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An Insight of Zinc Oxide Nanoparticles (ZnO NPs): Green Synthesis, Characteristics and Agricultural Applications

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Nanoscience represents a highly esteemed and significant emerging domain within contemporary scientific advancements. Continuous research in nanotechnology facilitates the development and commercialization of various nanoproducts globally. The unique dimensions and properties of nanoparticles have garnered considerable attention on an international scale. Good transparency, high electron mobility, wide bandgap, high thermal and mechanical stability at room temperature and luminescence are some of the important properties of these nanoparticles. Zinc oxide nanoparticles (ZnO NPs) are particularly noteworthy due to their applications across diverse industries, including gas sensors, biosensors, cosmetics, drug delivery systems, and agricultural practices. ZnO NPs exhibit a broad spectrum of properties, encompassing optical, electrical, piezoelectric, physical, semiconducting, and antimicrobial characteristics. Furthermore, these nanoparticles hold substantial promise for enhancing agricultural productivity. ZnO NPs can be synthesized through various methods, including chemical, hydrothermal, and biological green synthesis techniques. Recently, there has been an increasing focus on the green synthesis of ZnO NPs utilizing different plant extracts or microbial interventions. This biobased approach is considered safer and more environmentally sustainable compared to traditional chemical and physical synthesis methods. This review article primarily addresses the green synthesis, characterization, and agricultural applications of ZnO NPs.

Keywords: Agricultural applications; Green synthesis; Nanoparticles; ZnO NPs.

In the current era, Nanotechnology is one of the most important emerging fields of science and technology. Its multifaceted applications can revolutionize the scientific world [1]. This technology has huge applications in various sectors like optics, electronics, biomedical science, agriculture, and some sectors of material sciences.

Nanotechnology deals with the fundamental and applied studies of nanostructures/nanoparticles, i.e. their synthesis, characterization, and applications in various sectors. The nanoparticles (NPs) are the atomic or molecular aggregates of basic elements usually having a size of not more than 100 nm. These NPs are derived forms of basic elements made by modifying them[2] and now have altered atomic and/or molecular properties[3]. The significantly unique properties of each NP invented so far, have motivated many scientists working in this developing field of nanoscience. So far, several metal oxide NPs have been produced having significant applications in various sectors (Fig. 1). In their efforts, few

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scientists has studied how fertilizers prepared from NPs behave in the field and also compared with other studies and recommended the use of nano-fertilizer for sustainable agriculture[4]. In a similar review report, overviewed the current status, challenges, and opportunities of NPs in agriculture to prepare nano-pesticides, nano-fertilizers, and detection of some plant diseases and agrochemicals in soil and plants[5]. Biogenic nanostructures have tremendous scope in improving the agricultural sector[6]. Some scientists are opining that NP-based smart fertilizers are very useful for sustainable agriculture with higher production[7-8]. Therefore, its fact proving that the metal NPs have immense applications in the agricultural sector and are useful for achieving goals of higher production and sustainable agricultural development [9] (Fig. 2).

Among several newly synthesized NPs, ZnO is considered as the most important ones in its nanostructure and applications[10].

Zinc oxide (ZnO) nanoparticles have a wide range of applications due to their unique physical and chemical properties. They are being used in biomedical applications[118], environmental applications, and industrial applications including applications in agriculture.

The present article is focused on various aspects of ZnO NPs including their green biosynthesis, characterization, properties, and applications in the agricultural sector.

Zinc oxide nanoparticles (ZnO NPs)

ZnO, or zinc oxide, is an inorganic substance. The main look of ZnO is that of a white, water-insoluble powder. Because of its special qualities, zinc oxide (ZnO) is frequently added to a wide range of products, including paints, ointments, ceramics, cements, lubricants, plastics, sealants, batteries, ferrites, and fire retardants. Additionally, it serves as a Zn nutrient in some foods[11].

