

BIOGENIC SYNTHESIS OF ZnO NANOPARTICLES AND THEIR APPLICATIONS. (REVIEW)

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ABSTRACT: The biogenic synthesis of nanoparticles by plant source or microorganism is green and eco-friendly technology. ZnO Nanoparticles are semiconductor and piezoelectric material that is used for diverse purposes like solar and oxide fuels, electronics, sensor technologies, optical devices, light and heat stabilization, drug delivery as well as in the treatment of cancer. The association between nanotechnology and biological sciences is tremendous as all realistic biologic are based on nanoscale dimensions. The aim of this study is to present a review of the synthesis of ZnO nanoparticles from biological routes i.e. by plant source and microorganism, characterization and their properties like antibacterial, antifungal, photocatalytic activity as well as anticancer activity.

INTRODUCTION:

Nanotechnology encompasses the imaging, measuring, modeling and manipulating matter at the nanoscale. These nanoparticles have large surface area as compared to the macro-sized particles. Due to the large percentage of atoms at their surface, these manipulated particles show high surface reactivity [1]. Their chemical, electrical, mechanical, structural, optical and morphological properties can be modified by reducing the size of particles which increases the particle surface areas and surface energy. These unique properties enable the nanoparticles to interact with biomolecules in distinctive mode, which results into the transformation of inner cellular structures [2]. These nanomaterials have tremendous applications in the field of Nanobiotechnology and applied and basic sciences, food processing, agriculture and biomedicine [3].

ZnO, functional, promising and versatile inorganic compound, is a white crystalline powder that is insoluble in water. ZnO NPs have wide applications in rubber, ceramics and pharmaceutical industry. It is also frequently used in heat stabilization, light stabilization, pigmentation, activation, acceleration, cosmetics, adhesive, photocopying and paints [4]. One of the most promising application is in solar cell diodes, catalysis and sensors [5].

ZnO is n-type semiconductor by virtue of its properties like wide band gap, high electron mobility, high excitation binding energy of 60meV, good transparency, strong room temperature luminescence and radiation hardness [6]. The band gap of 3.37eV made it favorable in the field of energy saving or heat protecting windows, a transparent electrode in electro crystal display and in electronics as a thin film transistor and light emitting diodes [5]. A piezoelectric property makes it suitable for convertor, energy generator and photocatalyst in the production of hydrogen. [7] ZnO NPs also behave as a chemotherapeutic agent against cancer cells [8]. Due to its biodegradability and biocompatibility, it is an excellent material for biomedicine.

Metal Oxide NPs have drawn more attention due to its novel properties and application in many industries, but it is still essential to fabricate the high quality and ultra-fine powder and control the powder properties that confirmed the performance and microstructure of the final commodity [9]. Metal oxide, i.e. ZnO NPs have been synthesized by various techniques such as sol gel method [10,11,12], polyol methods

[13,14,15], hydrothermal synthesis [16,17,18], precipitation method [19,20,21,22], microwave technique [23,24,25,26], electrochemical method [27,28], sonochemical method [29,30,31], micro emulsion method [32,33] and made it possible to attain the product with various size, shape and structures. The major disadvantage of these techniques is difficulties of separation and purification of these NPs from surfactants, organic solvents and toxic materials. As the plant and plant extracts are natural surfactants, non-pollutant and eco-friendly substitute of chemical and physical methods [34]. The biogenic synthesis of NPs is an eco-friendly approach for the synthesis of NPs and plants are the best candidate for large scale biosynthesis of NPs.

Nanoparticle Synthesis by Plant Extract:

The utilization of plants for the synthesis of nanoparticles has drawn more attention due to single step biosynthesis process [35]. Plants are the best candidate for the synthesis of nanoparticles because (i). Free of toxicants (ii). Natural surfactants and capping agent. (iii) Possess phytochemicals readily provided by plants.

