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Field Application of ZnO and TiO_2 Nanoparticles on Agricultural Plants

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Abstract: Engineered nanoparticles (ENPs) have potential application in precision farming and sustainable agriculture. Studies have shown that ENPs enhance the efficiency of the delivery of agrochemicals and thus, have the potential to positively affect the environment, thereby improving the growth and health of the crops. However, the majority of the research on the effects of ENPs on plants and in agricultural applications have been limited to controlled laboratory conditions. These conditions do not fully consider various aspects inherent to the growth of agricultural plants in fields under changing weather and climate. Some of the most investigated ENPs in the agricultural research area are ZnO nanoparticles (ZnO NPs) and TiO_2 nanoparticles (TiO_2 NPs). ZnO NPs have the potential to increase crop production and stress resistance, mainly by the slow release of Zn ions to crops. Unlike ZnO NPs, TiO_2 NPs have less well-understood means of action, and are generally considered as plant growth promoter. This mini review presents information compiled for ZnO and TiO_2 NPs, their influence on agricultural plants with emphasis on particularly effect on plant growth, nutrient distribution and pollution remediation under field conditions. It is concluded that in order to gain a broader perspective, more field studies are needed, particularly multigeneration studies, to fully understand the effects of the ENPs on agricultural plants' growth and improvement of their health.

Keywords: crops; nanofertilizer; foliar application; field research; nanoparticle; plant health; crop production

1. Introduction

Nanotechnology plays an increasingly important role in most areas of human activity. Engineered nanoparticles (ENPs) have catalytic, photovoltaic, energetic, and sensory applications in diverse industries [1–8]. Moreover, biomedicine utilises ENPs as part of nano-vaccines, drug delivery, and diagnostic systems [9–12]. However, our knowledge about the effects of nanoparticles (NPs), especially ENPs, in the agricultural sector is still relatively sparingly explored and investigated.

The interaction of ENPs with plants has been studied for about two decades. The initial research articles were mostly focused on the toxicity of ENPs on the plants; nevertheless, there were also few articles discussing their potential beneficial effects on crops [13–16]. At the same time, the first articles about the biosynthesis of nanomaterials by plants or plants extracts were published [17], which were partially inspired by the observations that NPs naturally form in the rhizosphere of plants [18,19]. At first, toxicity tests focused mostly on the short-term effects of the ENPs in seeds, seedlings, and young plants [20]. Early reviews concerned with ecotoxicology towards plants were published around the year 2008 [21–24] and were mostly concerned with research on the plant toxicity and interactions that were lacking for the higher plants at that time. The early studies on beneficial effects showed that, at optimum concentrations, ENPs might improve enzyme activities, photosynthesis, nitrogen absorption, and growth parameters of early seedlings [14,15,25–27].

Moreover, the preliminary reports on the effect of ENPs on plants grown in fields were published between the years 2010 and 2015 [28]. These studies showed the need to explore further the effects and interaction of ENPs under more realistic conditions as the underlying trend from laboratory experiments involved the application of higher doses of the nanoparticles which were toxic to the plants. In contrast, at appropriate lower concentrations, many ENPs were found to positively affect the plants' growth, health, and quality [28,29]. For example, TiO_2 NPs applied on barley during stem elongation and a second time during the four-leaf stage at concentrations of 0.01 to 0.03% increased grain yield and the weight of 1000 grains [30]. Peanut plants also responded positively to low concentrations of ZnO NPs, and higher concentrations of 2000 mg $Zn \cdot L^{-1}$ revealed inhibitory effects [29]. Mostly, both ZnO and TiO_2 NPs are only toxic at high concentrations, i.e., concentrations higher than 2000 $mg \cdot L^{-1}$ [29]. Thus, both types of nanoparticles were found to be interesting for further field application, and their properties were also studied in this context. In recent studies on the interaction of ENPs with plants, the application of low, yet still effective, concentrations of ZnO and TiO_2 NPs was investigated [31,32], and a new avenue of research was opened, where these nanomaterials can be applied not only to promote growth and agricultural productivity but also to alleviate abiotic and biotic stresses [33–35]. Both ZnO and TiO_2 NPs were found to alleviate stresses caused by drought and heavy metals such as Cd. Further, these studies were performed under field conditions [33–35].

This mini review aims to summarise and discuss the finding of the field application of one of the most commonly used ENPs, ZnO and TiO_2 NPs, on agricultural plants. Application methods of ENPs to plants are briefly compared, and ENP effects on the growth, health, and yields of plants are discussed for both ZnO and TiO_2 NPs. Some of the areas that need further investigation are low and effective concentrations of ENPs and spray additives such as adjuvants that may enhance the foliar application of ENPs. More research on the application of ENPs in field conditions is also needed to increase the knowledge about the benefits and risks of using ENPs in agriculture and to help us produce crops sustainably.

2. ZnO NPs and Application in Agriculture

ZnO NPs are an amphoteric semiconductive material with a wide band gap (Eg = 3.37 eV) [36]. Because of their unique properties, such as high binding energy, refractive index, thermal conductivity, piezoelectric nature, high absorbance of UV light, and antibacterial properties, these are widely used in various applications [37]. Moreover, as an added advantage, the above-mentioned properties are highly tuneable. Their size can be altered from a few nanometres to the upper limit of nanoparticle size definition (100 nm), and their shape can be easily adjusted by selecting the appropriate method of synthesis [37]. Different synthesis techniques have been used to produce ZnO NPs, including mechanochemical processes, controlled precipitation, sol-gel, solvothermal, hydrothermal methods, methods using emulsions and microemulsions, growing from a gas phase, pyrolysis spray methods, and others [37]. A broad range of shapes, such as flowerlike structures, nanorods, nanotubes and spherical or oblong nanoparticles, can be easily synthesised [37,38]. The surface of ZnO NPs is often modified to enhance their stability in colloidal suspension, to improve their positive effects on plants and to reduce their potential toxicity. The modification of their surface can be obtained by treatment with the inorganic compounds such as SiO_2, Al_2O_3, etc., simple organic compounds, e.g., silanes or organic acids, and by more complex polymeric matrices [37]. Often biosynthesis of ZnO NPs is selected for agricultural applications since it is anticipated to create eco-benign nanomaterial [39]. Bare and surface-modified ZnO NPs were used in the laboratory, greenhouse, and field experiments on crop plants due to their UV protective, and antimicrobial properties besides their nutritional role as slow releasing Zn source for plants [31,38–42]. ZnO NPs easily dissolve compared with some other ENPs [43], such as TiO_2 NPs, which affect plant health partly by their nano-specific properties, but also in larger part by the release of the Zn, which is essential to many processes on the cellular level [44]. In addition, ZnO NPs are reported to have an ability to decrease the effect of environmental stresses on plants, such as drought [45], temperature [46], metals, metalloids [47,48], and salt [49]. When applied at suitable concentrations, ZnO NPs increase plants' seed germination [50], growth [51], the activity of antioxidants and protein production [52,53], chlorophyll content [54] and photosynthesis [55], production of oils and seeds [31,32], and uptake of essential elements [56].