Zinc oxide (ZnO) can be found in nature as zincites, which are found throughout the earth's lower crust. However, most commercially wanted ZnO, which is needed to make a variety of goods, is often made synthetically. In materials research, ZnO is typically referred to as an II–VI semiconductor due to its special qualities. Strong room-temperature luminescence, large band gap, high electron mobility, and superb transparency are only a few of the special qualities of ZnO semiconductors [12].

ZnO crystals are remarkable in that they feature a wurtzite (B4) type structure. The unit cell of the structure is hexagonal and has two lattice parameters. This structure exhibits the sp3 covalent bonding that results in the non-centrosymmetric structure[13–14]. Each anion is surrounded by four cations at the corners of the tetrahedron, with the tetrahedral coordination. It is the most prevalent and reliable ZnO structure. The other two crystalline forms of zinc oxide are rocksalt and cubic zincblende[15].

With an approximate hardness of 4.5 on the Mohs scale, zinc oxide is a relatively soft material[16]. Compared to other comparable III-V semiconductors, it has smaller elastic constants. Biosynthesized ZnO NPs come in a variety of shapes, such as rod-shaped, cubic, spherical, triangular, acicular, pyramid-like, hexagonal, spherical, and hexagonal wurtzite, among others. Accordingly, wurtzite, zinc-blende, and rock-salt are the three most well-known crystalline forms of ZnO (Fig. 3). The nano-structure sizes and various physical and chemical characters shown by ZnO NPs are well reported by earlier workers[15-16, 121].

Green Synthesis of ZnO NPs

At least one biological system is involved in every kind of green synthesis of nanoparticles. Green synthesis methods are less polluting, more economical, safer, and produce less pollution overall. Green synthesis is thought to be a secure substitute for NPs' chemical and physical synthesis. This method is ecofriendly and avoid use of toxic chemicals. In earlier reports, Singh et al.[17] concentrated on the biological synthesis and characterization of ZnO NPs. The green synthesis of nanoparticles (NPs) involves the use of various biological systems, such as fungi, yeast, bacteria, and higher plant extracts[18]. However, because it requires the precise and involved process of maintaining cell culture, intracellular synthesis, and multiple steps of purification, the synthesis of NPs using microbes is a little challenging.

Due to its lack of use of hazardous compounds or solvents and safety compared to traditional chemical and physical methods, green synthesis of nanoparticles has garnered a lot of attention recently. It is simple to scale up for higher production, environmentally friendly, and reasonably priced [19]. Toxic chemicals, energy, pressure, and high temperatures are not used while preparing nanoparticles using green synthesis [20].

The green approach reduces pollution risk by preventing the risk of producing waste along with desired products. In green synthesis, the primary focus is on the selection of reagents, that must be nature friendly. Undoubtedly, physical and chemical methods of production of NPs are quick, easy, and less laborious than green synthesis, which is better and environmentally affordable [21-24, 118]. Therefore, to achieve sustainable developmental goals, it is urgent to use eco-friendly green methods to reduce the pollution rinks and use green resources to produce the nanoparticles.

Plant-mediated synthesis of ZnO NPs

Plant-mediated synthesis of ZnO NPs involves use of plant extracts to facilitate the reduction of zinc ions into nanoparticles. This eco-friendly approach utilizes phytochemicals in plants, which act as both reducing agents and stabilizers, leading to the formation of ZnO NPs without the need for toxic chemicals.

The biological synthesis of nanoparticles through plant mediation is regarded as one of the most popular environmentally friendly processes. To produce the nanoparticles, the extract from the plants or plant parts must be combined with a metal salt solution (Fig. 3). Anatas and Warner[25] created ZnO NPs using an extract from *Coriandrum sativum* leaves in light-colored nanostructures, in accordance with previous research. ZnO NPs were also synthesized using *Calotropis gigantia* leaf extract, as reported by a group of scientists; the ZnO NPs obtained in this study appeared as a powder with a pale yellowish color. They also stated that the milky latex of *Calotropis procera* [26] is used in the biosynthesis of ZnO NPs. In another case, for ZnO NPs synthesis, leaf extract from *Acalypha indica* was also utilized.

