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# A Review on Properties, Green Synthesis and Applications of Zinc Oxide Nanoparticles(ZnONPs) - An Eco Friendly Approach

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**Abstract :**

In recent era Zinc oxide nanoparticle (ZnO NPs) is the second most abundant metal oxide after iron and it is cost effective, safe, and as well as it can be prepared easily. Zinc oxide nanoparticle appears to be white powder and insoluble in water. Zinc oxide nanoparticle has an energy band of 3.37 eV and a bonding energy of 60 meV, which provides its excellent chemical, electrical, and thermal stabilities. Zinc oxide nanoparticle is also known for its low toxicity and high UV-absorption making it a good candidate to be used in the biomedical field. One of the advantages of using zinc oxide nanoparticle in the biomedical field is because they act as a good surface material. Zinc oxide nanoparticle is naturally known as a strong resistance of microbes. Due to these reasons zinc oxide nanoparticle is extensively used for biological labelling, biological sensing, drug delivery, gene delivery, and in agriculture. This review aims to summarize the basic structural configuration, green synthesis approaches of ZnO NPs and its application in various biomedical fields.

**Keywords:** Zinc oxide nanoparticles, UV-absorption, green synthesis, biomedical fields, nanomedicine, agriculture.

**INTRODUCTION**

Now-a-days Zinc oxide nanoparticles (ZnONPs) have become a promising molecule in the field of nanotechnology. ZnO NP appears to be white powder and insoluble in water. Different types of inorganic metal oxides have been synthesized but of all those metal oxides, ZnO NPs is of maximum in use. This particle has believed as nontoxic, safe, biocompatible, inexpensive to produce and can be prepared easily and used as additive into countless materials like plastics, glass, cement, car tyres, lubricants, paints, ointments, adhesives, pigments, foods (source of Zn nutrient), batteries, fire retardants, etc. ZnO NPs have been commercially used in cosmetics, as drug carriers, and fillings in pharmaceutical products [10,33]. Zinc and oxygen belongs to the 2<sup>nd</sup> and 6<sup>th</sup> groups of the periodic table so that ZnO is often called as II-VI semi conductor. Zinc oxide nanoparticle has an energy band of 3.37 eV and a bonding energy of 60 meV, which provides its excellent chemical, electrical, and thermal stabilities like high catalytic activity, UV filtering properties, anti-inflammatory, wound healing properties, etc [11,36]. Zinc oxide nanoparticle is also known for its low toxicity and high UV-absorption making it a good candidate to be used in the biomedical field. One of the advantages of

using zinc oxide nanoparticle in the biomedical field is because they act as a good surface material. Zinc oxide nanoparticle is naturally known as a strong resistance of microbes. Due to these reasons zinc oxide nanoparticle is extensively used for biological labelling, biological sensing, drug delivery, gene delivery and also in agricultural field [44].

## PROPERTIES OF ZINC OXIDE NANOPARTICLES

### Physical Properties

Zinc oxide (ZnO) has been of great interest because of its excellent physical properties, such as low cost, non toxicity, high thermal stability, photosensitivity, advanced optical properties, and eco-friendly nature [54,47]. Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zinc blende. The wurtzite structure is most common and stable at ambient conditions. At optimum pressure and temperature, ZnO crystallized in the wurtzite (B4 type) structure shown in Fig. 1. Therefore, ZnO has been widely used in many fields, such as adsorption, paint, cosmetic, superconductor, and catalyst [17,18,27,28,45,51]. ZnO should have a sufficient structure area and morphology to allow the diffusion of active species and electron transfer [6]. ZnO with the wide band gap energy (3.37 eV) and the high exciton binding energy (60 meV) could absorb a larger fraction of the UV spectrum to oxidize harmful organic substances [25,39,55].