3. TiO_2 NPs and Application in Agriculture

TiO_2 NPs are insoluble semiconductive material with a high refractive index, UV absorption, photocatalytic, and antimicrobial properties. These have highly tuneable properties partially because these ENPs exhibit diverse crystal symmetries represented by mineral phases such as anatase, brookite, or rutile. Each crystal structure has unique features that can benefit its application; most commonly, the suitable mineral form is selected for its lower or higher photocatalytic ability [57]. The size can be adjusted from a few nanometres up to 100 nm in any dimension, and the shape of TiO_2 NPs can be tuned during their synthesis to obtain both nanorods and spherical nanoparticles [58]. Different types of synthesis protocols have been used for the production of TiO_2 NPs to create nanomaterials of specific properties, e.g., sol, sol-gel, micelle, solvothermal, and hydrothermal methods, vapour deposition, and many others [59]. Because of their properties, TiO_2 NPs have a wide range of applications in diverse fields of human activity, including agriculture. Similar to ZnO NPs, surface properties of TiO_2 NPs are often modified to help with their stability or to increase their positive effects and decrease their toxicity [57–59]. Their environmental applications include water purification, degradation of pollutants, antimicrobial coating, biosensing, and drug delivery [60–64]. TiO_2 NPs have been applied to protect seeds, enhance plant growth and germination, control crop diseases [65], degrade pesticides and detect their residues [66]. In addition, these NPs have been reported to increase root and shoot growth, seed or produce yield, and improve plant health. An increase in chlorophyll production, soluble leaf protein [67], and carotenoids content [68], and increase in uptake of several essential elements [69] was also reported. Environmental stresses, such as drought in wheat [70] and high Cd levels in maize [71], were also alleviated significantly with the use of TiO_2 NPs.

4. Application of ENPs in Field Conditions

ENPs can be applied to plants in three different ways when grown in field conditions: (1) seed application, (2) soil application, and (3) foliar application. Sometimes, seed application is combined with either soil or foliar application [72]. Most of the time, the foliar application is preferred since a much lower concentration of ENPs is sufficient to obtain positive effects for plants. ENPs are not transformed to less available forms in soil, and this application carries less risk of contaminating the soil by high concentrations of ENPs on their multi-year use [42]. Nevertheless, even foliar application carries its own risks; namely, the application can be potentially dangerous for unprotected workers applying the spray. If it is applied under windy conditions, there is a risk of air pollution for the surrounding area [42]. When foliar and soil application was compared for maize by Umar et al. [73], foliar application improved the grain Zn concentration more. However, soil application was also effective, and the differences between the application were found to be non-significant in other measured parameters, such as plant height, fresh and dry weight of shoots, photosynthetic and transpiration rate [73]. Foliar application has its own quirks. Good timing for foliar application needs to be selected, and various times of application and number of applications were chosen in the field studies [30,53,73,74]. Usually, more than one application of ENPs (i.e., up to three times) was sprayed on plants for one growing season in reviewed studies [29,54,73]. Even though more applications may be preferable, a foliar application may lead to the degradation of leaf structures by photocatalytic properties of ENPs [75], and multiple applications are labour intensive and less economically viable [76]. The application of the ENPs was made during several different growth stages, including leaf development, four-leaf stage, 6–9 leaf stage, stem elongation, flower-bud formation [30,53,73] or just the date after sowing was mentioned without a reference to an external source with recommendation [29] or no reference to the time of application at all [74]. The selection times of the ENPs applications often follow the literature on the growth stages of plants, such as Meier [77]. Both morning and evening/night applications have their own reason to be chosen. Mostly, an application under the low wind, no rain, and low humidity conditions is preferred. In the morning, the temperature is low, and plant stomata are open. Thus, there is a greater chance of ENP absorption. However, sunlight may increase evaporation, degradation of ENP surface coatings [78], and photo corrosion of ENPs [79] that may lead to diminished gains when compared with night application. At some locations, night-time may be the only time where the aforementioned conditions can be met. Research performed on conventional fertilisers or pesticides does not provide a clear answer to day-timing and is either inconclusive or mostly species-specific and specific to applied fertiliser or herbicide. Thus, research regarding the time of application during a day will be needed in the future [80–83]. The range of ENP concentrations applied on leaves have been diverse, and ranged from a relatively low (2.6 $mg \cdot L^{-1}$) [31,32] to a relatively high concentration of 2000 $mg \cdot L^{-1}$ [73]. There is also an indication from pot experiments that multiple applications of ENPs on plants have a better effect on plant growth and health. Further, multiple applications can be performed at a lower concentration of the ENPs in total, which reduces the costs of ENPs and the risk of soil contamination [72]. The combined application of ZnO NPs along with iron oxide NPs was more effective compared with the application of just ZnO NPs or iron oxide NPs [74]. When it comes to the application itself, TiO_2 NPs and ZnO NPs were applied as aqueous suspensions [73,84], or adjuvants were added to the colloidal solution to facilitate the penetration of nanoparticles across wax sub-structures [31,32]. The influence of the surface functionalisation of ENPs and additives such as adjuvants in the suspension may result in improvement in growth and other agriculturally important parameters [33,54]. The surface functionalisation of ENPs can improve the dispersion and stability of NPs and can allow the tailored incorporation of compounds or moieties on NPs surface, acting as plant stimulants [85]. For this and other reasons, the application of biologically synthesised ENPs is a trend in fertilisers and other agrichemicals [31–33]. Properties affecting the application of ENPs on leaves in field conditions can be viewed in Figure 1.

4.1. Seed Application and Effects

To date, only a few studies have been published that were concerned with the field application of ZnO NPs (Table 1) or TiO_2 NPs (Table 2). However, none of the field studies were performed on the effect of seed application of these ENPs. Seed application is made via soaking of the seed with ENP suspension of different concentrations. Its purpose is to either provide easily available micronutrients in the case of ZnO NPs or to protect the seed via the catalytic and antimicrobial effects of ZnO and TiO_2 NPs [25,29,72]. These ENPs improve seed germination and the seed vigour index, as well as plant height, growth and the dry weight of roots, and growth and the dry weight of shoots at later stages [25,29,72]. Effective concentrations are plant species dependant, but, for example, were found to be 400 to 1000 mg·L^{-1} for ZnO NPs in peanuts [29], and 500 to 4000 mg·L^{-1} for TiO_2 NPs in spinach [25]. Yet, since there are no published field studies, there is a lack of knowledge concerning the real-world effects of such application.

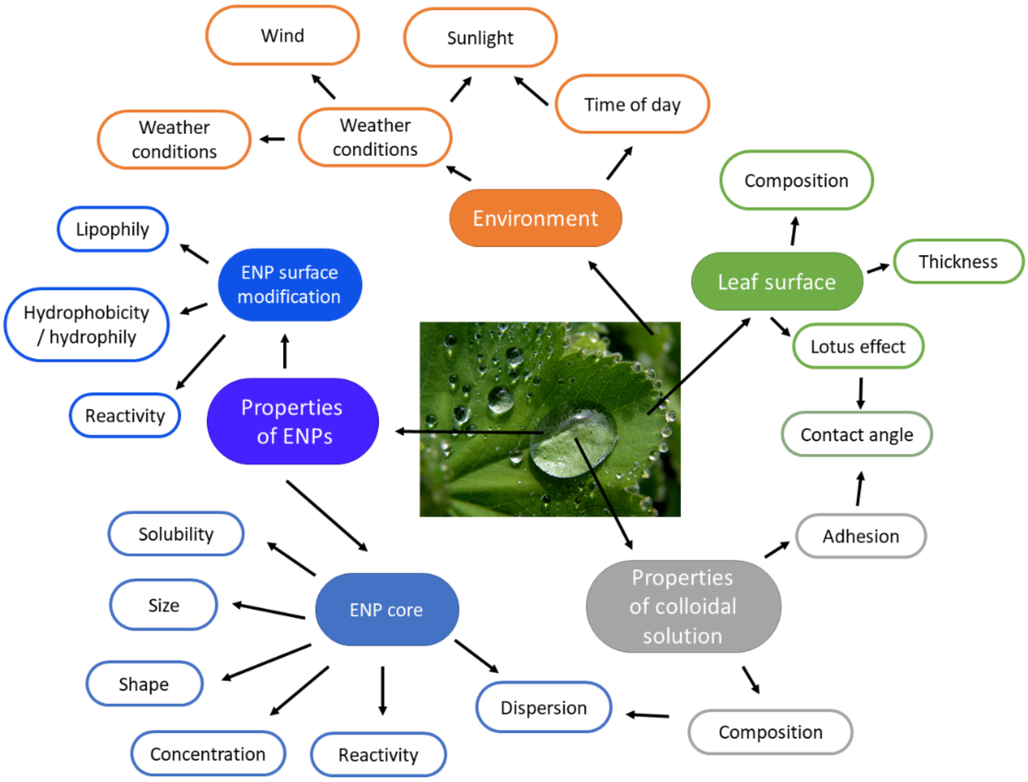

Figure 1. Properties affecting the application of ENPs on leaves in field conditions.

