the analyte and two chromophores (molecules that emit fluorescence) of different colours. When the receptor is empty, the chromophores are separated, and only one of them can emit its characteristic fluorescence. However, when the analyte binds to the receptor, the chromophores come into contact, and the emitted fluorescence is different (based on a phenomenon called Förster Resonance Energy Transfer — FRET (see Table 1). In this way, the presence or absence of the analyte can be linked to the type of emitted fluorescence, and its concentration can even be measured based on the intensity of that fluorescence. This type of nanobiosensor can provide *in vivo* information of molecule concentrations, protein activity (enzymes), and ion dynamics [23].

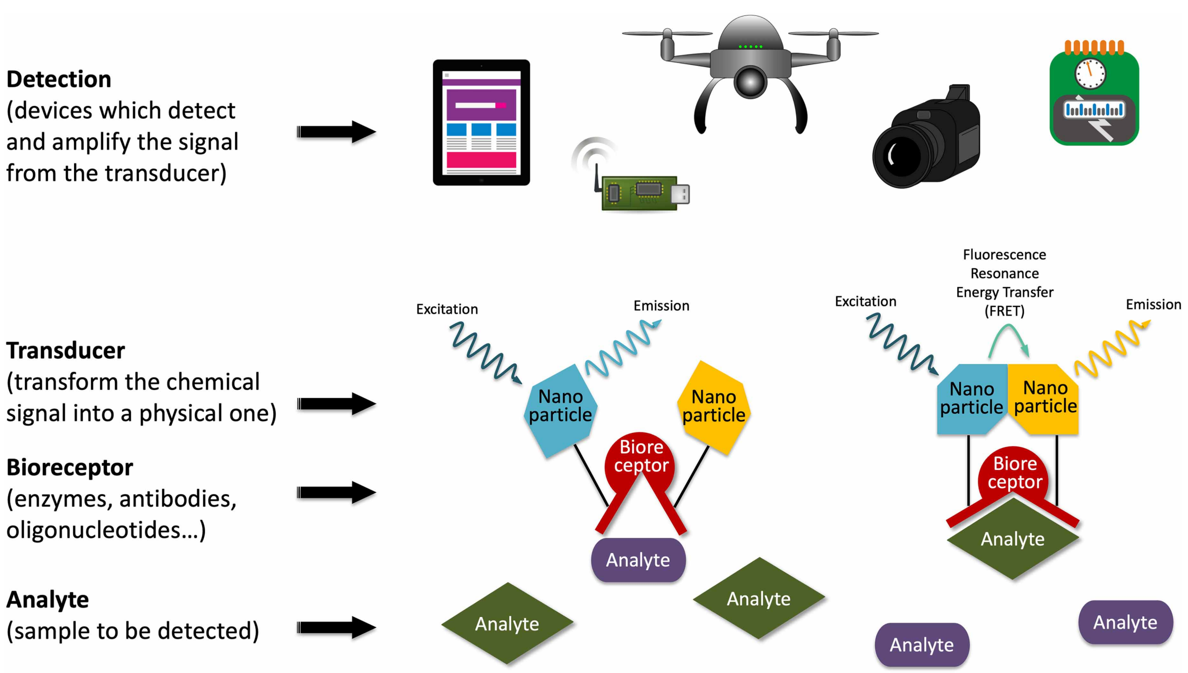

Figure 2. Schematic representation of major components of nanobiosensors and their mechanism.

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Table 1 Summary of nanobiosensors for plant pathogen detection or disease control

Target	Sensor component	Detection mechanism	Sensitibility	References
Fenitrothion	Nano TiO_2/nafion composite	Electrochemistry	0.2 μM	[12]
Organophosphate-based pesticides	Carbon nanotubes	Electrochemistry	0.145 ppb	[13]
Methyl parathion and chlorpyrifos	Carbon nanotubes wrapped by ssDNA[1]	Enzymatic reaction	1×10^{-12} M	[14]
Urea, urease	Gold nanoparticles	Colorimetry	5 μM, 1.8 U/L	[15]
Volatile substances (toxic gases)	multidimensional carbon nanostructures	Radio frequency signals	5 ppm	[16]
R. Solanacearum	Au NPs[2] functionalised with ssDNA	Colorimetry	15 ng	[17]
P. Stewartii sbusp. stewartii	Au NPs	Electrochemistry	7.8×10^3 cfu/ml	[18]
P. Ramorum	Ag NPs	SERS[3]	N/A	[19]
T. Harzianum	ZnO NPs–chitosan nanocomposite	Electrochemistry	1.0×10^{-19} mol L^{-1}	[20]
Citrus Tristeza	CdTe QD[4]-Rd	FRET[5]	220 ng ml^{-1}	[21]
Release of kasugamycin	Zn QD	N/A	N/A	[22]

[1]Single-standed DNA;
[2]Nanoparticles;
[3]Surface-enhanced Raman spectroscopy;
[4]Quantum dot;
[5]Fluorescence resonance energy transfer.