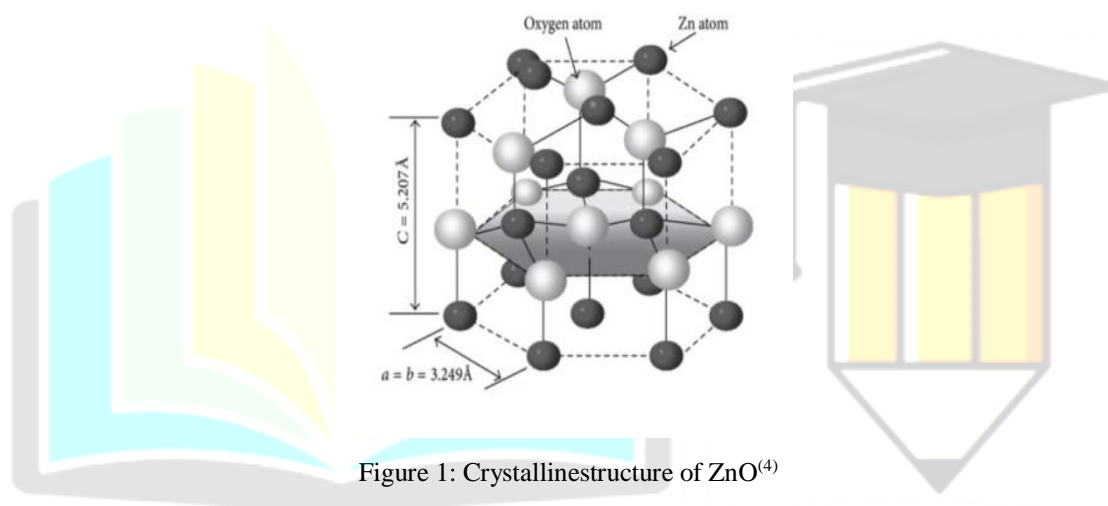


Figure 1: Crystalline structure of ZnO<sup>(4)</sup>

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<b>Molar Mass</b>	81.408 g/mol
<b>Odor</b>	odourless
<b>Density</b>	5.606 g/cm <sup>3</sup>
<b>Melting point</b>	1975 °c (Decompose)
<b>Boiling point</b>	2360 °c
<b>Solubility In Water</b>	0.16 mg/100 ml(30 °c)
<b>Band Gap</b>	3.3 eV
<b>Refractive Index (n<sub>p</sub>)</b>	2.0041

Table 1: Physical properties of ZnO

### Optoelectronic Properties

The most important factor responsible for a material to show a better optoelectronic property is the large exciton binding energy and this property is possessed by Zinc oxide having binding energy of 60 meV which could be attained at and above room temperature due to excitonic recombination. ZnO has large direct band gap of ~3.3 eV at room temperature so the pure ZnO has a transparent nature and it is colourless. The process of optical absorption and emission have been influenced by bound excitons which are extrinsic transition related to dopants or defects thereby usually responsible for creating discrete electronic states in the band gap. Further band gap can be placed from ~3–4 eV, alloying with cadmium oxide or magnesium oxide. Even in the absence of intentional doping, most ZnO has n-type character. The electron mobility of ZnO varies with temperature and has a maximum of ~2000 cm<sup>2</sup>/(V·s) at ~80 K. Data on hole mobility are scarce with values in the range 5- 30 cm<sup>2</sup>/(V·s). Due to the absence of p-type ZnO its electronic and optoelectronic applications which usually require junctions of n-type and p-type material [5]. Also high breakdown stress and high saturation velocity of zinc oxide increases its demand for the different electronic application. The excellent emitting power of ZnO has been investigated through different reports and line width of excitonic recombination is as narrow as 40 μeV with fine spectroscopic details have been observed. The refractive index of wurtzite ZnO as reported is  $n_w = 2.008$  and  $n_e = 2.029$ .