Table 1. Effects of ZnO NPs in higher plants grown under the field conditions.

Plant Name	Size of ZnO NPs	Additional Compounds	Concentrations	Type of Application	Number of Times Applied	Effects of ZnO NPs	Reference
Arachis hypogaea L.	25 nm	no	133 mg Zn·L^{-1}	Foliar	2	Increased plant height, pods per plant, filled pods per plant	[29]
Zea mays L.	25 nm	no	50, 100, 200, **400**, 600, 800, 1000, 1500, 2000 mg Zn·L^{-1}	Foliar	2	Increased plant height, leaf area, dry weight, grain yield, cob length	[86]
Daucus carota L.	n.a.	no	50, 100, **150** mg ZnO·L^{-1}	Foliar	1	Increased plant height, number of leaves	[74]
Setaria italica L.	20 nm	adjuvant SILWET STAR®	2.6 mg Zn·L^{-1}	Foliar	2	Increased total nitrogen, content of oil, dry mass, decreased content of starch	[32]
Helianthus annuus L.	20 nm	adjuvant SILWET STAR®	2.6 mg Zn·L^{-1}	Foliar	2	Differences in leaf surfaces' trichomes diversity, ratio, width, and length, increase in head diameter, weight of dry seed head, weight of thousand seeds, grain yield, content of oil	[31]

Table 1. *Cont.*

Plant Name	Size of ZnO NPs	Additional Compounds	Concentrations	Type of Application	Number of Times Applied	Effects of ZnO NPs	Reference
Linum usitatissimum L.	<40 nm	no	20, **40**, **60** mg ZnO·L^{-1}	Foliar	2	Increased shoot length, fresh and dry weight, root length, fresh and dry weight, number of fruiting branches, capsules, biological yield per plant, seed and straw yield, weight of 1000 seeds, oil content, seed, oil, biological and straw yield	[84]
Zea mays L.	30–70 nm (width), 160 nm (length)	no	Soil: 8 kg Zn·ha^{-1} **Foliar: 2% Zn solution**	Soil or foliar	1	Improved maize growth, yield and grain Zn contents, increased chlorophyll contents, maximum value of photosynthetic rate, transpiration rate	[73]
Triticum aestivum L.	20–30 nm	no	25 mg Zn·l^{-1}	Foliar	3	Enhanced wheat growth, yield, nutrients uptake, chlorophyll, carotenoids contents and antioxidants activities and reduced electrolyte leakage under Cd stress	[34]

The **bold** marks the concentration with the highest positive effects.

Table 2. Effects of TiO_2 NPs in higher plants grown under the field conditions.

Plant Name	Size of TiO_2 NPs	Additional Compounds	Concentrations	Type of Application	Number of Times Applied	Effects of TiO_2 NPs	Reference
Hordeum vulgare L.	n.a.	no	100, 200, **300** mg·L^{-1}	Foliar	2	Increased plant height, grain yield, dry biomass, weight of 1000 grains	[30]
Coriandrum sativum L.	20 nm	no	2, 4, **6** mg·L^{-1}	Foliar	2	Increased the plant height, number of branches, fruit yield, increase in amino acids, total sugars, total phenols, total indoles, and pigments	[87]
Hordeum vulgare L.	<100 nm	no	2000 mg·L^{-1}	Foliar	2	Increased days to anthesis, chlorophyll content, straw yield, number of grains per spike	[88]
Vitis vinifera L.	28 nm	no	1000 mg·L^{-1}	Foliar	1	Metabolic (nonstomatal) inhibition of the photosynthesis	[89]
Vitis vinifera L.	28 nm	no	1000 mg·L^{-1}	Foliar	1	Boosted the total phenolic content and biosynthesis of the leaf flavanols, increased K, Mg, Ca, B, and Mn levels	[90]
Helianthus annuus L.	20–30 nm	adjuvant SILWET STAR®	2.6 mg·L^{-1}	Foliar	2	Increased head diameter, dry-seed head weight, yield and thousand seed weight, increased oil content, improvement in physiological parameters	[31]

Table 2. *Cont.*

Plant Name	Size of TiO_2 NPs	Additional Compounds	Concentrations	Type of Application	Number of Times Applied	Effects of TiO_2 NPs	Reference
Triticum aestivum L.	10–13 nm 6–8 nm	Leaf extract surface modification during synthesis	100 mg·L^{-1}	Foliar	2	Increased straw and grain yields, chlorophyll contents, plant height, reduced oxidative stress under Cd stress, decreased Cd in wheat straw, roots, grains, better effect by green synthesised NPs	[33]
Helianthus annuus L.	<25 nm	no	25, **50** mg·L^{-1}	Foliar	2	Alleviated adverse effect of water deficiency stress on growth, achene quality and biodiesel yield	[35]

The **bold** marks the concentration with the highest positive effects.

4.2. Soil Application and Root Path

ENPs can be applied directly to the soil to improve the growth and vitality of plants that absorb them or the released nutrients from them via the root system. At the root interface, larger nanoparticles mostly attach to the surface and may release nutrients via dissolution, and smaller nanoparticles can be absorbed and transported along apoplast or symplast pathways [42,65]. Root application is highly influenced by the complex soil environment, and ENPs are more prone to aggregation, or they can be attached to particle surfaces and unavailable for plants. Moreover, soil and or rhizosphere microbial communities may be influenced [42,65]. Because of all of these factors, not many soil applications of ENPs were made under field conditions, and we report only one instance of root application of ZnO NPs and no TiO_2 NP root application. Umar et al. [73] tried both soil and foliar application of ZnO NPs on maize. Foliar treatment of ZnO NPs has shown the highest increase in grain Zn concentrations and the highest chlorophyll content. Other parameters were also higher compared with both control and soil application. However, soil and foliar application were not significantly different. Soil application improved shoot fresh and dry weight, root dry weight, transpiration rate, photosynthetic rate, and chlorophyll content [73].

4.3. Foliar Application and Translocation Path

ENPs applied on leaves are mostly translocated to plants via stomata or, more rarely, cuticle structures [42,65]. In the case of ZnO NPs, the Zn may be slowly released from these ENPs and absorbed in its ionic species [73]. Depending on their size and dissolution, they can be translocated to other parts of a plant [42,65].