Variations in the content of reactive oxygen species (H_2O_2), sugars (glucose, sucrose), ions (Ca^{2+}, H^+), and plant hormones (ethylene, abscisic acid, jasmonic acid, etc.) are often related to the health status of the plant, and there are nanobiosensors designed to measure their concentrations [23]. Nanobiosensors also play valuable roles in plant breeding and culturing, with the purpose of improving crop productivity and quality. Many nanomaterials are used to deliver nutrients and pesticides to particular target points in plants [5,24]. Detecting and controlling the use of pesticides, fertilisers, as well other chemical compounds, provide convenient information for precision farming [25], where detection of pesticides residues has several advantages such as low detection, sensitivity, high selectivity, and fast responses. Several types of nanobiosensors (enzyme, optical, and electrochemical sensors) have been developed to detect pesticide mixtures [12,26], organophosphorus pesticides [13] or even particular pesticides such as methyl parathion or chlorpyrifos [14]. In addition, an accurate and rapid estimation of nutrient concentrations in soil would increase the productivity, reduce cost to farmers, and reduce leaching of unutilised fertilisers. Thus, detection of urea, urease activity, and urease inhibition are possible by the development of a nanobiosensor based on gold nanopaticles (Au NPs) [15].

Designs based on carbon nanotubes, quantum dots (QDs), and plant viruses take advantage of the inherent properties of nanomaterials to convert chemical signals into optical signals [23]. Non-invasive electronic systems have also been developed to be placed on leaf surfaces using nano-scale carbon structures, which can be highly useful for measuring volatile substances [16]. The use of nanobiosensors for pest detection has provided rapid and accurate results compared with the time-consuming conventional methods (manually observing), allowing for plants to be quickly protected. Detailed reviews on NP-based biosensors used for plant pathogen detection, their detection mechanisms, and performance have been published elsewhere [5,7,8,10,25,26].

Inorganic nanomaterials such as Ag, Au and metal oxide NPs are commonly used as nanobiosensors. For example, Khaledian et al. [17] used Au NPs functionalised with single-stranded oligonucleotides to detect the genomic DNA of the devastating causal agent of potato bacterial wilt, *Ralstonia solanacearum*. Gold NPs have also been used in the detection of the plant bacterial pathogen *Pantoea stewartii* [18]. The detection method was developed using horseradish peroxidase labelled antibodies in an electrochemical enzyme linked

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immunoassay. Silver nanorods have been employed for the identification of the plant pathogen *Phytophthora ramorum* from real samples using surface enhanced Raman spectroscopy [19]. Siddiquee et al. [20] developed a DNA biosensor using zinc oxide NPs/chitosan nanocomposites to identify the presence of *Trichoderma harzianum*, a soil-borne fungus that has been successfully used as a biological control agent against various plant pathogens.

Carbon dots (CDs) are the new alternative to the conventional semiconductors QDs. Their low toxicity and high biocompatibility are ideal characteristics for using them as nanobiosensors in the detection of microorganism. For example, Safarnejad et al. described a QD-based complex nanobiosensor against the *Citrus Tristeza* virus, which is responsible for one of the most important diseases of citrus in the world. To achieve this goal, a fluorescence resonance energy transfer approach was used [21]. Additionally, surface-functionalised QDs are used as controlled release NFs for delivering the natural antibiotic kasugamycin in plant disease management [22].

Nanoformulations: crop protection and production

Our agriculture is intricately linked to the application of agrochemicals to maintain yields, whether to improve the nutritional status of crops or to combat pests and diseases. However, the efficiency of both fertilisers and pesticides remains relatively low, with a significant amount of the product being lost due to factors such as volatilisation, leaching, immobilisation, decomposition, etc. When chemical fertilisers are applied in bulk, plants cannot take them all at once, resulting in a cycle of re-application that increases costs [27]. In fact, studies have revealed that half of the applied nitrogen fertilisers are lost into water and air [28]. Besides the financial cost, this poses an environmental problem, as all the active substance that does not reach its target (the plant or the pathogen) ends up in the surrounding ecosystem (soil, water, other living organisms, etc.). Furthermore, the pesticide contamination of surface and ground water has resulted in loss of freshwater content available for human consumption [29]. This is where nanotechnology can be useful, making a significant contribution by increasing the efficiency and safety of treatments through NFs (Figure 3). As with every new technology that has advantages, there are also drawbacks using nanotechnology in agriculture. Some of the