In a report, authors demonstrated the synthesis of ZnO NPs using plant extract of *Atalantia monophyla* and further characterized them and assessed their antimicrobial activity [28]. A few other similar reports include that of synthesis of ZnO NPs using various plant materials and using those for different applications [29-31].

In 2020, Azeez and Himdad, synthesized the ZnO NPs using *Eucalyptus globulus* leaf extract, characterized them, and reported the medicinal usefulness of these NPs [32]. Some other reports also revealed the green synthesis of ZnO NPs from *Cisuss quadrangularis*, characterized them and demonstrated their antimicrobial, antioxidant and anticancer potential [33, 119-120].

It was also demonstrated ZnO NPs as bio-stimulator; they synthesized ZnO NPs from the leaf extract of *Agathosma betulina* and used to mitigate the abiotic stress in *Sorghum bicolor* [34]. In 2023,

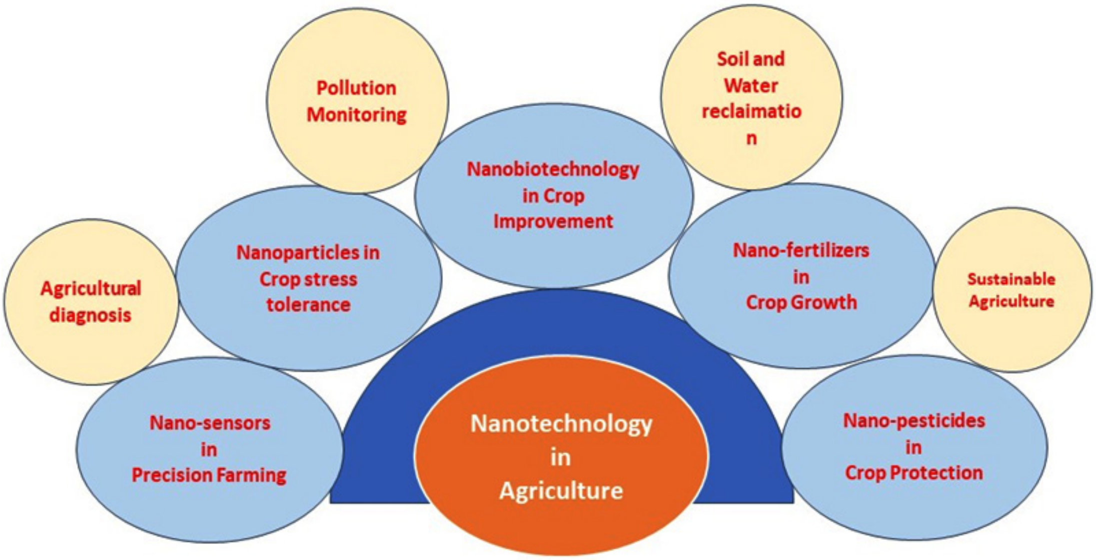

Fig. 1. Applications of nano-particles/ Nanotechnology in agriculture sector

another report came up to gave a detailed account of the synthesis, characterization, modifications, and applications of ZnO NPs in food and agriculture [35]. The general process for synthesis of NPs is presented in fig. 4.

Microbe-mediated synthesis of ZnO NPs

Microbe-mediated synthesis of zinc oxide nanoparticles (ZnO NPs) is an eco-friendly and cost-effective method that leverages the natural capabilities of microorganisms. It is one of the most popular methods of NP synthesis. But this NP synthesis method is a little difficult [36]. Accordingly, a few investigations have documented the environmentally friendly synthesis of ZnO-NP utilizing bacteria, fungi, yeast, and algae [37]. A few factors need to be taken into account first when it comes to microbe-mediated NPs synthesis, including the type of microbes used, particular growth conditions, and the biosynthesis pathway (intracellular or extracellular). The majority of the time, rod/cubic was produced using *Sphingobacterium thalpophilum, Staphylococcus aureus,* and *Bacillus megaterium*. They also reported particle sizes ranging from 10 to 95 nm and a variety of shapes, such as acicular, multiform, and triangular. Certain fungi, such as *Candida albicans* and *Aspergillus niger*, were utilized to create spherical or