Most often, ZnO NPs were applied at two important stages of plant growth. The first application is mostly made during the leaf development stage, e.g., day 27 after sowing for foxtail millet [32] and day 40 for sunflower [31]. The second application is mainly performed during the stem elongation phase before flowering, such as day 53 for foxtail millet [32] and day 80 for sunflower [31]. Just one application at the stage of leaf growth was studied by Umar et al. [73]. Moreover, the application of ZnO NPs at three different stages of plant growth during the growing season was studied by Hussain et al. [34]. TiO_2 NPs, of which Ti is neither considered an essential element nor are easily dissolvable [91], share many similar positive effects on plants with ZnO NPs. To the best of our knowledge, and similar to the ZnO NPs, only a few studies have been performed with the application of TiO_2 NPs in field conditions, and all of them used foliar application as the preferred method to deliver the ENPs. One or two applications were used at important stages of plant growth (Table 2).

The available reports demonstrated the concentration-dependent efficacy, and hence, different concentrations of ZnO NPs were used in the studies. A high concentration, 2%

Zn solution, was found to be effective in application on maize [73]. However, most of the studies were conducted involving the application of ZnO NPs within the concentration range of 20 to 150 mg·L^{-1} [29,34,74,84]. In addition, it was observed that ZnO NPs can be highly effective even at a low concentration of 2.6 mg·L^{-1}, increasing plant health and yields, including enhanced oil content in foxtail millet and sunflower, and weight of a thousand seeds, grain yields, and head diameter in sunflower [31,32].

Three different concentration ranges of TiO_2 NPs were used to improve plants' growth and yield parameters and health [30,31,87–90]. At high concentrations of 1000 or 2000 mg·L^{-1} of TiO_2 NPs, both positive and negative effects of the TiO_2 NPs were observed [88–90]. Teszlák et al. [89] observed inhibition of photosynthesis when they applied TiO_2 NPs at 1000 mg·L^{-1} to a grapevine. However, at the same time, they also observed a higher content of K, Ca, Mg, and P in leaves treated with TiO_2 NPs. In their follow up study, in addition to increased K, Mg, Ca, B, and Mn micronutrient levels in leaves, Kőrösi et al. [90] also found that TiO_2 NPs induced photocatalytic stress that improved the antioxidant capacity and phenolic content in the leaves of the grapevine. Kőrösi et al. [90] proposed that the proper dosage of TiO_2 NPs may positively affect the upregulation of antioxidant defence, and their photoactivity destroys the pathogens on leaves. Moreover, TiO_2 NP upregulation of antioxidant defence reduced oxidative stress under heightened Cd concentrations and decreased Cd amounts in wheat straw, roots, and grains, which may help with the growth of cereals in areas where the soil is contaminated with Cd [33].

In other studies, the application of TiO_2 NPs at a lower concentration range of 25 to 300 mg·L^{-1} was found to have promising positive effects on plant height, straw and grain yields, dry biomass, the weight of 1000 grains, and chlorophyll contents [30,33,35]. The TiO_2 NPs at these concentrations also helped to manage water stress, probably via the build-up of phenolic compounds in leaves. Phenolic compounds stabilise reactive oxygen species in plant cells and increase cell wall thickness, which slows the movement of water out of the cells [35]. In addition, TiO_2 NPs synthesised by the green method with plant extracts exhibited a significantly better effect when compared with TiO_2 NPs synthesised via the sol-gel method [33]. It was proposed that this effect can be caused by the presence of the plant extract traces on the TiO_2 NPs surface or their slightly smaller size (6 to 8 nm for green synthesised TiO_2 NPs compared with 10 to 13 nm for chemically synthesised ones) [33].

Low concentrations of TiO_2 NPs, i.e., 2 to 6 mg·L^{-1} were also used, and these were reported to affect physiological and yield parameters positively, such as head diameter, dry-seed head weight, yield and thousand seed weight, increased oil content in sunflower [31] Moreover, these were also found to increase the plant height, a number of branches, fruit yield, increase in amino acids, total sugars, total phenols, total indoles, and pigments in coriander [87]. The results of these two studies showed that TiO_2 NPs can be used at very low concentrations, which should be beneficial for financial reasons, and the potential risk of soil contamination with TiO_2 NPs. Additionally, the application of such low concentrations can significantly lower the risk of toxicity towards people or animals who would consume the treated crops.

Compared with a conventional source of Zn at the same concentration, such as soluble $ZnSO_4$ or bulk (microparticulate) ZnO, foliar application of ZnO NPs was found to be more effective in increasing the dry weight of shoots, photosynthetic rate, transpiration, and chlorophyll values in maize and the foliar application was observed to be better than their soil application [73]. However, the cob weight in maize was improved more via soil application of ZnO NPs compared with foliar application. Other yield parameters were mostly exhibited statistically insignificant differences between soil and foliar applications [73]. ZnO NPs have a similar penetration and translocation of Zn within plants compared with dissolved $ZnSO_4$, and these are generally better translocated through plants than their bulk counterparts which can result in higher concentrations of Zn in stem, leaves and grains [73]. Yet, not all studies result in ZnO NPs being a superior application technique to their bulk counterparts. For example, according to Sadak and Bakry [84], the soil-applied

ZnO NPs did not improve plant growth parameters over bulk ZnO. ZnO NPs sometimes show improvement over conventional dissolvable forms of Zn. When these were administered to maize at lower concentrations of 400 mg $Zn{\cdot}L^{-1}$, compared with 2000 mg $Zn{\cdot}L^{-1}$ applied in the form of $ZnSO_4$. The NPs provided a noticeable increase in plant height, leaf area, dry weight, grain yield, cob length, and a number of grains per row [86]. Similarly, Prasad et al. [29] found that just 133 mg $Zn{\cdot}L^{-1}$ of ZnO NPs of foliar spray performed better than 2000 mg $Zn{\cdot}L^{-1}$ of chelated Zn when applied on peanut plants.

ZnO NPs supplement essential micronutrient Zn to crops mostly to enhance their growth and yields. Likewise, this supplemented Zn can be transported in plants to edible parts such as leaves, seeds, fruit, or other edible parts. Prasad et al. [29] reported a 2-fold increase in the content of zinc in both leaves and kernel of peanut treated by foliar application of ZnO NPs Zn compared with control. In maize, the application of ZnO NPs at 100 mg $Zn{\cdot}L^{-1}$ resulted in 37% higher Zn accumulation in grains [86]. Similarly, after foliar application of ZnO NPs at 2000 mg $Zn{\cdot}L^{-1}$, Umar et al. [73] observed increased concentrations of Zn in maize grains up to 82% over control. Foliar application of Zn on wheat resulted in approximately 59% higher concentration in grains compared with control [34].

In addition to increasing yields, ZnO NPs may be used in cases when the soil is contaminated with Cd since their foliar application reduced the Cd uptake in grain and improved the grain quality of wheat. ZnO NPs were also used in combination with other NPs, Fe based and Si-based NPs, and when used together, these ENPs had a positive synergistic effect on the amelioration of Cd stress [34].