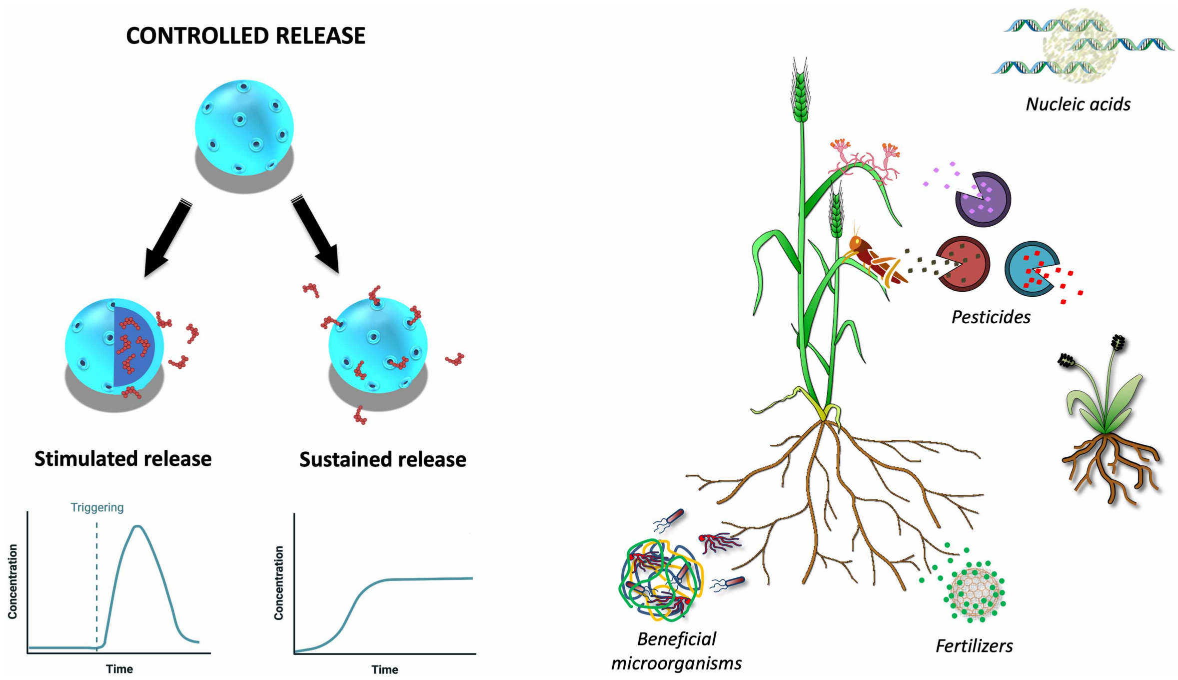

Figure 3. Enhanced characteristics of nanoformulations.

(**A**) Types of controlled release of exogenous cargo. NPs and NFs can release the active substance in response to stimulus or continuously over time. (**B**) Nanoformulations can be used for multiple plant protection purposes such as pest control (fungi, bacteria, virus, insects), weed control, pesticide remediation, enhancing beneficial microorganism from soil, etc.

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biggest concerns associated with its use go from high reactivity and variability, environmental impact, to safety concerns for farmers and consumers. However, using nanomaterials as platforms for the application of active substances (whether fertilisers or pesticides) offers several powerful advantages [30]:

Protection against degrading agents (pH, light, temperature, microorganisms, etc.): encapsulating the product in a nanocapsule provides a protective cover that prevents the deterioration of the active substance, allowing for a reduction in the effective applied dose. This also opens the possibility of using naturally occurring agrochemicals, which easily decompose in the environment and are less persistent, whose sensitivity to degradation has hindered their use until now [31,32].

Controlled release: nanocapsules and NPs can be designed and prepared to release the active substance suddenly in response to a specific stimulus (e.g. a pH change when reaching an insect's stomach or the action of an enzyme) or to release it continuously over time [33,34] (Figure 3).

Control of solubility in both aqueous and lipid media, facilitating penetration and movement in different tissues [35].

Attachment of biomolecules for specific functions: nucleic acids (DNA, RNA), antibodies, proteins, lipids, etc., can be attached to the surface of nanomaterials with the ability to recognise other substances. In this way, nanomaterials can be directed and concentrated in specific areas of organisms, tissues or cells, where they can later release their chemical cargo [36,37].

NFs are new-age materials with endless nano-scale based delivery systems. Some representative NFs designs, which vary in size from 10 nm to more than 100 nm, are based on: liposomes, niosomes, phytosomes, microgels, multiple emulsions, nanoemulsions, microclusters, solid lipid NPs, nanostructured lipid carriers, biopolymeric NPs, gold NPs, self-assembled micelle, silica NPs, graphene NPs, and mesoporous NPs [10,38]. To improve the properties of active components, NFs are synthesised through encapsulation, i.e. entrapment of the active molecule inside the nanocarriers, or complexation, i.e. covalent attachment of active molecules to nanocarriers. The interaction, uptake, and translocation of NFs by plants is highly dependent of several factors such as plant physiology, surface charge of NFs itself, shape, size, and physico-chemical properties [39]. Thus, diverse crops belonging to different species have shown diverse patterns of accumulation and absorption of different types of NFs [40,41]. Table 2 summarises some examples of NFs for crop protection and production.

These NFs can be used to improve existing strategies and products traditionally used in agriculture or to create new approaches and solutions [54] (Figure 3). In the former case, the aim is often to achieve better application through controlled and localised release of existing and marketed active substances. This type of strategy is particularly useful for fertilisers, as it prevents losses due to leaching and decomposition, allowing nutrients to be available to the plant when and where they are needed [55]. Nanofertilisers or smart fertilisers are NFs (polymers) mainly based on NPs that provide nutrients to plants or enhance the effect of conventional

Table 2 Some examples of nanoformulations for crop protection and production

Agrochemical type	Nanodevice	Composition	Active ingredient	References
Fertilisers	Nanoparticle	Calcium phosphate	Urea	[42]
	Nanocomposite	Starch, hydroxyapatite	Urea, phosphate	[43]
Fungicides	Nanoparticle	Selenium	-	[44]
	Nanoparticle	Cyclodextrins	Thiabendazole, carbendazim, fuberidazole	[45]
	Nanodisk	Phospholipids, apolipoprotein A-I	Amphotericin B	[46]
Insecticides	Nanoparticle	Sodium alginate	Imidacloprid	[47]
	Nanoparticle	SiO_2	-	[48]
Herbicides	Nanocomposite	Zn–Al layered double hydroxide	2,4-dichlorophenoxyacetate	[49]
	Nanocapsule	Chitosan, alginate, tripolyphosphate	Imazapir, imazapyc	[50]
Bactericides	Nanoparticle	MgO	-	[51]
Antivirals	Clay nanosheet	Layered double hydroxide	Double-stranded RNA	[52]
Nematicides	Viral capsid	Red clover necrotic mosaic virus	Abamectin	[53]