### Antimicrobial Properties

Mechanisms of antimicrobial actions of ZnO materials have been explained in association with particular interaction based on their unique physicochemical properties of Zn<sup>2+</sup> ion release, adsorption, and ROS generation [42], and the intracellular responses in microorganisms of energy metabolism inhibition; lipid peroxidation, and cell membrane damage; and DNA replication disruption, as well as DNA break [7,26] (Figure 2). The Zn<sup>2+</sup> ions that are released from ZnO NPs induce an antimicrobial response in microorganisms due to interference in metabolic processes and disturbance in enzymatic systems [22,23]. ZnO NPs also have functions of particle adsorption to the bio membrane via a charge–charge interaction, and ROS generation as photocatalysts under UV and visible light irradiation [1,9,21,38]. Positively charged surfaces of ZnO NPs interact with the negatively charged cell wall or bio membrane of microorganisms [14]. They are internalized into the microorganisms after adsorption resulting in loss of cell integrity based on cell wall or membrane rupture, and further mediate oxidative stress owing to lipid peroxidation leading to DNA damage. Based on the fundamental mechanisms of action, ZnO NPs have a differential susceptibility against pathogenic microorganisms, affected by their physicochemical characteristics including morphology, particle size, and porosity [9,55,19,14].

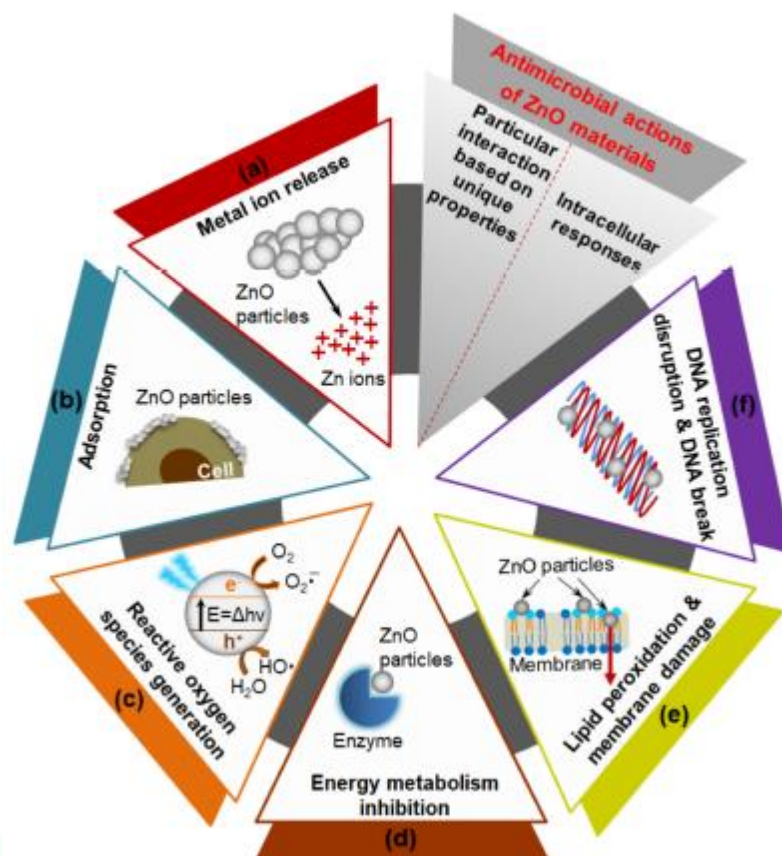


Figure 2. Mechanisms of zinc oxide (ZnO) materials used in antimicrobial applications<sup>(7,26)</sup>

### GREEN SYNTHESIS OF ZINC OXIDE NANOPARTICLES (ZnO NPs)

The synthesis of ZnO NPs is generally divided into physical and chemical methods, which have the disadvantages of high energy consumption, low purity, uneven particle size distribution, high cost, large quantities of secondary waste, and irreversible pollution of the environment. As applications in which ZnO NPs are utilized increase in number, their synthesis using methods in which the environment is protected is of wide concern, principally because the concept of environmental protection is now deeply rooted in the expectations of the population. Green methods of synthesis refer to those in which microorganisms, enzymes, and plant extracts are used in the fabrication process. No toxic materials should be used, and the process is combined with low energy consumption. It has the advantages of environmental sustainability, eco-friendliness, and low cost, and is therefore, an attractive alternative to traditional physical and chemical methods [22].