5. Conclusions and Future Research Needs

The ZnO and TiO_2 NPs can be used as highly effective and inexpensive alternatives to conventional fertilisers with great potential to enhance plant growth and health and to lower the applied materials at the same time. The ENPs can offer an effective strategy to increase micronutrient uptake to edible plant parts and, thus, prevent malnutrition. However, when applied on leaves, ZnO and TiO_2 NPs being photoreactive, their dosage and high solar exposure may boost antioxidant systems in leaves but also may overwhelm the defence systems and result in damage at higher doses. Thus, further research and development of the use of low and still effective concentrations of ZnO and TiO_2 NPs, adjuvants that help with absorption, and ENPs that protect plants from abiotic stresses are still needed to utilise their potential to have larger-scale economic implications. ENPs exhibit the potential to significantly improve the agricultural yields even at relatively low concentrations; yet, there are still some risks to the consumers or the plants these ENPs are applied on that need to be further studied. Because of this, more thorough studies on dose-dependent responses under the field conditions are needed, with emphasis on lower concentrations applied. Field experiments with ENPs are still relatively sparse; hence, further extensive studies in this field are urgently required to fully understand the scale and different aspects that pertain to their potential to improve agriculture. More research also needs to be performed to mitigate potential unwanted effects during foliar application of ENPs that can lead to contamination of the surrounding area to ensure that the foliar application of ENPs is in line with environmental goals of soil protection and climate crisis mitigation. One of the avenues to decrease the risk of ENPs, is their green synthesis with biomolecules of bacteria, algae, fungi, or plants. However, only a few studies have compared such effects, and there are still some knowledge gaps that should be studied more thoroughly. For example, it is not yet known if the increased positive effects of biosynthesised ENPs come from the reduction in their size. The effects may also come from the surface functionalisation of ENPs by the extracts used in their synthesis that contain biomolecules that can improve the health of plants. The ENPs act via slowly releasing essential nutrients and their effect is also derived from their nanoscale size. In the future, studies on multiple generations of plants should be undertaken to assess the potential safety risks in the long term.

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References

1. Ayati, A.; Ahmadpour, A.; Bamoharram, F.F.; Tanhaei, B.; Mänttäri, M.; Sillanpää, M. A review on catalytic applications of Au/TiO_2 nanoparticles in the removal of water pollutant. *Chemosphere* **2014**, *107*, 163–174. [CrossRef]
2. Moezzi, A.; McDonagh, A.M.; Cortie, M.B. Zinc oxide particles: Synthesis, properties and applications. *Chem. Eng. J.* **2012**, *185–186*, 1–22. [CrossRef]
3. Williams, B.P.; Qi, Z.; Huang, W.; Tsung, C.-K. The impact of synthetic method on the catalytic application of intermetallic nanoparticles. *Nanoscale* **2020**, *12*, 18545–18562. [CrossRef] [PubMed]
4. Sutarlie, L.; Ow, S.Y.; Su, X. Nanomaterials-based biosensors for detection of microorganisms and microbial toxins. *Biotechnol. J.* **2017**, *12*. [CrossRef] [PubMed]
5. Ismael, M. A review and recent advances in solar-to-hydrogen energy conversion based on photocatalytic water splitting over doped-TiO_2 nanoparticles. *Sol. Energy* **2020**, *211*, 522–546. [CrossRef]
6. Esfe, M.H.; Kamyab, M.H.; Valadkhani, M. Application of nanofluids and fluids in photovoltaic thermal system: An updated review. *Sol. Energy* **2020**, *199*, 796–818. [CrossRef]
7. Vinitha, V.; Preeyanghaa, M.; Vinesh, V.; Dhanalakshmi, R.; Neppolian, B.; Sivamurugan, V. Two is better than one: Catalytic, sensing and optical applications of doped zinc oxide nanostructures. *Emergent Mater.* **2021**. [CrossRef]
8. Selvakumar, D.; Nagaraju, P.; Arivanandhan, M.; Jayavel, R. Metal oxide–grafted graphene nanocomposites for energy storage applications. *Emergent Mater.* **2021**. [CrossRef]
9. Pippa, N.; Gazouli, M.; Pispas, S. Recent Advances and Future Perspectives in Polymer-Based Nanovaccines. *Vaccines* **2021**, *9*, 558. [CrossRef]
10. Wang, W.; Liu, X.; Zheng, X.; Jin, H.J.; Li, X. Biomineralization: An Opportunity and Challenge of Nanoparticle Drug Delivery Systems for Cancer Therapy. *Adv. Healthc. Mater.* **2020**, *9*, 2001117. [CrossRef]
11. Wu, X.; Yang, H.; Yang, W.; Chen, X.; Gao, J.; Gong, X.; Wang, H.; Duan, Y.; Wei, D.; Chang, J. Nanoparticle-based diagnostic and therapeutic systems for brain tumors. *J. Mater. Chem. B* **2019**, *7*, 4734–4750. [CrossRef] [PubMed]
12. Antunes, A.; Popelka, A.; Aljarod, O.; Hassan, M.K.; Kasak, P.; Luyt, A.S. Accelerated Weathering Effects on Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PHBV/TiO2 Nanocomposites. *Polymers* **2020**, *12*, 1743. [CrossRef] [PubMed]
13. Changmei, L.; Chaoying, Z.; Junqiang, W.; Guorong, W.; Mingxuan, T. Research of the effect of nanometer materials on germination and growth enhancement of Glycine max and its mechanism. *Soybean Sci.* **2002**, *21*, 168–171.
14. Hong, F.; Yang, F.; Liu, C.; Gao, Q.; Wan, Z.; Gu, F.; Wu, C.; Ma, Z.; Zhou, J.; Yang, P. Influences of Nano-TiO_2 on the chloroplast aging of spinach under light. *Biol. Trace Elem. Res.* **2005**, *104*, 249–260. [CrossRef]
15. Hong, F.; Zhou, J.; Liu, C.; Yang, F.; Wu, C.; Zheng, L.; Yang, P. Effect of nano-TiO_2 on photochemical reaction of chloroplasts of spinach. *Biol. Trace Elem. Res.* **2005**, *105*, 269–279. [CrossRef]
16. Yang, L.; Watts, D.J. Particle surface characteristics may play an important role in phytotoxicity of alumina nanoparticles. *Toxicol. Lett.* **2005**, *158*, 122–132. [CrossRef]
17. Shankar, S.S.; Ahmad, A.; Sastry, M. Geranium Leaf Assisted Biosynthesis of Silver Nanoparticles. *Biotechnol. Prog.* **2003**, *19*, 1627–1631. [CrossRef]
18. Manceau, A.; Nagy, K.L.; Marcus, M.A.; Lanson, M.; Geoffroy, N.; Jacquet, T.; Kirpichtchikova, T. Formation of Metallic Copper Nanoparticles at the Soil−Root Interface. *Environ. Sci. Technol.* **2008**, *42*, 1766–1772. [CrossRef]
19. Lanson, B.; Marcus, M.A.; Fakra, S.; Panfili, F.; Geoffroy, N.; Manceau, A. Formation of Zn–Ca phyllomanganate nanoparticles in grass roots. *Geochim. Cosmochim. Acta* **2008**, *72*, 2478–2490. [CrossRef]
20. Lin, D.H.; Xing, B.S. Phytotoxicity of nanoparticles: Inhibition of seed germination and root growth. *Environ. Pollut.* **2007**, *150*, 243–250. [CrossRef]