Anjali Oudhia successfully fabricated the ZnO nanoparticles of 25nm diameter by simple, low cost, green method using Neem (*Azadirachta Indica*) leaf extract as a template and reducing agent exhibiting antimicrobial activity against *E.coli*. [36].

The reduction of ZnO nanoparticles was carried out by stirring the *Corymbia Citriodora* leaf extract and Zinc nitrate solution at 80 C for 48 h [37]. By using *Catharanthus Roseus* (*I. G.Don*, leaf extract, ZnO NPs with the size ranging from 23-57nm and their antibacterial activity against *Pseudomonas Aevraginosa* has been studied by G.Bhumi [38]. The visibility of the yellow color solution was observed at 30 C for 24 h indicate the development of ZnO NPs using *Trifolium Pratense*, flower extract [39]. The flower extract of *Cassia Densistipulata Taub* has ability to reduce the Zn²⁺ to Zn (0) by the formation of ZnO NPs [40].

Gunalan Sangeetha reported the biosynthesis of ZnO NPs by reducing the Zinc Nitrate and Sodium Hydroxide at room temperature, while the size and shape of ZnO NPs can be controlled by changing the concentration of *Aloe Barbadosensis Miller* leaf extract. The fabricated NPs have size ranges from 25-45nm with the average size of 35nm showed photocatalytic activity [41], Antibacterial as well as antimicrobial activity [42].

The extracellular biosynthesis of ZnO NPs by aqueous leaf extract of *Corriandum Sativum* [43], *Acalypha Indica* [44], *Pongamia Pinnata* leaf extract [45] are reported to produce ZnO NPs. The flower extract of *Cassia Auriculata* was also used for the fabrication of ZnO NPs [46]. *Aloe Vera* leaf extract has been detected to produce rod shape ZnO NPs and their antimicrobial activity against gram positive and gram negative bacteria has been evaluated [8]. Hibiscus Rosa-Sinesis seems to be the best candidate for the ZnO NPs of 30-35nm size [47].

Table No 1: Biogenic Sources of certain Nanoparticles

Source	Size and Shape	References
Leaf Extract:		
Azadirachta Indica (Neem)	25nm	36
Corymbia Citriodra	64nm	37
Parthenium Hysterophonics	27nm, Spherical 84nm, Hexagonal	70
Catharanthus Roseus	23-57nm	38
Aloe Barbadenese Miller	25-45nm	41
Olea Europea	500nm	48
Hibiscus-Rosa Sinesis	30-35nm	47
Corriandum Sativum	66nm	43
Aloe Vera	500nm	8
Acalypha Indica	100-200nm	44
Pongamia Pinnata	23nm	45
Tabernamontana	36nm, Spherical	57
Ocimum Tenuiflorum	11-25nm, Hexagonal	51
Camellia Sinesis	9-10nm, Spherical	53
Thevetia Peruviona	53nm, Triangular	56
Flower Extract:		
Trifolium Pratense	-	39
Cassia Densilipulate	-	40
Cassia Auriculata	-	46
Stem Extract:		
M. Mercurialis L. Benth	-	58
Tinospora Cordifolia	37-42nm	49
Root Extract:		
Zingiber Officinale (Ginger)	30-50nm	50
M. Mercurialis L. Benth	-	58
Peel Extract:		
Punica Granatum	50-100nm, Spherical, Square	52
Bacterias:		
Aeromonas Hydrophila	42-64nm	59

The fabrication of ZnO NPs by utilization of *Olea Europea* leaf extract has also been reported with its optical properties [48]. Jannatul Firdose fabricated the ZnO NPs utilizing six Plant Exrtacts: (i)*Senna Auriculata* (ii). *Pyrus Communis*

(iii).*Eichhornia Crassipes* (iv) *Annona Reticulata* (v). *Amaranthus Dubius* (vi).*Curcuma Rubescens*. Phytochemicals like flavonoids, alkaloids, proteins are responsible for the reduction of zinc sulphide to ZnO having spherical shape and size less than 100nm [4]. Spherical ZnO NPs with size 37-42nm have been synthesized by using stem extract of *Tinospora Cordifolia* which reduce Zinc acetate hydrate into ZnO in the presence of NaOH [49].