ZnO NPs with a particle size of 10–61 nm were also prepared using certain yeast strains, such as *Pichia kudriavzevii* and *P. fermentans*. The beneficial effects of ZnO NPs on the physiological, nutritional, and quantitative characteristics of Foxtail millet [38] were documented by Kolencík et

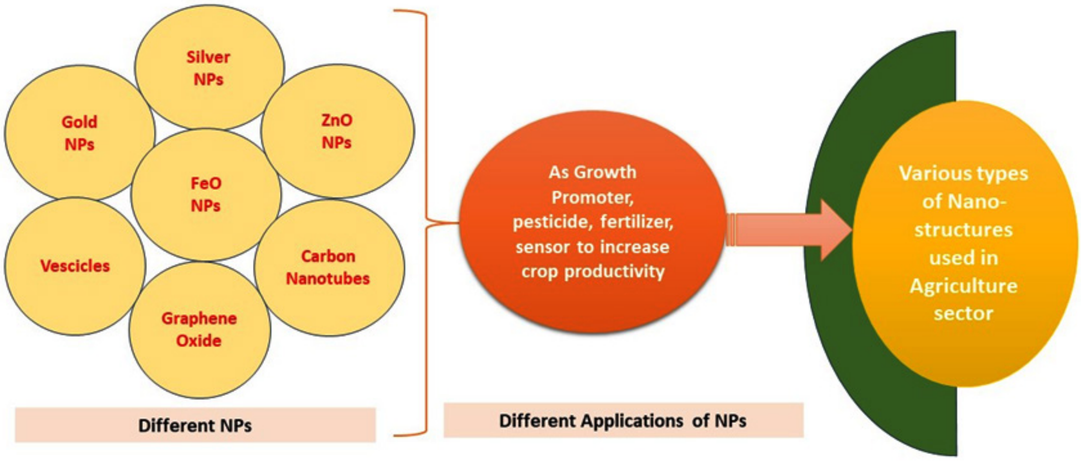

Fig. 2. Use of various Nanoparticles for different applications in the Agriculture sector.

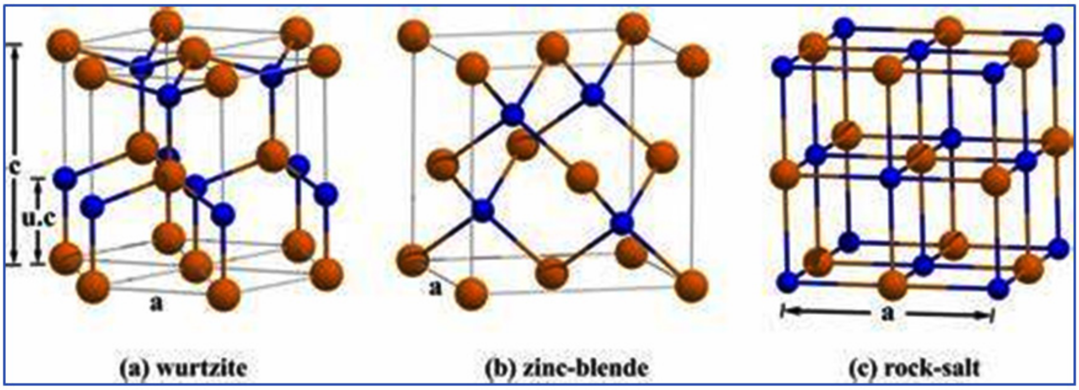

Fig. 3. Various crystalline structures of ZnO

al. For this purpose, the algae *Sargassum muticum* and *Chlamydomonas reinhardtii* have also been used safely[39–40]. Nevertheless, little is known about the mechanism underlying the microbial synthesis of ZnO-NP [41,42].

Some of the important reports indicating the biological synthesis of ZnO NPs are presented in Table 1.

Properties of ZnO NPs

The ZnO NPs possess some unique properties. They have mostly a diameter of less than 100nm. They have a relatively larger surface area. They are semiconductor materials and usually have a band gap energy of 3.37 eV. They are non-toxic and environment-friendly NPs. Some of the major Physical properties are listed below (Table- 2).