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fertilisers when they are applied in small amounts. The size and high volume to surface area make them more efficient than the conventional ones. In addition, they move faster than the conventional fertilisers. Based on the exogenous cargo, there are three categories of nano fertilisers: (i) macronutrient nanofertilisers, (ii) micronutrient nano- fertilisers, and (iii) nanoparticulate nano fertilisers [10]. There are different types of NPs employed for the generation of nanofertilisers with different compositions, benefits, and active compounds; these have been addressed elsewhere [8,10,28,56].

As alternative solutions to the conventional agrochemicals, some NPs have the ability to stimulate the natural defences of plants, possess inherent microbiological activity or incorporate new substances and products with highly specific action or natural origin [30,57]. NFs offer an excellent alternative for safe and highly efficient delivery of biomolecules such as microRNA, CRISPR–Cas, and RNA interference (RNAi) for plant protection [36]. For example, the technology of RNAi is a perfect candidate to be coupled with NFs that protect the nucleic acid and allow its release at specific times and locations to silence specific phytopathogenic genes and prevent infections [30,52]. Siddiqui et al. [58] suggested that silicon dioxide NPs (SiO_2 NPs) may improve the natural defence mechanisms of *Cucurbita pepo* plants in response to salt stress by improving the transpiration rate, water use efficiency, total chlorophyll, and carbonic anhydrase activity.

NPs also protect plants from abiotic stress including drought, temperature fluctuations, salinity, alkalinity, and mineral and metal toxicity [10]. Thus, NPs, especially Au counterparts, can mimic the activity of antioxidant enzymes working as nano-enzymes in mitigating the oxidative stress [59]. Furthermore, cerium NPs (CeO NPs) could increase the tolerance against abiotic stress in plants by regulating essential pathways. Thus, CeO NPs are well-suitable to mitigate the effects of excessive ROS production by acting as ROS scavengers when transitioning easily between the Ce^{3+} and Ce^{4+} oxidation states [60,61]. Wu et al. [62] demonstrated that CeO NPs could increase *Arabidopsis* plants tolerance to salinity stress by directly acting on the cytosolic Na^+/K^+ ratio (improving K^+ retention and reducing Na^+ efflux), resulting in improving plant leaf photosynthetic performance and biomass. Additionally, phytohormones play important roles in responses against abiotic stress [33]. Silica NPs loaded with abscisic acid resulted in prolonged release of the exogenous cargo in *Arabidopsis thaliana* plants, improving the drought resistance in seedlings [63]. In addition to the enzymatic defence system against abiotic stress provided by the NPs indicated so far, titanium dioxide NPs (TiO_2 NPs) protect plants by using an alternative gene regulation mechanism. For example, TiO_2 NPs were able to trigger the expression of essential non-coding RNA to protect plants in response to heavy metal stress [64].

Considerations and challenges for real-field applications

While the published results in the field of nanotechnology in agriculture are increasingly promising, and there are already numerous patents and commercial products available [54], it is difficult to adapt such products into practical applications in the field. First, research work in this area tends to be highly complex and requires multidisciplinary teams with expertise in chemistry, physics, biology, and agronomy, among others, along with the use of sophisticated equipment (e.g. particle accelerators — synchrotrons). Second, the behaviour of nanomaterials can depend significantly on factors such as plant species and physiology so results obtained from one crop (especially regarding NFs) may not be directly applicable to others [39]. Third, agriculture often operates on tight profit margins, so the cost of using nanomaterials for large-scale field applications must be relatively low, otherwise, farmers may not be able to adopt them [39,54]. Additionally, it is crucial to consider the potential environmental impact and food safety of these products, which has resulted in a growing trend towards using natural nanomaterials (biopolymers) that are non-toxic and easily degradable [39,54].

Finally, one of the major challenges is the application of many of these nanodevices to crops, as it often incurs additional costs for farmers. A nanoagrochemical should ideally be applicable in the same way as conventional agrochemicals (using machinery, irrigation, etc.), depending on its mode of action and function. However, it would be highly advantageous if they could be incorporated as seed coatings, which would significantly reduce costs. Nanobiosensors can be more problematic in this regard, as specific methods would need to be designed for their release onto crops; some of them may be useless or may be too costly in many situations, such as non-invasive electronic systems on leaves, unless they are used for perennial crops (e.g. fruit trees).

To address many of these challenges, it is imperative to develop research focused on field applications [39,54]. Many of the studies conducted so far lack real-field trials and are limited to extrapolating results obtained in the laboratory or under controlled conditions (greenhouses or growth chambers). Field trials in agronomy are equivalent to clinical trials in medicine, and even if a product performs well in the laboratory, it does not guarantee effectiveness under real conditions, or there may be challenges in its manufacturing and/or

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distribution. Therefore, conducting experiments with different crops in experimental plots, comparing them to conventional products to assess efficiency, and following the usual practices of farmers is the only way to validate whether a nanotechnology application will have a significant impact on agriculture.