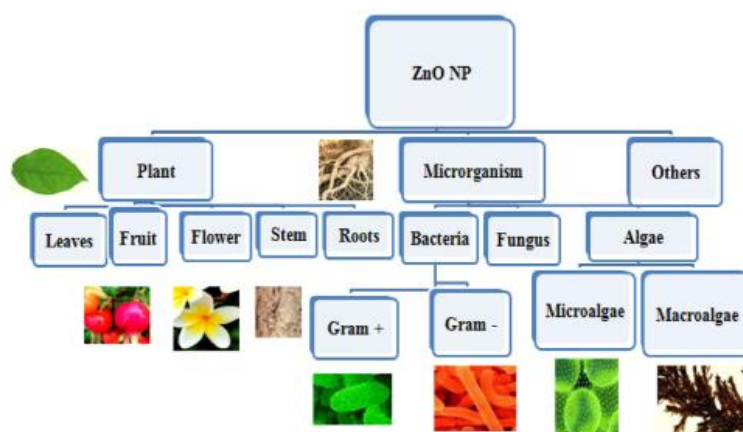


Figure 3: Zinc oxide nanoparticle synthesis by using different sources<sup>(1)</sup>

**ZnO NPs synthesis by using plant extract:**

Plant mediated synthesis of nanoparticles (NPs) is a revolutionary technique that has wide range of applications in agriculture, food industry and medicine (Table 1). Due to the physio-chemical properties of plant based NPs, this method also offer an added advantage of increased life span of NPs that overcome the limitations of conventional chemical and physical methods of NPs synthesis [33]. Plants possess rich genetic variability with respect to number of biomolecules and metabolites like proteins, vitamins, coenzymes based intermediates, phenols, flavonoids and carbohydrates. These plant metabolites contain hydroxyl, carbonyl, and amine functional groups that react with metal ions and reduce their size into nano range. These molecules not only help in bioreduction of the ions to the nano scale size, but they also play a pivotal role in the capping of the nanoparticles which is important for stability and biocompatibility [34].

Table 1: Plant mediated synthesis of ZnO nanoparticles (NPs)<sup>(1)</sup>

Sl. No	Plant Species	Common Name	Part parts used	Size (nm)	Shape	Functional Group
1	<i>Azadirachta indica</i> L. (Meliaceae)	Neem	Fresh leaves	18 (XDR)	Spherical	Amine, Alcohol, Ketone, Carboxylic acid
2	<i>Azadirachata indica</i> L. (Meliaceae)	Neem	Leaf	9.6-25.5 (TEM)	spherical	Amide II stretching band, C-N stretching band of aliphatic,aromatic amide, an aliphatic amine, alcohol, phenol, secondary amine, C-H of alkane and aromatics, C = C-H of alkynes, C = O, C-C of an alkane
3	<i>Aloe vera</i> L. (Liliaceae)	Ghrita-kumari	Leaf extract	8-20 (XRD)	Spherical, oval, hexagonal	O-H of phenol, amines, O-H of alcohol and C-H of alkanes, the amide of protein and enzymes.
4	<i>Aloe vera</i> L. (Liliaceae)	Ghrita-kumari	Freeze Dried	25-26 (TEM SEM)	Spherical, hexagonal	None
5	<i>Pongamia pinnata</i> L. (Fabaceae)	Indian Beech	Fresh leaves	26 (XRD)	Spherical, hexagonal nano rod	O-H stretching, C = O stretching of carboxylic acid or their ester, C-O-H bending mode
6	<i>Pontederia crassipes</i> Mart. (Pontederiaceae)	Water Hyacinth	Fresh leaves	32-36 (SEM & TEM), 32 (XRD)	Spherical without aggregation	None
7	<i>Cocos nucifera</i> L. (Arecaceae)	Coconut	Coconut water	20-80 (TEM), 21.2 (XRD)	Spherical and predominately hexagonal	O-H of alcohol and carboxylic acid, C = O of ketones, C-N of aromatic and aliphatic amines
8	<i>Moringa oleifera</i> Lam. (Moringaceae)	Drumstick tree	Leaf	24 (XRD), 16-20 (FE-SEM)	Spherical and granular nano sized	O-H, C-H of alkane, C = O of alcohol, carboxylic acid