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The complete reduction of ZnO NPs by root extract of *Zingiber Officinale* has been observed at room temperature after 2h with continuous stirring [50]. The hexagonal shape ZnO NPs (11-25nm) has been fabricated in 40-45min through the reduction of Zn ions by the utilization of *Ocimum Tenuiflorum* leaves extract [51]. *Punica Grantum* peel extract is traced to be produced spherical and square like structure ZnO NPs (50-100nm) and its efficiency against *Aspergillus Niger* and *Proteus Vulgaris* has been studied [52]. *Citrus Aurantifolia* has lead to the formation of Spherical ZnO NPs with particle size ranges from 9-10nm [53].

The biosynthesis of ZnO NPs have also been investigated by Rajesh Kumar Shah, using green tea *Camellia Sinensis* as a reducing and stabilizing agent and evaluates their antimicrobial activity against gram positive bacteria, gram negative bacteria as well as against fungal strains [54]. Seaweeds like *Sargassum Myriocystum* is a natural bio surfactant that is used as strong reducing and stabilizing agent to produce 36nm particle size ZnO NPs [55]. Triangular ZnO NPs with particle size 53nm has been biosynthesize by using *Thevetia Pervuiona* leaves extract [56].

Rajeshwari Sivaraj reported the formation of stable, spherical ZnO NPs by utilizing the 50% concentration of *Tabernamontana* leaf extract and exhibits the effective cytotoxic effect against MCF-7 breast cancer cell lines with an IC₅₀ value of 30.65 µg/ml/2h by MTT assay [57]. M.Manokali utilize the leaf, stem, roots, and fruit of a medicated plant, *M. Mercurialis L.Benth*, to produce ZnO NPs and found that the protein, steroids and alkaloids are responsible for the reduction of zinc nitrate and enhance the stability of ZnO NPs [58].

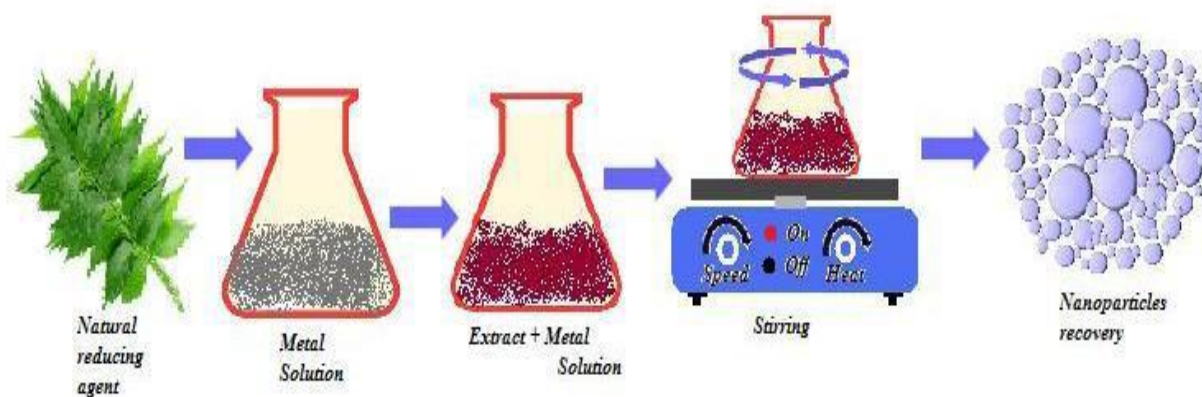


Figure 1. Synthesis of Nanoparticle from plant extract

Synthesis of ZnO NPs by Bacterias:

42-64nm size ZnO NPs synthesized by utilizing reproducible bacteria *Aeromonas Hydrophila* exhibit greater degree of hindrance against *Pseudomonas Aeruginosa* and *Aspergillus Flavus* [59].