21. Klaine, S.J.; Alvarez, P.J.J.; Batley, G.E.; Fernandes, T.F.; Handy, R.D.; Lyon, D.Y.; Mahendra, S.; McLaughlin, M.J.; Lead, J.R. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* **2008**, *27*, 1825–1851. [CrossRef]
22. Handy, R.D.; von der Kammer, F.; Lead, J.R.; Hassellöv, M.; Owen, R.; Crane, M. The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology* **2008**, *17*, 287–314. [CrossRef] [PubMed]
23. Navarro, E.; Baun, A.; Behra, R.; Hartmann, N.B.; Filser, J.; Miao, A.-J.; Quigg, A.; Santschi, P.H.; Sigg, L. Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. *Ecotoxicology* **2008**, *17*, 372–386. [CrossRef]
24. Handy, R.D.; Owen, R.; Valsami-Jones, E. The ecotoxicology of nanoparticles and nanomaterials: Current status, knowledge gaps, challenges, and future needs. *Ecotoxicology* **2008**, *17*, 315–325. [CrossRef] [PubMed]
25. Zheng, L.; Hong, F.; Lu, S.; Liu, C. Effect of nano-TiO_2 on strength of naturally aged seeds and growth of spinach. *Biol. Trace Elem. Res.* **2005**, *104*, 83–91. [CrossRef]
26. Gao, F.; Hong, F.; Liu, C.; Zheng, L.; Su, M.; Wu, X.; Yang, F.; Wu, C.; Yang, P. Mechanism of nano-anatase TiO_2 on promoting photosynthetic carbon reaction of spinach: Inducing complex of Rubisco-Rubisco activase. *Biol. Trace Elem. Res.* **2006**, *111*, 239–253. [CrossRef]
27. Yang, F.; Hong, F.; You, W.; Liu, C.; Gao, F.; Wu, C.; Yang, P. Influence of nano-anatase TiO_2 on the nitrogen metabolism of growing spinach. *Biol. Trace Elem. Res.* **2006**, *110*, 179–190. [CrossRef]
28. Du, W.; Gardea-Torresdey, J.L.; Ji, R.; Yin, Y.; Zhu, J.; Peralta-Videa, J.R.; Guo, H. Physiological and Biochemical Changes Imposed by CeO_2 Nanoparticles on Wheat: A Life Cycle Field Study. *Environ. Sci. Technol.* **2015**, *49*, 11884–11893. [CrossRef]
29. Prasad, T.N.V.K.V.; Sudhakar, P.; Sreenivasulu, Y.; Latha, P.; Munaswamy, V.; Reddy, K.R.; Sreeprasad, T.S.; Sajanlal, P.R.; Pradeep, T. Effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut. *J. Plant Nutr.* **2012**, *35*, 905–927. [CrossRef]
30. Moaveni, P.; Farahani, H.A.; Maroufi, K. Effect of TiO_2 nanoparticles spraying on barley (*Hordeum vulgare* L.) under field condition. *Adv. Environ. Biol.* **2011**, *5*, 2220–2223.
31. Kolenčík, M.; Ernst, D.; Urík, M.; Ďurišová, L'.; Bujdoš, M.; Šebesta, M.; Dobročka, E.; Kšiňan, S.; Illa, R.; Qian, Y.; et al. Foliar Application of Low Concentrations of Titanium Dioxide and Zinc Oxide Nanoparticles to the Common Sunflower under Field Conditions. *Nanomaterials* **2020**, *10*, 1619. [CrossRef] [PubMed]
32. Kolenčík, M.; Ernst, D.; Komár, M.; Urík, M.; Šebesta, M.; Dobročka, E.E.; Černý, I.; Illa, R.; Kanike, R.; Qian, Y.; et al. Effect of foliar spray application of zinc oxide nanoparticles on quantitative, nutritional, and physiological parameters of foxtail millet (Setaria italica l.) under field conditions. *Nanomaterials* **2019**, *9*, 1559. [CrossRef]
33. Irshad, M.A.; ur Rehman, M.Z.; Anwar-ul-Haq, M.; Rizwan, M.; Nawaz, R.; Shakoor, M.B.; Wijaya, L.; Alyemeni, M.N.; Ahmad, P.; Ali, S. Effect of green and chemically synthesized titanium dioxide nanoparticles on cadmium accumulation in wheat grains and potential dietary health risk: A field investigation. *J. Hazard. Mater.* **2021**, *415*, 125585. [CrossRef]
34. Hussain, A.; Rizwan, M.; Ali, S.; ur Rehman, M.Z.; Qayyum, M.F.; Nawaz, R.; Ahmad, A.; Asrar, M.; Ahmad, S.R.; Alsahli, A.A.; et al. Combined use of different nanoparticles effectively decreased cadmium (Cd) concentration in grains of wheat grown in a field contaminated with Cd. *Ecotoxicol. Environ. Saf.* **2021**, *215*, 112139. [CrossRef] [PubMed]
35. Khattak, A.; Ullah, F.; Shinwari, Z.K.; Mehmood, S. The effect of titanium dioxide nanoparticles and salicylic acid on growth and biodiesel production potential of sunflower (*Helianthus annuus* L.) under water stress. *Pak. J. Bot.* **2021**, *53*, 1987–1995. [CrossRef]
36. Klingshirn, C.; Fallert, J.; Zhou, H.; Sartor, J.; Thiele, C.; Maier-Flaig, F.; Schneider, D.; Kalt, H. 65 years of ZnO research—Old and very recent results. *Phys. Status Solidi* **2010**, *247*, 1424–1447. [CrossRef]
37. Kołodziejczak-Radzimska, A.; Jesionowski, T. Zinc Oxide—From Synthesis to Application: A Review. *Materials* **2014**, *7*, 2833. [CrossRef]
38. Sabir, S.; Arshad, M.; Chaudhari, S.K. Zinc oxide nanoparticles for revolutionizing agriculture: Synthesis and applications. *Sci. World J.* **2014**, *2014*, 8. [CrossRef] [PubMed]
39. Saravanan, A.; Kumar, P.S.; Karishma, S.; Vo, D.V.N.; Jeevanantham, S.; Yaashikaa, P.R.; George, C.S. A review on biosynthesis of metal nanoparticles and its environmental applications. *Chemosphere* **2021**, *264*, 128580. [CrossRef]
40. Tarafdar, J.C.; Agrawal, A.; Raliya, R.; Kumar, P.; Burman, U.; Kaul, R.K. ZnO Nanoparticles Induced Synthesis of Polysaccharides and Phosphatases by Aspergillus Fungi. *Adv. Sci. Eng. Med.* **2012**, *4*, 324–328. [CrossRef]
41. Raliya, R.; Tarafdar, J.C. ZnO Nanoparticle Biosynthesis and Its Effect on Phosphorous-Mobilizing Enzyme Secretion and Gum Contents in Clusterbean (*Cyamopsis tetragonoloba* L.). *Agric. Res.* **2013**, *2*, 48–57. [CrossRef]
42. Raliya, R.; Saharan, V.; Dimkpa, C.; Biswas, P. Nanofertilizer for Precision and Sustainable Agriculture: Current State and Future Perspectives. *J. Agric. Food Chem.* **2018**, *66*, 6487–6503. [CrossRef] [PubMed]
43. Bian, S.-W.W.; Mudunkotuwa, I.A.; Rupasinghe, T.; Grassian, V.H. Aggregation and Dissolution of 4 nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid. *Langmuir* **2011**, *27*, 6059–6068. [CrossRef]
44. Singh, P.; Arif, Y.; Siddiqui, H.; Sami, F.; Zaidi, R.; Azam, A.; Alam, P.; Hayat, S. Nanoparticles enhances the salinity toxicity tolerance in *Linum usitatissimum* L. by modulating the antioxidative enzymes, photosynthetic efficiency, redox status and cellular damage. *Ecotoxicol. Environ. Saf.* **2021**, *213*, 112020. [CrossRef]