Summary

- The study of NFs–plant interaction is an important point to consider in the understanding of the physiological and biochemical responses in plants.
- Nanobiosensors and NFs have the potential to revolutionise farming practices and contribute to sustainable and efficient agriculture.
- Continued research and development in nanotechnology for agriculture is needed to address challenges such as climate change, crop yield plateaus, and negative environmental impacts.
- There is a requirement to execute large trials based on the lack of knowledge in some critical areas such as toxicity and bioaccumulation of the NFs and physico-chemical interaction of NFs with soil.
- Governments should develop open awareness programs to educate farmers and consumers about nanotechnology for its successful implementation in agriculture. This way, people, and specially farmers, would not be as reluctant to purchase products developed using the technology of novel NFs-based agrochemicals.

Competing Interests
The authors declare that there are no competing interests associated with the manuscript.

Abbreviations
CDs, carbon dots; NFs, nanoformulations; NP, nanoparticle; QDs, quantum dots; RNAi, RNA interference.

References

1 Shang, Y., Hasan, M.K., Ahammed, G.J., Li, M., Yin, H. and Zhou, J. (2019) Applications of nanotechnology in plant growth and crop protection: a review. *Molecules* **24**, 2558 https://doi.org/10.3390/molecules24142558
2 Kwak, S.Y., Wong, M.H., Lew, T.T., Bisker, G., Lee, M.A., Kaplan, A. et al. (2017) Nanosensor technology applied to living plant systems. *Annu. Rev. Anal. Chem.* **10**, 113–140 https://doi.org/10.1146/annurev-anchem-061516-045310
3 Zhang, X., Zhang, J. and Zhu, K.Y. (2010) Chitosan/double-stranded RNA nanoparticle-mediated RNA interference to silence chitin synthase genes through larval feeding in the African malaria mosquito (*Anopheles gambiae*). *Insect Mol. Biol.* **19**, 683–693 https://doi.org/10.1111/j.1365-2583.2010.01029.x
4 Majumdar, S. and Keller, A.A. (2021) Omics to address the opportunities and challenges of nanotechnology in agriculture. *Crit. Rev. Environ. Sci. Technol.* **51**, 2595–2636 https://doi.org/10.1080/10643389.2020.1785264
5 Shawon, Z.B., Hoque, M.E. and Chowdhury, S.R. (2020) Nanosensors and nanobiosensors: Agricultural and food technology aspects. In *Nanofabrication for Smart Nanosensor Applications* (Pal, K. and Gomes, F., eds), pp. 135–161, Elsevier, Amsterdam
6 Kashyap, P.L., Kumar, S., Jasrotia, P., Singh, D.P. and Singh, G.P. (2019) Nanosensors for Plant Disease Diagnosis: Current Understanding and Future Perspectives. In *Nanoscience for Sustainable Agriculture* (Pudake, R., Chauhan, N. and Kole, C., eds), Springer, Cham (Switzerland) https://doi.org/10.1007/978-3-319-97852-9_9
7 Li, Z., Yu, T., Paul, R., Fan, J., Yang, Y. and Wei, Q. (2020) Agricultural nanodiagnostics for plant diseases: recent advances and challenges. *Nanoscale Adv.* **2**, 3083–3094 https://doi.org/10.1039/C9NA00724E
8 Chhipa, H. (2019) Applications of nanotechnology in agriculture. *Methods Microbiol.* **46**, 115–142 https://doi.org/10.1016/bs.mim.2019.01.002
9 Wang, D., Saleh, N.B., Byro, A., Zepp, R., Sahle-Demessie, E., Luxton, T.P. et al. (2022) Nano-enabled pesticides for sustainable agriculture and global food security. *Nat. Nanotechnol.* **17**, 347–360 https://doi.org/10.1038/s41565-022-01082-8
10 Mittal, D., Kaur, G., Singh, P., Yadav, K. and Ali, S.A. (2020) Nanoparticle-based sustainable agriculture and food science: recent advances and future outlook. *Front. Nanotechnol.* **2**, 579954 https://doi.org/10.3389/fnano.2020.579954
11 Rai, V., Acharya, S. and Dey, N. (2012) Implications of nanobiosensors in agriculture. *J. Biomater. Nanobiotechnol.* **3**, 315–324 https://doi.org/10.4236/jbnb.2012.322039

