



Green Synthesis and Characterization of Zinc Oxide Nanoparticles by Using Numerous Plants: A Review

Harshal S Kharde*, Sandeep R Gadhave, Gokul J Pawar, Akash R Ranmale

Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and commerce, Pravaranagar, Maharashtra, India.

*Corresponding author: harshalkharde123456@gmail.com

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ABSTRACT

Nanotechnology deals with the production and usage of material with nanoscale dimension. The nanoscale dimension provides nanoparticles with a large surface area to volume ratio and thus very specific properties. Zinc oxide nanoparticles (ZnO NPs) had been in recent studies due to its large bandwidth and high exaction binding energy and it has potential applications like antibacterial, antifungal, anti-diabetic, anti-inflammatory, wound healing, antioxidant and optic properties. Due to the large rate of toxic chemicals and extreme environment employed in the physical and chemical production of these NPs, green methods employing the use of plants, fungus, bacteria and algae have been adopted. This review is a comprehensive study of the synthesis and characterization methods used for the green synthesis of ZnO NPs using different biological sources.

Keywords: Green synthesis, Zinc oxide, Nanoparticles, Biological.

INTRODUCTION

Nanomaterials are particles with nanoscale dimension, and nanoparticles are very small particles with enhanced catalytic reactivity, thermal conductivity, non-linear optical performance and chemical steadiness owing to its large surface area to volume ratio.^[1] Nanoparticles (NPs) are considered nano antibiotics because of their antimicrobial activities.^[2] Nanoparticles have been integrated into various industrial, health, food, feed, space, chemical, and cosmetics industries of consumers, which calls for a green and environment-friendly approach to their synthesis.^[3]

Methods of Nanoparticle Synthesis

Two approaches have been suggested for nanoparticle synthesis: Bottom-up and top-down approaches. The top-down approach involves milling or attrition of large macroscopic particles. It involves synthesizing large-scale patterns initially and then reducing it to the nanoscale level through plastic deformation. This technique cannot be employed for large-scale production of nanoparticles because it is a costly and slow process.^[4] Interferometric Lithography (IL) is the most common technique that employs the top-down approach for nanomaterial synthesis.^[5] This technique involves the synthesis of nanoparticles from already miniaturized atomic components through self-assembly. This includes formation through physical and chemical means. It is a comparatively cheap approach.^[6] It is based on kinetic and thermodynamic equilibrium approach. The kinetic approach involves MBE (molecular beam epitaxial).

Different Methods used in Nanoparticle Synthesis

In the physical method, physical forces are involved in the attraction of nanoscale particles and the formation of large, stable, well-defined nanostructures. Its example includes nanoparticle synthesis through the colloidal dispersion method. It also includes basic techniques like vapor condensation, amorphous crystallization, physical fragmentation and many others.^[7-10] Nanoparticle synthesis is mediated by physical, chemical and green methods.^[11-13] The physical method involves using costly equipment, high temperature and pressure,^[14] and a large space area for setting up machines. The chemical method involves the use of toxic chemicals, which can prove to be hazardous for the environment and the person handling them. The literature states that some of the toxic chemicals we use in physical and chemical methods may reside in the NPs formed, which may prove hazardous in their application in the medical sciences.^[15] Thus, we needed an environment-friendly and cost-effective method for nanoparticle synthesis. The physical process involves the use of high vacuum in processes like pulsed laser deposition, MBE (molecular beam epitaxial), thermal evaporation etc. [16] and chemical methods include chemical micro emulsion, wet chemical, spray pyrolysis, electrode position,^[16] chemical and direct precipitation and microwave-assisted combustion.^[17] Physical and chemical methods need Additional capping and stabilizing agents.^[18-21]

Green Approach

Biosynthesis of nanoparticles is synthesizing nanoparticles using microorganisms and plants with biomedical applications. This is an