9	<i>Santalum album</i> L. (Santalaceae)	Sandal wood	Leaves	100(DLS & SEM), 70–140 (TEM)	Nano rods	N-H stretching of amide II, carboxylate group, carbonyl group
10	<i>Gossypium herbaceum</i> L. (Malvaceae)	Cotton	Cellulose fibre	13 (XRD)	Wurtzite, spherical, nano rod	O-H, [C = O, C-O, C-O-C] (due to Zn precursor)

### ZnO NPs synthesis using microorganisms:

NPs involve unicellular and multicellular biological entities including bacteria [24], yeast [31], fungi [40], virus [4] and algae [32]. These methods are cheap, non-toxic and eco-friendly. The microbes act as a tiny nano-factory in reducing the metal ions into metal NPs with the involvement of enzymes and other biomolecule compounds secreted or produced by the microbes. Nevertheless, only a few microbes are reported to have the capability to synthesise ZnO NPs. Microbes such as bacteria, fungi, and yeast play an important role in the biological synthesis of metal and metal oxide NPs. In the last decade, the use of microbes has gained increased interest in which there have been many studies conducted using various microorganisms' models. Nevertheless, the biological synthesis of ZnO NPs using microbes still remains unexplored. Table 2 summarizes several of microbes that mediate the synthesis of ZnO NPs including their size, shape and special applications. Biological synthesis using microbes offers an advantage over plants since microbes are easily reproduced. Nonetheless, there are many drawbacks pertaining to the isolation and screening of potential microbes. The main drawback includes cost-effective of the synthesis processes as it is time-consuming and involves the use of chemical for growth medium. The presence of various enzymes, protein and other biomolecules from microbes plays a vital role in the reduction process of NPs. These multiple organic components secreted in the suspension or growth medium attributed to the formation of multiple sizes, shape with mono- and poly dispersed NPs [23]. Moreover, the protein secreted from microbes could act as a capping agent that confers stability of NPs formation.

Table 2: Microorganisms mediated synthesis of ZnO nanoparticles (NPs)<sup>(1)</sup>

Sl No	Types of Microorganisms	Family	Size	Shape	Functional Group
1	<i>Aeromonas hydrophila</i> (Bacteria)	Pseudomonadaceae	57.72 (AFM), 42–64 (XRD)	Spherical, oval	Phosphorus compound, monosubstituted alkynes
2	<i>Lactobacillus sporogens</i> (Bacteria)	Bacillaceae	5–15 (TEM), 11 (XRD)	Hexagonal unit cell	-
3	<i>Serratia ureilytica</i> (HM475278) (Bacteria)	Enterobacteriaceae	170–250 (30 min), 300–600 (60 min), 185–365 (90 min) [SEM]	Spherical to nanoflower shaped	-