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12 Kumaravel, A. and Chandrasekaran, M. (2011) A biocompatible nano TiO_2/nafion composite modified glassy carbon electrode for the detection of fenitrothion. *J. Electroanal. Chem.* **650**, 163–170 https://doi.org/10.1016/j.jelechem.2010.10.013
13 Joshi, K.A., Tang, J., Haddon, R., Wang, J., Chen, W. and Mulchandani, A. (2005) A disposable biosensor for organophosphorus nerve agents based on carbon nanotubes modified thick film strip electrode. *Electroanalysis* **17**, 54–58 https://doi.org/10.1002/elan.200403118
14 Viswanathan, S., Radecka, H. and Radecki, J. (2009) Electrochemical biosensor for pesticides based on acetylcholinesterase immobilized on polyaniline deposited on vertically assembled carbon nanotubes wrapped with ssDNA. *Biosens. Bioelectron.* **24**, 2772–2777 https://doi.org/10.1016/j.bios.2009.01.044
15 Deng, H., Hong, G., Lin, F., Liu, A., Xia, X. and Chen, W. (2016) Colorimetric detection of urea, urease, and urease inhibitor based on the peroxidase-like activity of gold nanoparticles. *Anal. Chim. Acta* **915**, 74–80 https://doi.org/10.1016/j.aca.2016.02.008
16 Lee, K., Park, J., Lee, M.S., Kim, J., Hyun, B.G., Kang, D.J. et al. (2014) *In-situ* synthesis of carbon nanotube–graphite electronic devices and their integrations onto surfaces of live plants and insects. *Nano Lett.* **14**, 2647–2654 https://doi.org/10.1021/nl500513n
17 Khaledian, S., Nikkhah, M., Shams-bakhsh, M. and Hoseinzadeh, S. (2017) A sensitive biosensor based on gold nanoparticles to detect *Ralstonia solanacearum* in soil. *J. Gen. Plant Pathol.* **83**, 231–239 https://doi.org/10.1007/s10327-017-0721-z
18 Zhao, Y., Liu, L., Kong, D., Kuang, H., Wang, L. and Xu, C. (2014) Dual amplified electrochemical immunosensor for highly sensitive detection of *Pantoea stewartii* subsp. *stewartii*. *ACS Appl. Mater. Interfaces* **6**, 21178–21183 https://doi.org/10.1021/am506104r
19 Yüksel, S., Schwenkbier, L., Pollok, S., Weber, K., Cialla-May, D. and Popp, J. (2015) Label-free detection of *Phytophthora ramorum* using surface-enhanced Raman spectroscopy. *Analyst* **140**, 7254–7262 https://doi.org/10.1039/C5AN01156F
20 Siddiquee, S., Rovina, K., Yusof, N.A., Rodrigues, K.F. and Suryani, S. (2014) Nanoparticle-enhanced electrochemical biosensor with DNA immobilization and hybridization of *Trichoderma harzianum* gene. *Sensing Biosens. Res.* **2**, 16–22 https://doi.org/10.1016/j.sbsr.2014.06.002
21 Safarnejad, M.R., Samiee, F., Tabatabie, M. and Mohsenifar, A. (2017) Development of quantum dot-based nanobiosensors against *citrus tristeza virus* (CTV). *Sens. Transducers* **213**, 54 https://www.sensorsportal.com/HTML/DIGEST/P_RP_0227.htm
22 Liang, Y., Duan, Y., Fan, C., Dong, H., Yang, J., Tang, J. et al. (2019) Preparation of kasugamycin conjugation based on ZnO quantum dots for improving its effective utilization. *Chem. Eng. J.* **361**, 671–679 https://doi.org/10.1016/j.cej.2018.12.129
23 Giraldo, J.P., Wu, H., Newkirk, G.M. and Kruss, S. (2019) Nanobiotechnology approaches for engineering smart plant sensors. *Nat. Nanotechnol.* **14**, 541–553 https://doi.org/10.1038/s41565-019-0470-6
24 Shukla, P., Chaurasia, P., Younis, K., Qadri, O.S., Faridi, S.A. and Srivastava, G. (2019) Nanotechnology in sustainable agriculture: studies from seed priming to post-harvest management. *Nanotechnol. Environ. Eng.* **4**, 1–5 https://doi.org/10.1007/s41204-019-0058-2
25 Duhan, J.S., Kumar, R., Kumar, N., Kaur, P., Nehra, K. and Duhan, S. (2017) Nanotechnology: the new perspective in precision agriculture. *Biotechnol. Rep.* **15**, 11–23 https://doi.org/10.1016/j.btre.2017.03.002
26 Kaushal, M. and Wani, S.P. (2017) Nanosensors: frontiers in precision agriculture. In *Nanotechnology: an Agricultural Paradigm* (Prasad, R., Kumar, M., Kumar, V., eds), pp. 279–291, Springer, Singapore
27 Zulfiqar, F., Navarro, M., Ashraf, M., Akram, N.A. and Munné-Bosch, S. (2019) Nanofertilizer use for sustainable agriculture: advantages and limitations. *Plant Sci.* **289**, 110270 https://doi.org/10.1016/j.plantsci.2019.110270
28 Arora, S., Murmu, G., Mukherjee, K., Saha, S. and Maity, D. (2022) A comprehensive overview of nanotechnology in sustainable agriculture. *J. Biotechnol.* **355**, 21–41 https://doi.org/10.1016/j.jbiotec.2022.06.007
29 Uqab, B., Mudasir, S. and Nazir, R. (2016) Review on bioremediation of pesticides. *J. Bioremediat. Biodegrad.* **7**, 2 https://doi.org/10.4172/2155-6199.1000343
30 Vurro, M., Miguel-Rojas, C. and Pérez-de-Luque, A. (2019) Safe nanotechnologies for increasing the effectiveness of environmentally friendly natural agrochemicals. *Pest Manag. Sci.* **75**, 2403–2412 https://doi.org/10.1002/ps.5348
31 Pinto, T.V., Silva, C.A., Siquenique, S. and Learmonth, D.A. (2022) Micro-and nanocarriers for encapsulation of biological plant protection agents: a systematic literature review. *ACS Agric. Sci. Technol.* **2**, 838–857 https://doi.org/10.1021/acsagscitech.2c00113
32 Pérez-de-Luque, A. (2023) Can nanotechnology improve the application of bioherbicides? *Pest Manag. Sci.* https://doi.org/10.1002/ps.7526
33 Sampedro-Guerrero, J., Vives-Peris, V., Gomez-Cadenas, A. and Clausell-Terol, C. (2023) Efficient strategies for controlled release of nanoencapsulated phytohormones to improve plant stress tolerance. *Plant Methods* **19**, 1–20 https://doi.org/10.1186/s13007-023-01025-x
34 Li, Q., Li, X. and Zhao, C. (2020) Strategies to obtain encapsulation and controlled release of small hydrophilic molecules. *Front. Bioeng. Biotechnol.* **8**, 437 https://doi.org/10.3389/fbioe.2020.00437
35 Mandaji, C.M., da Silva Pena, R. and Chisté, R.C. (2022) Encapsulation of bioactive compounds extracted from plants of genus Hibiscus: a review of selected techniques and applications. *Food Res. Int.* **151**, 110820 https://doi.org/10.1016/j.foodres.2021.110820
36 Mujtaba, M., Wang, D., Carvalho, L.B., Oliveira, J.L., Espirito Santo Pereira, A.D., Sharif, R. et al. (2021) Nanocarrier-mediated delivery of miRNA, RNAi, and CRISPR-Cas for plant protection: current trends and future directions. *ACS Agric. Sci. Technol.* **1**, 417–435 https://doi.org/10.1021/acsagscitech.1c00146
37 Zhang, J., Li, H., Zhong, X., Tian, J., Segers, A., Xia, L. et al. (2022) RNA-interference-mediated aphid control in crop plants: a review. *Agriculture* **12**, 2108 https://doi.org/10.3390/agriculture12122108
38 Han, H.S., Koo, S.Y. and Choi, K.Y. (2022) Emerging nanoformulation strategies for phytocompounds and applications from drug delivery to phototherapy to imaging. *Bioact. Mater.* **14**, 182–205 https://doi.org/10.1016/j.bioactmat.2021.11.027
39 Pérez-de-Luque, A. (2017) Interaction of nanomaterials with plants: what do we need for real applications in agriculture? *Front. Environ. Sci.* **5**, 12 https://doi.org/10.3389/fenvs.2017.00012
40 Cifuentes, Z., Custardoy, L., de la Fuente, J.M., Marquina, C., Ibarra, M.R., Rubiales, D. et al. (2010) Absorption and translocation to the aerial part of magnetic carbon-coated nanoparticles through the root of different crop plants. *J. Nanobiotechnol.* **8**, 1–8 https://doi.org/10.1186/1477-3155-8-26
41 Larue, C., Veronesi, G., Flank, A.M., Surble, S., Herlin-Boime, N. and Carrière, M. (2012) Comparative uptake and impact of TiO2 nanoparticles in wheat and rapeseed. *J. Toxicol. Environ. Health A* **75**, 722–734 https://doi.org/10.1080/15287394.2012.689800
42 Ramírez-Rodríguez, G.B., Miguel-Rojas, C., Montanha, G.S., Carmona, F.J., Dal Sasso, G., Sillero, J.C. et al. (2020) Reducing nitrogen dosage in *Triticum durum* plants with urea-doped nanofertilizers. *Nanomaterials* **10**, 1043 https://doi.org/10.3390/nano10061043