Many studies have been conducted on the fundamental and distinctive optic characteristics of ZnONPs/ nano - structures as well as their Photoluminescence spectra [72]. The presence O_2 is found to have a significant impact on the photoresponse ability based on measurements of ZnO nanowire photoconductivity. Photogenerated electrons dramatically boost the conductivity when illuminated. O2 molecules re-adsorb onto the nanowire surface when the light is turned off, lowering the conductivity [73–74]. ZnO NPs nanobelts are used to prepare nanocantilever and nano-resonators and the nanowires show semiconductor properties[75, 119]. Good transparency, high electron mobility, wide bandgap, high thermal and mechanical stability at room temperature and luminescence are some of the important properties of these nanoparticles [121].

Agricultural Applications of ZnONPs

In the current era, nanotechnology seems to be one of the most important solutions for different agricultural issues. Since the last few decades, nanotechnology has received more attention globally. The ultimate impact is the development of a few new and unique methods for improving agricultural production. The applications of nanoscience increase agricultural production through various delivery systems viz. nano-pesticides, nano-fertilizers, nano-fungicides, nano-herbicides, and nano-sensors for the identification of various crop diseases, monitoring plant, monitoring animal health, management of post-harvest issues related to fruits, seeds and grains, etc. [11, 74-76]. The continuous research and practical applications of ZnO NPs has emerged as vital components of sustainable agricultural production.

The applications of nanotechnology and nanoscience in the field of agriculture provides some effective alternatives especially in

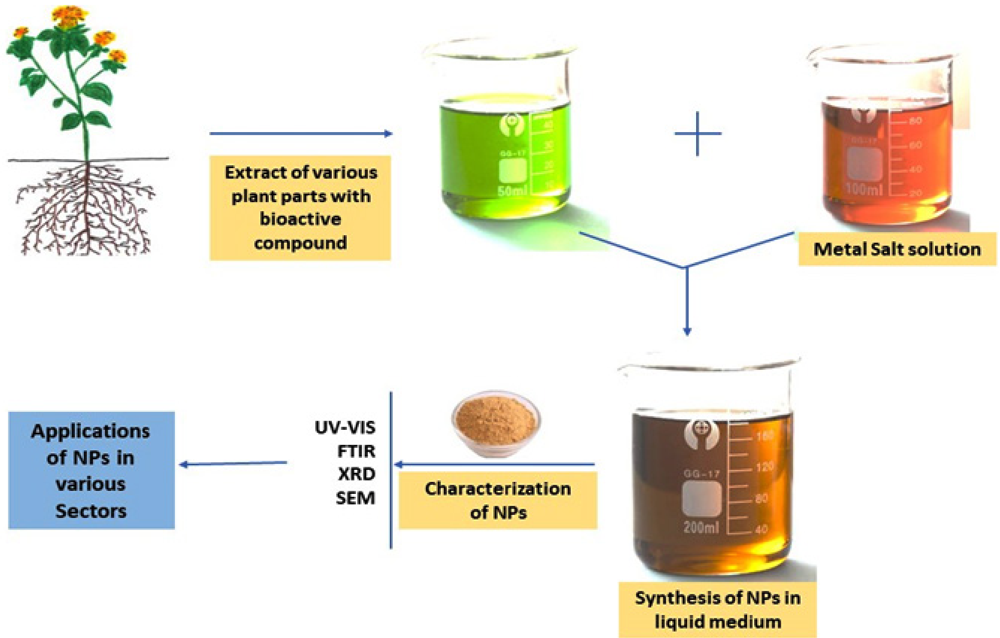

Fig. 4. Schematic presentation of biological synthesis of NPs, its characterization and application in agriculture

delivering nutrient richness, herbicide resistance in crops, improvement of soil fertility, tolerance of abiotic stress in plants, and general crop protection. Currently, entire globe is facing some high-impact issues related to the ever-increasing demand for more and safer foods and dealing with the environmental damage caused by anthropogenic agencies. Earlier reports indicate that nanomaterials have some potential applications in agricultural field such as increased plant growth and development, enhanced quality of crop, quantity wise increase in the crops production and controlling or managing agricultural crop diseases [77-79]. Some of these important reports indicated the role of ZnO NPs and their derivatives in increasing crop production are discussed below.