environment-friendly, cost-effective, biocompatible, safe, green approach.^[22] Green synthesis includes synthesis through plants, bacteria, fungi, algae etc. They allow large-scale production of ZnO NPs free of additional impurities.^[23] NPs synthesized from a biomimetic approach show more catalytic activity and limit the use of expensive and toxic chemicals. These natural strains and plant extracts secrete some phytochemicals that act as both reducing agent and capping or stabilization agent; for example, synthesis of ZnO nanoflowers of uniform size from cell soluble proteins of *B. lichen* form is showed enhanced photocatalytic activity and photo stability clearly depicted by 83% degradation of methylene blue (MB) pollutant dye in the presence of ZnO nanoflowers considering the fact that self-degradation of MB was null (observed through the control value) and through three repeated cycles of the experiment at a different time interval, degradation was found at 74% which clearly showed photo stability of ZnO nanoflowers produced.^[24] Oblate spherical and hexagonal-shaped ZnO NPs of size ranging from 1.2 to 6.8 nm have been synthesized using fungal strain *Aspergillus fumigatus* TFR-8 and these NPs showed stability for 90 days confirmed by measuring hydrodynamic diameter of NPs using particle size analyzer which showed agglomeration formation of NPs only after 90 days suggesting high stability of NPs formed using the fungal strain.^[25] ZnO NPs of size 36 nm synthesized from seaweed *Sargassum myriocystum* (microalgae) obtained from the gulf of Mannar showed no visible changes even after 6 months, demonstrating the stability of NPs formed. From FTIR result studies, it has been confirmed that fucoidan-soluble pigments secreted from microalgae were responsible for the reduction and stabilization of the NPs. Plant parts like roots, leaves, stems, seeds, and fruits have also been utilized for NP synthesis as their extract is rich in phytochemicals that act as both reducing and stabilization agents.^[26-32] ZnO NPs synthesized from *Trifolium pratense* flower extract showed similar peaks in the UV-vis spectrophotometer after 24, 48, 72, 96 and 120 hours of NP formation, showing the NPs' stability.^[33] Similarly, the fruit extract of *Rosa canina* acted as both a reducing and stabilizing agent for synthesized ZnO NPs, confirmed by FTIR studies. Biocapping is done by carboxylic and phenolic acid present in fruit extract. Spherical-shaped ZnO NPs were formed by Aloe vera leaf extract where free carboxylic and the amino group of plant extract acted as both reducing and capping agents.

Zinc Oxide Nanoparticles

ZnO is an n-type semiconducting metal oxide. Zinc oxide NP has drawn interest in the past two to three years due to its wide applicability in electronics, optics, and biomedical systems.^[34-40] Several types of inorganic metal oxides have been synthesized and remained in recent studies like TiO₂, CuO and ZnO of all these metal oxides, ZnO NPs is of maximum interest because they are inexpensive to produce, safe and can be prepared easily.^[41] US FDA has enlisted ZnO as generally recognized as safe (GRAS) metal oxide.^[42] ZnO NPs exhibit tremendous semiconducting properties because of its large band gap (3.37 eV) and high excitation binding energy (60 meV) like high catalytic activity, optic, UV filtering, anti-inflammatory and wound healing properties.^[43-49] Due to its UV filtering properties, it has been extensively used in cosmetics like sunscreen lotions.^[50] It has a wide range of biomedical applications, such as drug delivery, anticancer, anti-diabetic, antibacterial, antifungal, and agricultural

properties.^[51-55] Although ZnO is used for targeted drug delivery, it still has the limitation of cytotoxicity, which has yet to be resolved.^[56] ZnO NPs have a very strong antibacterial effect at a very low concentration of gram-negative and gram-positive bacteria as confirmed by the studies, they have shown a strong antibacterial effect than the ZnO NPs synthesized chemically.^[57-59] They have also been employed for rubber manufacturing, paint, for removing sulfur and arsenic from water, protein adsorption properties, and dental applications. ZnO NPs have piezoelectric and pyroelectric properties.^[60,61] They are used for the disposal of aquatic weeds, which is resistant to all types of eradication techniques like physical, chemical and mechanical means.^[62] ZnO NPs have been reported in different morphologies like nanoflake, nanoflower, nanobelt, nanorod and nanowire.

LITERATURE STUDY

Due to the increasing popularity of green methods, different works have been done to synthesize ZnO NPs using different sources like bacteria, fungi, algae, plants, and others.