45. Dimkpa, C.O.; Andrews, J.; Sanabria, J.; Bindraban, P.S.; Singh, U.; Elmer, W.H.; Gardea-Torresdey, J.L.; White, J.C. Interactive effects of drought, organic fertilizer, and zinc oxide nanoscale and bulk particles on wheat performance and grain nutrient accumulation. *Sci. Total Environ.* **2020**, *722*, 137808. [CrossRef] [PubMed]
46. Hassan, N.S.; El Din, T.A.S.; Hendawey, M.H.; Borai, I.H.; Mahdi, A.A. Magnetite and Zinc Oxide Nanoparticles Alleviated Heat Stress in Wheat Plants. *Curr. Nanomater.* **2018**, *3*, 32–43. [CrossRef]
47. Rizwan, M.; Ali, S.; Zia ur Rehman, M.; Adrees, M.; Arshad, M.; Qayyum, M.F.; Ali, L.; Hussain, A.; Chatha, S.A.S.; Imran, M. Alleviation of cadmium accumulation in maize (*Zea mays* L.) by foliar spray of zinc oxide nanoparticles and biochar to contaminated soil. *Environ. Pollut.* **2019**, *248*, 358–367. [CrossRef]
48. Rizwan, M.; Ali, S.; ur Rehman, M.Z.; Maqbool, A. A critical review on the effects of zinc at toxic levels of cadmium in plants. *Environ. Sci. Pollut. Res.* **2019**, *26*, 6279–6289. [CrossRef]
49. Torabian, S.; Zahedi, M.; Khoshgoftarmanesh, A. Effect of Foliar Spray of Zinc Oxide on Some Antioxidant Enzymes Activity of Sunflower under Salt Stress. *J. Agric. Sci. Technol.* **2016**, *18*, 1013–1025.
50. García-López, J.I.; Zavala-García, F.; Olivares-Sáenz, E.; Lira-Saldívar, R.H.; Díaz Barriga-Castro, E.; Ruiz-Torres, N.A.; Ramos-Cortez, E.; Vázquez-Alvarado, R.; Niño-Medina, G. Zinc Oxide Nanoparticles Boosts Phenolic Compounds and Antioxidant Activity of *Capsicum annuum* L. during Germination. *Agronomy* **2018**, *8*, 215. [CrossRef]
51. Singh, J.; Kumar, S.; Alok, A.; Upadhyay, S.K.; Rawat, M.; Tsang, D.C.W.; Bolan, N.; Kim, K.-H. The potential of green synthesized zinc oxide nanoparticles as nutrient source for plant growth. *J. Clean. Prod.* **2019**, *214*, 1061–1070. [CrossRef]
52. Venkatachalam, P.; Priyanka, N.; Manikandan, K.; Ganeshbabu, I.; Indiraarulselvi, P.; Geetha, N.; Muralikrishna, K.; Bhattacharya, R.C.; Tiwari, M.; Sharma, N.; et al. Enhanced plant growth promoting role of phycomolecules coated zinc oxide nanoparticles with P supplementation in cotton (*Gossypium hirsutum* L.). *Plant Physiol. Biochem.* **2017**, *110*, 118–127. [CrossRef]
53. Salama, D.M.; Osman, S.A.; Abd El-Aziz, M.E.; Abd Elwahed, M.S.A.; Shaaban, E.A. Effect of zinc oxide nanoparticles on the growth, genomic DNA, production and the quality of common dry bean (Phaseolus vulgaris). *Biocatal. Agric. Biotechnol.* **2019**, *18*, 101083. [CrossRef]
54. Pullagurala, V.L.R.; Adisa, I.O.; Rawat, S.; Kalagara, S.; Hernandez-Viezcas, J.A.; Peralta-Videa, J.R.; Gardea-Torresdey, J.L. ZnO nanoparticles increase photosynthetic pigments and decrease lipid peroxidation in soil grown cilantro (Coriandrum sativum). *Plant Physiol. Biochem.* **2018**, *132*, 120–127. [CrossRef]
55. Faizan, M.; Faraz, A.; Yusuf, M.; Khan, S.T.; Hayat, S. Zinc oxide nanoparticle-mediated changes in photosynthetic efficiency and antioxidant system of tomato plants. *Photosynthetica* **2018**, *56*, 678–686. [CrossRef]
56. Peralta-Videa, J.R.; Hernandez-Viezcas, J.A.; Zhao, L.; Diaz, B.C.; Ge, Y.; Priester, J.H.; Holden, P.A.; Gardea-Torresdey, J.L. Cerium dioxide and zinc oxide nanoparticles alter the nutritional value of soil cultivated soybean plants. *Plant Physiol. Biochem.* **2014**, *80*, 128–135. [CrossRef] [PubMed]
57. Macwan, D.P.; Dave, P.N.; Chaturvedi, S. A review on nano-TiO_2 sol–gel type syntheses and its applications. *J. Mater. Sci.* **2011**, *46*, 3669–3686. [CrossRef]
58. Silva, R.M.; TeeSy, C.; Franzi, L.; Weir, A.; Westerhoff, P.; Evans, J.E.; Pinkerton, K.E. Biological Response to Nano-Scale Titanium Dioxide (TiO_2): Role of Particle Dose, Shape, and Retention. *J. Toxicol. Environ. Heal. Part A* **2013**, *76*, 953–972. [CrossRef]
59. Chen, X.; Mao, S.S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107*, 2891–2959. [CrossRef] [PubMed]
60. Mahlambi, M.M.; Ngila, C.J.; Mamba, B.B. Recent Developments in Environmental Photocatalytic Degradation of Organic Pollutants: The Case of Titanium Dioxide Nanoparticles—A Review. *J. Nanomater.* **2015**, *2015*, 790173. [CrossRef]
61. Han, C.; Lalley, J.; Namboodiri, D.; Cromer, K.; Nadagouda, M.N. Titanium dioxide-based antibacterial surfaces for water treatment. *Curr. Opin. Chem. Eng.* **2016**, *11*, 46–51. [CrossRef]
62. Yan, X.; Yuan, K.; Lu, N.; Xu, H.; Zhang, S.; Takeuchi, N.; Kobayashi, H.; Li, R. The interplay of sulfur doping and surface hydroxyl in band gap engineering: Mesoporous sulfur-doped TiO_2 coupled with magnetite as a recyclable, efficient, visible light active photocatalyst for water purification. *Appl. Catal. B Environ.* **2017**, *218*, 20–31. [CrossRef]
63. George, J.M.; Antony, A.; Mathew, B. Metal oxide nanoparticles in electrochemical sensing and biosensing: A review. *Microchim. Acta* **2018**, *185*, 358. [CrossRef]
64. Jarosz, M.; Pawlik, A.; Szuwarzyński, M.; Jaskuła, M.; Sulka, G.D. Nanoporous anodic titanium dioxide layers as potential drug delivery systems: Drug release kinetics and mechanism. *Colloids Surf. B Biointerfaces* **2016**, *143*, 447–454. [CrossRef] [PubMed]
65. Servin, A.; Elmer, W.; Mukherjee, A.; De la Torre-Roche, R.; Hamdi, H.; White, J.C.; Bindraban, P.; Dimkpa, C. A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield. *J. Nanoparticle Res.* **2015**, *17*, 92. [CrossRef]
66. Aragay, G.; Pino, F.; Merkoçi, A. Nanomaterials for Sensing and Destroying Pesticides. *Chem. Rev.* **2012**, *112*, 5317–5338. [CrossRef]
67. Raliya, R.; Biswas, P.; Tarafdar, J.C. TiO_2 nanoparticle biosynthesis and its physiological effect on mung bean (*Vigna radiata* L.). *Biotechnol. Rep.* **2015**, *5*, 22–26. [CrossRef] [PubMed]
68. Raliya, R.; Nair, R.; Chavalmane, S.; Wang, W.-N.; Biswas, P. Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (*Solanum lycopersicum* L.) plant. *Metallomics* **2015**, *7*, 1584–1594. [CrossRef] [PubMed]