From previous studies, it is evident that scientists have synthesized ZnO NPs/nanopowder through various methods and successfully used these NPs as fertilizers and pesticides to improve crop productivity[80]. In the case of peanut crops, it was observed that treating seeds with different concentrations of ZnO NPs helps in promoting seed germination, seedling growth and vigor, and overall plant growth. ZnONPs have also been shown to be effective in promoting stem and root growth in peanut plants [81], and wheat yields grown from nanoparticle-treated seeds have been shown

Table 1. Green synthesis of ZnO nanoparticles from different biological sources

Sr. No.	Biological Sources	Synthesized From	References
1	NP Synthesis using bacteria	*Acinetobacter schindleri*	43
2		*Aeromonas hydrophila*	44
3		*Bacillus megaterium*	45
4		*Bacillus licheniformis*	46
5		*Lactobacillus johnsonii*	47
6		*Lactobacillus paracasei*	48
7		*Staphylococcus aureus*	49
8		*Serratia ureilytica*	50
9	NP Synthesis using fungi and yeast	*Alternaria alternata*	51
10		*Aspergillus niger*	52
11		*Aspergillus fumigatus*	53
12		*Aspergillus terreus*	54
13		*Candida albicans*	41
14		*Dictyota dichotoma*	55
15		*Pichia fermentas*	56
16		*Pichia kudriavzevii*	57
17		*Xylaria acuta*	58
18	Plant-mediated NP synthesis	*Agathosma betulina*	59
19		*Atalantia monophyla*	28
20		*Averrhoa bilimbi*	29
21		*Calliandra haematocephala*	60
22		*Calotropis procera*	61
23		*Cassia fistula*	62
24		*Cinnamomum Tamala*	30
25		*Cissus quadrangularis*	33
26		*Citrus aurantifolia*	63
27		*Eclipta alba*	64
28		*Elaeagnus angustifolia*	65
29		*Ficus carica*	66
30		*Moringa oleifera*	67
31		*Pongamia pinnata*	68
32		*Rosa canina*	69
33		*Tecosma castanifolia*	70
34		*Trianthema portulacastrum*	71

to increase total production by approximately 20–25% [82 - 83].

A few researchers demonstrated the application of ZnO quantum dots in the detection of pesticides in water [84]. Some biologists tested the potential of ZnO NPs as nano-fertilizers on rice [83, 85-86]. On the experimental basis, the positive impact of the foliar application of ZnO NPs on the quantitative, nutritional and physiological parameters of Foxtail millet was reported[38]. Somes researchers suggested that ZnO NPs improve the resistance and annual productivity of Mango trees grown in salty areas [87]. ZnO NPs also showed positive impact on the regulation of antioxidant enzymes, osmolytes, and some other agronomic characters in *Coriander* [88]. Some biologists also reported insecticidal and pesticidal activities of ZnO NPs [89-90]. In the same line of work, several workers suggested and demonstrated innovations in modern nanotechnology for sustainable

Table 2. Some important properties of ZnO NPs

Properties	Types of ZnO NPs and their values/features
Crystal Structure	Wurtzite/ Zinc-blende/ Rock-Salt Wurtzite: Hexagonal, Zinc blende: Cubic, Rock Salt: Halite/
Density	5.606 g/cm3
Melting Point	2248 K
Boiling Point	2630 K
Relative dielectric constant	8.66
Band Gap	3.37 eV

Table 3. Some reported agricultural applications and experimental results of ZnO nanoparticles