Green synthesis of ZnO NPs using plant extract

Plant parts like leaf, stem, root, fruit, and seed have been used for ZnO NPs synthesis because of the exclusive phytochemicals that they produce.^[63,64] Using natural extracts of plant parts is a very eco-friendly, cheap process that does not involve using any intermediate base groups.^[65] It takes much less time, does not involve using costly equipment and precursors, and gives a highly pure and quantity-enriched product free of impurities.^[66] Plants are most preferred source of NPs synthesis because they lead to large-scale production and production of stable, varied in shape and size NPs.^[67] Bio-reduction involves reducing metal ions or metal oxides to 0 valence metal NPs with the help of phytochemicals like polysaccharides, polyphenolic compounds, vitamins, amino acids, alkaloids, terpenoids secreted from the plant.^[66,67] Most commonly applied method for simple preparation of ZnO NPs from leaves or flowers is where the plant part is washed thoroughly in running tap water and sterilized using double distilled water (some use Tween 20 to sterilize it). Then, the plant part is kept for drying at room temperature, followed by weighing and crushing it using a mortar and pestle. Milli-Q H₂O is added to the plant part according to the desired concentration and the mixture is boiled under continuous stirring using a magnetic stirrer.^[68] The solution is filtered using Whatman filter paper and the obtained clear solution was used as a plant extract (sample). Some volume of the extract is mixed with 0.5 Mm of hydrated Zinc nitrate, zinc oxide, or zinc sulfate and the mixture is boiled at desired temperature and time to achieve efficient mixing.^[69] Some perform optimization at this point using different temperatures, pH, exact concentrations, and time. The incubation period results in a change of color of the mixture to yellow which is a visual confirmation of the synthesized NPs.^[70] Then, UV-vis spectrophotometry is employed to confirm the synthesis of NPs followed by centrifugation of the mixture and drying the pellet in a hot air oven to get the crystal NPs.^[71] Further synthesized nanoparticles are characterized using X-ray diffractometer (XRD), energy dispersion analysis of X-ray (EDAX), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), atomic force

microscopy (AFM), thermal-gravimetric differential thermal analysis (TG-DTA), photoluminescence analysis (PL), X-ray photoelectron microscopy (XPS), Raman spectroscopy, attenuated total reflection (ATR), UV-visible diffuse reflectance spectroscopy (UV-DRS), and dynamic light scattering (DLS) methods.^[72,73] An experiment conducted by Jafarirad *et al.* compared the results of NPs obtained through 2 different techniques, conventional heating (CH) and microwave irradiation (MI), and results clearly demonstrated that MI takes less time for NPs synthesis attributed to the high heating rate that MI provides and thus faster reaction rate.^[74] Plants like *Anisochilus carnosus*, *Plectranthus amboinicus*,^[75] and *Vitex negundo*^[76] belonging to the Lamiaceae family have been extensively studied, which showed NPs formation of varied sizes and shapes like spherical, quasi-spherical, and hexagonal, rod-shaped with agglomerates. Results clearly indicated that with the increasing concentration of a plant extract, the size of synthesized NPs decreases.^[77] Results also compared the size ranges observed through different techniques like FE-SEM, TEM, XRD, which showed similar range values.^[78] SEM and EDAX showed similar results different from results of XRD. NPs synthesized from *Vitex negundo* leaf and flower showed a similar size of 38.17 nm confirmed by XRD analysis calculated through Debye-Scherrer equation.^[79] Leaves of *Azadirachta indica* of Meliaceae family have been most commonly used for the synthesis of ZnO NP.^[80] All experiments showed NPs in similar size range confirmed by XRD and TEM analysis with a spherical shape, hexagonal disc shape, and Nano buds. These studies elucidated the involvement of alcohol, amide, amine, alkane, carboxylic acid, and carbonate moieties in forming NPs, which were confirmed through FTIR studies. Fresh leaf extract and leaf peel of *Aloe vera* belonging to Liliaceae family. [81-84] Synthesized NPs showed a difference in size (NP synthesized from peel was greater in size confirmed by SEM and TEM analysis) but similar in shapes (hexagonal and spherical).^[85-88] NPs synthesized from extracts of *Agathosma betulina*, *Moringa oleifera*, *Pongamia pinnata*, *Plectranthus amboinicus*, *Nepheleium lappaceum* and *Calatropis gigantea* showed agglomerate formation.^[89,90]

Green synthesis of ZnO NPs using other green sources

Biocompatible chemicals are used as some other green sources for the synthesis of nanoparticles. It is a fast, economical process that eliminates the production of any kind of side product in nanoparticle nucleation and synthesis reaction. It leads to the formation of nanoparticles of a controlled shape and size with their well-dispersed nature.^[91] Nanoparticles synthesized through wet chemical method render them special properties like enhanced antibacterial efficiency up to 99.9% when coated on a cotton fabric.^[92] Table 5 illustrates a few other green sources that have been employed for the synthesis of ZnO NP.^[93,94]

CONCLUSION

The biosynthesis of nanoparticles using an eco-friendly approach has been the area of focused research in the last decade. Green sources stabilize and reduce agents for synthesizing shape and size-controlled nanoparticles. The future prospect of plant-mediated nanoparticle synthesis includes an extension of laboratory-based work to an industrial scale, elucidation of phytochemicals involved in the

synthesis of nanoparticles using bioinformatics tools and deriving the exact mechanism involved in inhibition of pathogenic bacteria. The plant-based nanoparticle can have huge applications in the food, pharmaceutical, and cosmetic industries and thus become a major area of research.

CONFLICTS OF INTEREST

Authors readily declare that the review article does not content any conflict of interest and is not associated with anyone.

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