69. Tan, W.; Du, W.; Barrios, A.C.; Armendariz, R.; Zuverza-Mena, N.; Ji, Z.; Chang, C.H.; Zink, J.I.; Hernandez-Viezcas, J.A.; Peralta-Videa, J.R.; et al. Surface coating changes the physiological and biochemical impacts of nano-TiO_2 in basil (Ocimum basilicum) plants. *Environ. Pollut.* **2017**, *222*, 64–72. [CrossRef]
70. Mustafa, H.; Ilyas, N.; Akhtar, N.; Raja, N.I.; Zainab, T.; Shah, T.; Ahmad, A.; Ahmad, P. Biosynthesis and characterization of titanium dioxide nanoparticles and its effects along with calcium phosphate on physicochemical attributes of wheat under drought stress. *Ecotoxicol. Environ. Saf.* **2021**, *223*, 112519. [CrossRef]
71. Lian, J.; Zhao, L.; Wu, J.; Xiong, H.; Bao, Y.; Zeb, A.; Tang, J.; Liu, W. Foliar spray of TiO_2 nanoparticles prevails over root application in reducing Cd accumulation and mitigating Cd-induced phytotoxicity in maize (*Zea mays* L.). *Chemosphere* **2020**, *239*, 124794. [CrossRef] [PubMed]
72. Mahdieh, M.; Sangi, M.R.; Bamdad, F.; Ghanem, A. Effect of seed and foliar application of nano-zinc oxide, zinc chelate, and zinc sulphate rates on yield and growth of pinto bean (Phaseolus vulgaris) cultivars. *J. Plant Nutr.* **2018**, *41*, 2401–2412. [CrossRef]
73. Umar, W.; Hameed, M.K.; Aziz, T.; Maqsood, M.A.; Bilal, H.M.; Rasheed, N. Synthesis, characterization and application of ZnO nanoparticles for improved growth and Zn biofortification in maize. *Arch. Agron. Soil Sci.* **2021**, *67*, 1164–1176. [CrossRef]
74. Elizabath, A.; Bahadur, V.; Misra, P.; Prasad, V.M.; Thomas, T. Effect of different concentrations of iron oxide and zinc oxide nanoparticles on growth and yield of carrot (*Daucus carota* L.). *J. Pharmacogn. Phytochem.* **2017**, *6*, 1266–1269.
75. Salehi, H.; Chehregani, A.; Lucini, L.; Majd, A.; Gholami, M. Morphological, proteomic and metabolomic insight into the effect of cerium dioxide nanoparticles to *Phaseolus vulgaris* L. under soil or foliar application. *Sci. Total Environ.* **2018**, *616–617*, 1540–1551. [CrossRef]
76. Fernández, V.; Brown, P.H. From plant surface to plant metabolism: The uncertain fate of foliar-applied nutrients. *Front. Plant Sci.* **2013**, *4*, 289. [CrossRef]
77. Meier, U. *Growth Stages of Mono-and Dicotyledonous Plants*; Blackwell Wissenschafts-Verlag: Berlin, Germany, 1997; ISBN 3826331524.
78. Guan, H.N.; Chi, D.F.; Yu, J.; Zhang, S.Y. Novel photodegradable insecticide W/TiO2/Avermectin nanocomposites obtained by polyelectrolytes assembly. *Colloids Surf. B Biointerfaces* **2011**, *83*, 148–154. [CrossRef]
79. Ma, H.; Wallis, L.K.; Diamond, S.; Li, S.; Canas-Carrell, J.; Parra, A. Impact of solar UV radiation on toxicity of ZnO nanoparticles through photocatalytic reactive oxygen species (ROS) generation and photo-induced dissolution. *Environ. Pollut.* **2014**, *193*, 165–172. [CrossRef]
80. Fageria, N.K.; Filho, M.P.B.; Moreira, A.; Guimarães, C.M. Foliar Fertilization of Crop Plants. *J. Plant Nutr.* **2009**, *32*, 1044–1064. [CrossRef]
81. Baligar, V.C.; Fageria, N.K.; He, Z.L. Nutrient use efficiency in plants. *Commun. Soil Sci. Plant Anal.* **2001**, *32*, 921–950. [CrossRef]
82. González-Melendi, P.; Fernández-Pacheco, R.; Coronado, M.J.; Corredor, E.; Testillano, P.S.; Risueño, M.C.; Marquina, C.; Ibarra, M.R.; Rubiales, D.; Pérez-de-Luque, A. Nanoparticles as smart treatment-delivery systems in plants: Assessment of different techniques of microscopy for their visualization in plant tissues. *Ann. Bot.* **2008**, *101*, 187–195. [CrossRef] [PubMed]
83. Fernández, V.; Eichert, T. Uptake of Hydrophilic Solutes Through Plant Leaves: Current State of Knowledge and Perspectives of Foliar Fertilization. *CRC Crit. Rev. Plant Sci.* **2009**, *28*, 36–68. [CrossRef]
84. Sadak, M.S.; Bakry, B.A. Zinc-oxide and nano ZnO oxide effects on growth, some biochemical aspects, yield quantity, and quality of flax (*Linum uitatissimum* L.) in absence and presence of compost under sandy soil. *Bull. Natl. Res. Cent.* **2020**, *44*, 98. [CrossRef]
85. Velasco, E.A.P.; Galindo, R.B.; Aguilar, L.A.V.; Fuentes, J.A.G.; Urbina, B.A.P.; Morales, S.A.L.; Valdés, S.S. Effects of the Morphology, Surface Modification and Application Methods of ZnO-NPs on the Growth and Biomass of Tomato Plants. *Molecules* **2020**, *25*, 1282. [CrossRef] [PubMed]
86. Subbaiah, L.V.; Prasad, T.N.V.K.V.; Krishna, T.G.; Sudhakar, P.; Reddy, B.R.; Pradeep, T. Novel Effects of Nanoparticulate Delivery of Zinc on Growth, Productivity, and Zinc Biofortification in Maize (*Zea mays* L.). *J. Agric. Food Chem.* **2016**, *64*, 3778–3788. [CrossRef] [PubMed]
87. Khater, M.S. Effect of Titanium Nanoparticles (TiO_2) on Growth, Yield and Chemical Constituents of Coriander Plants. *Arab J. Nucl. Sci. Appl.* **2015**, *48*, 187–194.
88. Janmohammadi, M.; Amanzadeh, T.; Sabaghnia, N.; Dashti, S. Impact of foliar application of nano micronutrient fertilizers and titanium dioxide nanoparticles on the growth and yield components of barley under supplemental irrigation. *Acta Agric. Slov.* **2016**, *107*, 265–276. [CrossRef]
89. Teszlák, P.; Kocsis, M.; Scarpellini, A.; Jakab, G.; Kőrösi, L. Foliar exposure of grapevine (*Vitis vinifera* L.) to TiO_2 nanoparticles under field conditions: Photosynthetic response and flavonol profile. *Photosynthetica* **2018**, *56*, 1378–1386. [CrossRef]
90. Kőrösi, L.; Bouderias, S.; Csepregi, K.; Bognár, B.; Teszlák, P.; Scarpellini, A.; Castelli, A.; Hideg, É.; Jakab, G. Nanostructured TiO_2-induced photocatalytic stress enhances the antioxidant capacity and phenolic content in the leaves of Vitis vinifera on a genotype-dependent manner. *J. Photochem. Photobiol. B Biol.* **2019**, *190*, 137–145. [CrossRef]
91. Zierden, M.R.; Valentine, A.M. Contemplating a role for titanium in organisms. *Metallomics* **2016**, *8*, 9–16. [CrossRef]