K.Prasad reported the fabrication of ZnO NPs at room temperature by using the reproducible probiotic microbe (*Lactobacillus Sporogens*) as a reducing and stabilizing agent. By alteration of pH and partial pressure of gaseous hydrogen, oxido-reductase activates that are pH sensitive and are capable of producing ZnO NPs. By the addition of nutrient medium such as carbohydrates, the oxidation-reduction potential is lowered, which enhances the growth of anaerobes in the presence of oxygen. By lowering the pH, oxidoreductase bound in membrane stimulates which enhance the ZnO NPs synthesis [60].

Mohd Zobair Hosain uses the *Bacillus cereus* as a bio templating agent for the synthesis of ZnO NPs of specific shape and dimension by a hydrothermal method. The interaction between ZnO and microbial cell involves the biochemistry and surface chemistry processes that is proposed mechanism for the fabrication of ZnO NPs [61].

Characterization:

The characterization of nano particles is meaningful to investigate and control the synthesis of nano particles and their application. Nanoparticle characterization can be accomplished by a wide range of techniques like scanning and transmission electron microscopy (SEM, TEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), dynamic light scattering (DLS), powder X-ray diffractometry (XRD), and UV- Vis spectroscopy. These techniques are significant to measure the parameters like particle size, shape, pore size, fractional dimensions, crystallinity and surface area.

SEM and TEM are used to measure the particle size while morphology i.e particle height and volume can be determined by AFM. Dynamic Light Scattering can be executed to govern the particle size distribution. Furthermore, X-Ray diffractometer is applied to find out the crystallinity and shape of particle whereas sample formation can be confirmed by using UV-Vis spectroscopy.

Applications:

Antimicrobial Activity:

The activity through which the bacterial growth can be inhibited is antibacterial activity and antibacterial agent is a drug that has ability to inhibit the growth of bacteria. Different methods are applicable to analyze antibacterial activity including agar dilution, broth dilution, disk diffusion, and the microtiter plate-based method [62]. The proposed mechanism for antibacterial activity may be direct interaction of ZnO NPs with cell wall, spoliation of bacterial cell stability or formation of reactive groups (ROS). Various factors affect the antibacterial activity like thermal annealing, ZnO defects, morphology, surface charge, particle size and concentration as well as UV illumination [63]

Lili He investigated the antifungal activity of ZnO NPs (70nm) against two post-harvest pathogenic fungi i.e. *Botrytis Cinerea* and *penicillium expansum*. ZnO NPs restrains the growth of *B.Cinerea* by agitating cellular function which influences the deformation in fungal hyphae [64]. ZnO NPs isolated from *Aeromonas Hydrophila*, has antibacterial activity against *Pseudomonas Aeruginosa* and *Aspergillus Flavus* [59]. ZnO NPs exhibit the robust bacterial activity against Gram-Positive and Gram-Negative Bacteria [45]. ZnO NPs fabricated from Neem (*azadirachta Indica*) showed excellent antibacterial activity against *E.Coli* [36].

Photocatalytic Activity:

A lot of research work has been done on the photocatalysis in recent years. In this process, oxidation reduction reaction is take place on the surface of catalyst which generates the electron-hole pair under the intensity of light. Organic pollutant can be oxidized through photogenerated hole in the presence of photocatalyst. One of the most commonly used photocatalyst is ZnO NPs [65].