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https://doi.org/10.1042/ETLS20230070

43 Giroto, A.S., Guimarães, G.G., Foschini, M. and Ribeiro, C. (2017) Role of slow-release nanocomposite fertilizers on nitrogen and phosphate availability in soil. *Sci. Rep.* **7**, 46032 https://doi.org/10.1038/srep46032

44 Nandini, B., Hariprasad, P., Prakash, H.S., Shetty, H.S. and Geetha, N. (2017) Trichogenic-selenium nanoparticles enhance disease suppressive ability of *Trichoderma* against downy mildew disease caused by *Sclerospora graminicola* in pearl millet. *Sci. Rep.* **7**, 2612 https://doi.org/10.1038/s41598-017-02737-6

45 Lezcano, M., Al-Soufi, W., Novo, M., Rodríguez-Núñez, E. and Tato, J.V. (2002) Complexation of several benzimidazole-type fungicides with α- and β-cyclodextrins. *J. Agric. Food Chem.* **50**, 108–112 https://doi.org/10.1021/jf010927y

46 Pérez-de-Luque, A., Cifuentes, Z., Beckstead, J.A., Sillero, J.C., Ávila, C., Rubio, J. et al. (2012) Effect of amphotericin B nanodisks on plant fungal diseases. *Pest Manag. Sci.* **68**, 67–74 https://doi.org/10.1002/ps.2222

47 Kumar, S., Bhanjana, G., Sharma, A., Sidhu, M.C. and Dilbaghi, N. (2014) Synthesis, characterization and on field evaluation of pesticide loaded sodium alginate nanoparticles. *Carbohydr. Polym.* **101**, 1061–1067 https://doi.org/10.1016/j.carbpol.2013.10.025

48 Ulrichs, C., Krause, F., Rocksch, T., Goswami, A. and Mewis, I. (2006) Electrostatic application of inert silica dust based insecticides onto plant surfaces. *Commun. Agric. Appl. Biol. Sci.* **71**, 171–178 https://pubmed.ncbi.nlm.nih.gov/17390789/