Sr. No.	Synthesis of NPs	Agricultural applications of NPs	References
1	Biological Synthesis	Growth promoter in Cotton (*Gossypium hirsutum* L.)	100
2		Nano-pesticides for crop plants	101
3		Bio- fungicides for strawberry crop protection	102
4		Mitigate drought-induced oxidative stress in tomato (*Lycopersicum esculentum*)	103
5		Antimicrobial and larvicidal activity	104
6		Improve plant growth and ameliorate drought stress in *Vigna radiata*	105
7		Nano-fertilizer to improve biochemical indices and growth of Maize (*Zea mays*)	106
8	Commercially available (Chemically or physically synthesized)	Enhance germination, growth and yield of peanut	81
9		Improves salt stress in finger millet	107
10		Nano-fertilizer for rice (*Oryza sativa*) production	108
11		To mitigate salt stress in Mango trees	87
12		Enhance the insecticidal activity of thiamethoxam	40
13		Modulate plant growth in tomato (*Lycopersicum esculentum*)	109
14		Tolerate Cold/ chilling stress in Rice	110
15		Improve seed germination and tolerate salt stress	111
16		Improve salt tolerance in tomato	112
17		Insecticidal activity against *s*ome fungi	113
18		Enhance drought tolerance in wheat	114
19		Under salt stress increases chlorophyll content and overall growth	99
20		Wheat grain biofortification	115
21		Tolerate Cd toxicity in rice	116-117

agriculture with increased production indicating the potential of Zinc oxide NPs boosting the yield and growth of several food crops [91-94]. Some were even more conclusively stated that metal oxides are more effective than other nanostructures [95-99]. Thus, ZnO NPs has some promising applications in agricultural sector including as fertilizer, as pesticides, to counter the plant's abiotic stresses, and promote plant growth. Some of the important reports indicating the agricultural applications of ZnO NPs are listed in table 3.

Zinc and ZnONPs have garnered considerably more attention than any other metal nanoparticles that have been synthesized by different researchers thus far as sustainable plant growth promotors and stimulators. They have reportedly demonstrated a positive effect on early flowering, yield, enzyme activity, and seed germination. Zn and ZnONPs have been shown to have detrimental effects as well; these primarily include toxicity to the chlorophyll apparatus, thylakoid degradation, cell cycle arrests, and DNA damage. ZnONPs' positive or negative effects are typically determined by the kind of species, size, concentrations, dosages, treatment strategies, plant developmental stage, genotype of the species, and environmental factors at play. ZnONPs do, however, accumulate in the ecosystem as a result of the increased use of these NPs. Understanding how ZnONPs alter and behave in intricate soil and plant systems is essential for the appropriate use and control of their release.

Overall Zinc oxide (ZnO) nanoparticles have high positive impact on agriculture by enhancing plant growth, improving nutrient uptake, and exhibiting antimicrobial properties that may reduce plant diseases. They can also help improve soil health and promote crop protection against pests.

CONCLUSION

Zinc oxide (ZnO) nanoparticles are a treasure trove for life scientists and hold great potential in various application fields. The synthesis of ZnO NPs by green plants and microorganisms is a significant advancement for the scientific community. ZnO NPs are found in three different forms namely wurtzite, zinc mixture and rock salt exhibiting unique characteristics. These NPs have enormous applications in various sectors such as biosensors, cosmetics, drug delivery systems, pharmaceuticals and agricultural applications. In agriculture, ZnO NPs have been successfully tested as plant growth promoters, significantly increasing seed germination, disease resistance, antioxidant capacity, and improving overall crop productivity. Overall, the various ZnO nanostructures developed under the nano-agriculture mission will be extremely helpful for agricultural sustainability. However, there is a need to test the ability of ZnO NPs to withstand various crop abiotic stresses and other physiological conditions that affect overall crop yield.

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Conflict of interest

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Data Availability Statement

This statement does not apply to this article.

Ethics Statement

This research did not involve human participants, animal subjects, or any material that requires ethical approval.

Informed Consent Statement

This study did not involve human participants, and therefore, informed consent was not required.

Authors Contribution

DKK : conceptualized this work; RRG : wrote the preliminary manuscript; DKK and RRG : made the necessary corrections and the approved draft was submitted in this final form to editor.

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