The photo catalytic Degradation of Mehtylene blue (MB) was estimated by ZnO NPs isolated from *Corymbia Citriodora* leaf extract under UV-Vis irradiation [37]. Chen Hao reported the photocatalytic degradation of Methylene Blue and Methyl Orange in the presence of Graphene-ZnO nanocomposites under solar irradiation. By increasing the ratio of grapheme, the absorption of sunlight is increased and ultimately effects the degradation of Methylene Blue and

Methyl Orange [66]. The photocatalytic reduction of Cr (IV) has been observed by using ZnO nanoparticles and it is concluded that by changing the morphology of NPs, the catalytic activity can either be enhanced or suppressed [67]. Methyl Orange shows 95% degradation under UV radiation utilizing ZnO NPs synthesized by Micro-wave assisted ball milling [68]. Sasan Rabieh investigated the effect of concentration of dye and ZnO NPs and pH on photocatalytic degradation of Malachite Green. It is observed that Malachite Green firstly adsorbed on the surface of ZnO NPs followed by degradation. While the hydroxyl group is the main reactive specie contributes in degradation [69].

Miscellaneous Applications:

ZnO NPs can also be used as an adsorbent to remove different type of pollutants. H₂S liberate from petroleum products accumulate in air and aquifers and cause pollution. The allowed concentration of H₂S liberated in environment should be less than 15ppm. To protect the environment and habitat, ZnO NPs can be effectively used to remove the H₂S [60].

Rajeshwari Sivaraj reported the cytotoxic effect of ZnO NPs against MCF-7 breast cancer cells having IC₅₀ value of 30.65 µg/ml/24 h by the MTT assay. The result shows that ZnO NPs exhibit best anticancer activity [57].

ZnO NPs also have an application in soil sciences and agriculture. ZnO NPs enhance the soil microbial population and soil exo-enzyme activities and as a result increase the growth activity of peanut plant (number of leaves, dry weight of roots and shoots, leaf surface area, root length, shoot length, plant height fresh and the total biomass) [56].

ZnO NPs can also be used in the manufacturing of various cross-linkage rubber products [71]. Przybyszewska *et al.* utilize the ZnO NPs of different dimension and morphology as a cross linking agent of carboxylated nitrile elastomer mainly to investigate the alliance between key features of ZnO NPs and its activity in cross linkage process [72]. It reveals that ZnO NPs enhance the mechanical property, tensile strength and higher cross link density of vulcanizates in comparison with micro size ZnO. Thomas *et al.* fabricated BIAT-capped ZnO (ZOB), the novel accelerators *N*-benzylimine aminothioformamide(BIAT)-capped-stearic acid-coated nano-ZnO (ZOBs), and stearic acid-coated nano zinc phosphate (ZPS) by sol gel method in order to determine the impact of capping compound on remedy and mechanical properties of natural rubber (NR). This capping technique can enhance the scorch safety of rubber compound by slow down the liberation of BIAT from the capped ZnO into the rubber matrix [73].

Sabura *et al.* synthesise nano zinc oxide of size ranging from 15-30nm by a solid-state pyrolytic method and used these ZnO NPs as a curing agent for neoprene rubber. He concluded that small concentration of ZnO is sufficient for curing and enhance the mechanical properties of neoprene rubber as compare to micro-sized ZnO [74].

As ZnO NPs have greater potential to absorb UV radiation, so used in sun creams, lotions [75]. As ZnO NPs exhibit excellent drying and antibacterial properties so widely used in the manufacturing of large variety of medicine. Due to its wound healing property, it is used in dermatological

substances versus inflammation and itching. It is also used as a dietary supplement and nutritional product [76].

ZnO NPs are used as self-cleaners, UV blockers and water repellent in the field of textile industry. ZnO NPs that are hydrothermally grown on SiO₂-cotted cotton fabric exhibit outstanding UV-blocking properties [77]. Ates *et al.* grown ZnO nanowires on the cotton fabrics by microwave-assisted hydrothermal method in order to find out the superhydrophobicity, self-cleaning and ultraviolet (UV) blocking properties [78].

CONCLUSION:

This review comprises of the biogenic synthesis, characterization and various application of ZnO NPs. The above mention method is low cost, single step and green method for the synthesis of metal oxides like ZnO NPs. As ZnO NPs are semiconductor and piezoelectric material, shows various applications in electronics, solar cell diodes, catalysis and sensors. It also shows excellent antimicrobial, photocatalytic and anticancer activity.

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