49 bin Hussein, M.Z., Yahaya, A.H., Zainal, Z. and Kian, L.H. (2005) Nanocomposite-based controlled release formulation of an herbicide, 2, 4-dichlorophenoxyacetate incapsulated in zinc–aluminium-layered double hydroxide. *Sci. Technol. Adv. Mater.* **6**, 956 https://doi.org/10.1016/j.stam.2005.09.004

50 Maruyama, C.R., Guilger, M., Pascoli, M., Bileshy-José, N., Abhilash, P.C., Fraceto, L.F. et al. (2016) Nanoparticles based on chitosan as carriers for the combined herbicides imazapic and imazapyr. *Sci. Rep.* **6**, 19768 https://doi.org/10.1038/srep19768

51 Imada, K., Sakai, S., Kajihara, H., Tanaka, S. and Ito, S. (2016) Magnesium oxide nanoparticles induce systemic resistance in tomato against bacterial wilt disease. *Plant Pathol.* **65**, 551–560 https://doi.org/10.1111/ppa.12443

52 Mitter, N., Worrall, E.A., Robinson, K.E., Li, P., Jain, R.G., Taochy, C. et al. (2017) Clay nanosheets for topical delivery of RNAi for sustained protection against plant viruses. *Nat. Plants* **3**, 16207 https://doi.org/10.1038/nplants.2016.207

53 Cao, J., Guenther, R.H., Sit, T.L., Lommel, S.A., Opperman, C.H. and Willoughby, J.A. (2015) Development of abamectin loaded plant virus nanoparticles for efficacious plant parasitic nematode control. *ACS Appl. Mater. Interfaces* **7**, 9546–9553 https://doi.org/10.1021/acsami.5b00940

54 Kah, M., Tufenkji, N. and White, J.C. (2019) Nano-enabled strategies to enhance crop nutrition and protection. *Nat. Nanotechnol.* **14**, 532–540 https://doi.org/10.1038/s41565-019-0439-5

55 Ramírez-Rodríguez, G.B., Dal Sasso, G., Carmona, F.J., Miguel-Rojas, C., Pérez-de-Luque, A., Masciocchi, N. et al. (2020) Engineering biomimetic calcium phosphate nanoparticles: a green synthesis of slow-release multinutrient (NPK) nanofertilizers. *ACS Appl. Bio Mater.* **3**, 1344–1353 https://doi.org/10.1021/acsabm.9b00937

56 Pestovsky, Y.S. and Martínez-Antonio, A. (2017) The use of nanoparticles and nanoformulations in agriculture. *J. Nanosci. Nanotechnol.* **17**, 8699–8730 https://doi.org/10.1166/jnn.2017.15041

57 Pérez-de-Luque, A. (2020) Guest edited collection: nanotechnology in agriculture. *Sci. Rep.* **10**, 15738 https://doi.org/10.1038/s41598-020-73198-7

58 Siddiqui, M.H., Al-Whaibi, M.H., Faisal, M. and Al Sahli, A.A. (2014) Nano-silicon dioxide mitigates the adverse effects of salt stress on *Cucurbita pepo* L. *Environ. Toxicol. Chem.* **33**, 2429–2437 https://doi.org/10.1002/etc.2697

59 Sharifi, M., Faryabi, K., Talaei, A.J., Shekha, M.S., Ale-Ebrahim, M., Salihi, A. et al. (2020) Antioxidant properties of gold nanozyme: a review. *J. Mol. Liquids* **297**, 112004 https://doi.org/10.1016/j.molliq.2019.112004

60 Saxena, R., Tomar, R.S. and Kumar, M. (2016) Exploring nanobiotechnology to mitigate abiotic stress in crop plants. *J. Pharm. Sci. Res.* **8**, 974–980 https://www.jpsr.pharmainfo.in/Documents/Volumes/vol8Issue09/jpsr08091607.pdf

61 Collin, B., Auffan, M., Johnson, A.C., Kaur, I., Keller, A.A., Lazareva, A. et al. (2014) Environmental release, fate and ecotoxicological effects of manufactured ceria nanomaterials. *Environ. Sci. Nano* **1**, 533–548 https://doi.org/10.1039/C4EN00149D

62 Wu, H., Shabala, L., Shabala, S. and Giraldo, J.P. (2018) Hydroxyl radical scavenging by cerium oxide nanoparticles improves *Arabidopsis* salinity tolerance by enhancing leaf mesophyll potassium retention. *Environ. Sci. Nano* **5**, 1567–1583 https://doi.org/10.1039/C8EN00323H

63 Sun, D., Hussain, H.I., Yi, Z., Rookes, J.E., Kong, L. and Cahill, D.M. (2018) Delivery of abscisic acid to plants using glutathione responsive mesoporous silica nanoparticles. *J. Nanosci. Nanotechnol.* **18**, 1615–1625 https://doi.org/10.1166/jnn.2018.14262

64 Frazier, T.P., Burklew, C.E. and Zhang, B. (2014) Titanium dioxide nanoparticles affect the growth and microRNA expression of tobacco (*Nicotiana tabacum*). *Funct. Integr. Genomics* **14**, 75–83 https://doi.org/10.1007/s10142-013-0341-4

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