4	<i>Chlamydomonas reinhardtii</i> (Microalgae)	Chlamydomonaceae	55–80 (HR-SEM), 21 (XRD)	Nanorod, nanoflower, porous nanosheet	C = O stretching, N-H bending band of amide I and amide II, C = O stretch of zinc acetate, C- O-C of polysaccharide
5	<i>Sargassum muticum</i> (Seaweeds)	Sargassaceae	30–57 (FE-SEM), 42 (XRD)	Hexagonal wurtzite	Asymmetric stretching band of the sulfate group, an asymmetric C-O band associated with C-O- SO <sub>3</sub> & -OH group, sulfated polysaccharides.
6	<i>Sargassum myriocystum</i> (Seaweeds)	Sargassaceae	46.6 (DLS), 20–36 (AFM)	Spherical, radial, triangle, hexagonal, rod	O-H and C = O stretching band, carboxylic acid
7	<i>Aspergillus fumigatus</i> (TFR-8) (Fungus)	Trichocomaceae	1.2–6.8 (DLS), 100 (agglomerate)	Oblate spherical and hexagonal forms aggregate	-
8	<i>Aspergillus terreus</i> (Fungus)	Trichocomaceae	54.8– 82.6 (SEM), 29 (XRD)	spherical	C-N bond of primary amine, C-O of primary alcohol, primary & secondary alcohol, N = O aromatic nitro compound, alkyl C = C, amide, open chain imino group
9	<i>Candida albicans</i> (Fungus)	Saccharomycetaceae	25 (XRD), 15– 25(SEM) , 20 (TEM)	Quasi- spherical, hexagonal phase (wurtzite Structure )	-

## APPLICATION OF ZINC OXIDE NANOPARTICLES

### Bioimaging with Zinc oxide nanoparticle :

The optical properties of ZnO nanoparticles can be tuned by doping with appropriate elements [52]. In one report, ZnO NPs has been doped with different cations (Co, Cu, or Ni) and stabilized in aqueous colloidal solutions, which are employed for cellular imaging studies in various cells [50]. It has been suggested that these small ZnO nanoparticles can penetrate into the cell nucleus. Since ZnO NPs exhibit efficient excitonic blue and near-UV emission, which can also have green luminescence related to oxygen vacancies [15, 48], many reports exist in the literature on the use of ZnO NPs for cellular imaging. Taking advantage of their intrinsic fluorescence, the penetration of ZnO nanoparticles

in human skin is imaged *in vitro* and *in vivo* [58]. It has been found that most ZnO nanoparticles stayed in the stratum corneum with low possibility to result in safety concerns. In another study, biocompatible ZnO NPs with nonlinear optical properties are synthesized, encapsulated within the nonpolar core of phospholipid micelles, and conjugated with folic acid (FA) for nonlinear optical microscopy [20]. The micelle encapsulated ZnO NPs are stable in aqueous solutions and FA-conjugated ZnO NPs are found to accumulate intracellularly throughout the cytoplasm, without inducing cytotoxicity in live cells. Recently, transferrin-conjugated green fluorescent ZnO NPs has also been reported for cancer cell imaging with minimum cytotoxicity [43].

#### **Drug Delivery with ZnO nanoparticles :**

ZnO NPs are versatile nano-platforms for not only bioimaging but also drug delivery applications, due to their large surface area, versatile surface chemistry, phototoxic effect, among others. *In vitro* studies have shown that ZnO nanoparticles can be highly toxic to cancer cells [16] or bacteria and leukemic T cells [49]. Therefore, not only have ZnO NPs been investigated as drug/gene delivery vehicles, they have also been studied for cancer therapy. One of the major obstacles in dendritic cell (DC)-based cancer immunotherapy is the development of a delivery system which can efficiently deliver target antigens into DCs [12]. Because of the large surface area, nanomaterials are promising candidates for this application. Recently, Fe<sub>3</sub>O<sub>4</sub>-ZnO core-shell nanoparticles with an average diameter of 16 nm has been prepared to deliver carcino-embryonic antigen into DCs, which could also serve as imaging contrast agents [8]. Antigen-bound nanoparticles have efficiently taken up by DCs *in vitro*, where the ZnO shell facilitated cell internalization and significantly reduced the incubation time needed for labeling DCs [56].

#### **Gene Delivery with ZnO nanoparticle :**

Gene therapy has attracted considerable interest over the last several decades for cancer treatment [30]. One major challenge of gene therapy is the development of safe gene vectors which can protect DNA from degradation and enable cellular uptake of DNA with high efficiency. A wide variety of nanomaterials have been investigated for gene delivery and gene therapy applications, including ZnO NPs which have shown promise in various literature reports. In a series of studies, three-dimensional tetrapod-like ZnO nanostructures has been investigated as gene vectors to deliver pEGFPN1 DNA (which contains the gene for green fluorescent protein) to A375 human melanoma cells [34,35]. The plasmid DNA (pDNA) has been attached to ZnO nanostructures via electrostatic interactions, and the three needle-shaped legs favoured the internalization of the tips within the cells for gene delivery. No significant cytotoxicity has been observed, which are reportedly attributed to the three dimensional geometry.

#### **Biosensor based on ZnO nanomaterials :**

Biosensors (e.g. photometric, calorimetric, electrochemical, piezoelectric, among others when categorized based on the detection principles) are widely used in healthcare, chemical/biological analysis, environmental monitoring, and food industry [57]. Nanomaterials, alone or in combination with biologically active substances, are attracting ever-increasing attention since they can provide a suitable platform for the development of high performance biosensors due to their unique properties [53]. For example, the high surface area of nanomaterials can be employed to immobilize various biomolecules such as enzymes, antibodies, and other proteins. In addition, they can allow for direct electron transfer between active sites of the biomolecules and the electrode.

#### **Role of ZnO NPs in Agriculture:**

Agriculture is backbone of third world economics but unfortunately now, the agriculture sector is facing various global challenges like climate changes, urbanization, sustainable use of resources, and environmental issues such as runoff, accumulation of pesticides and fertilizers; human population is increasing day by day and food demand is growing rapidly and estimated population increase in world from current level of 6 billion to 9 billion by 2050 is expected. So we must adopt efficient techniques to make agriculture more sustainable [13].



Nanotechnology has a dominant position in transforming agriculture and food production. Nanotechnology has a great potential to modify conventional agricultural practices. Most of the agrochemicals applied to the crops are lost and do not reach the target site due to several factors including leaching, drifting, hydrolysis, photolysis, and microbial degradation. Nanoparticles and nanocapsules provide an efficient means to distribute pesticides and fertilizers in a controlled fashion with high site specificity thus reducing collateral damage. Farm application of nanotechnology is gaining attention by efficient control and precise release of pesticides, herbicides, and fertilizers. Nanosensors development can help in determining the required amount of farm inputs such as fertilizers and pesticides. Nanosensors for pesticide residue detection offer high sensitivity, low detection limits, super selectivity, fast responses, and small sizes. They can also detect level of soil moisture and soil nutrients. Plants can rapidly absorb nanofertilizers. Nano-encapsulated slow release fertilizers can save fertilizer consumption and minimize environmental pollution [46].

## CONCLUSION

The rapid development of engineered nanoparticles (ENPs) has increased their applications in medical, engineering, cosmetic, food industry also in agriculture. However, the adverse effect of ENPs on environment, essential microorganisms, and human health has been suggested. The consequence of ingesting ENPs could be fatal to the host. Ironically, with the advertisement of nanomaterial containing products, no regulation has yet to be established regarding the use of ENPs in foods and agriculture. ZnO NPs have tremendous physical and optical properties. They also possess antimicrobial actions against some bacteria and fungi. As far as synthesis of zinc oxide nanoparticles is concerned they can be synthesized by chemical methods but in recent times due to evolution of green chemistry, biogenic synthesis of ZnO NPs is also possible by using different plant extracts. Concerned nanoparticles play a significant role in agriculture, where colloidal solution of ZnO NPs is used in nanofertilizers. Application of these nanoparticles to crops increases their growth and yield. As food demand is increasing day by day the yield of staple food crops is much low. So it is need of the hour to commercialize metal nanoparticles for sustainable agriculture.

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