

GREEN NANOPARTICLES A CRITICAL REVIEW**Govindaram Pallavi^{1*}, Ceema Mathew²**

¹Department of Pharmaceutical Analysis, Gokaraju Rangaraju College of Pharmacy,
Hyderabad-500 090, Telangana, India.

²Department of Pharmaceutical Chemistry, Gokaraju Rangaraju College of Pharmacy,
Hyderabad 500 090, Telangana, India.

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Corresponding Author*Govindaram Pallavi**

Department of Pharmaceutical
Analysis, Gokaraju Rangaraju College
of Pharmacy, Hyderabad-500 090,
Telangana, India.



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ABSTRACT

The rapid advancement of nanotechnology has positioned nanoparticles (NPs) as fundamental building blocks across diverse scientific and technological domains. These nanoscale materials, exhibiting unique physicochemical properties arising from their size (1-100 nm), are synthesized and manipulated through interdisciplinary efforts spanning chemistry, engineering, physics, and biology. While noble metal NPs, such as gold, silver, and platinum, have been extensively explored due to their remarkable properties, conventional chemical and physical synthesis routes often involve hazardous precursors and energy-intensive processes, raising significant ecological and health concerns. This necessitates the development of sustainable and environmentally benign NP production technologies.

KEYWORDS: Nanotechnology, Biosensors, Nanoimaging.

INTRODUCTION

Nanotechnology is a scientific discipline focused on the study of materials at the nanoscale, typically ranging from 1 to 100 nm. It operates at this tiny scale and offers numerous benefits across various fields of science, such as dentistry, pharmaceuticals, and bioengineering.^[1] Currently, various nanoparticle morphologies are being developed, including nanoshells, nanorods, nanoneedles, nanospheres, nanocubes, nanoplates, and more.^[2] This review examines current research focused on the environmentally-friendly synthesis of inorganic

nanoparticles (NPs), which offers several advantages over traditional methods that rely on chemical agents harmful to the environment. The article explores conventional synthesis techniques, highlighting recent advances in greener alternatives for producing metal, metal oxide, and other essential NPs. It also delves into the mechanisms of formation and the factors that influence the surface morphology, dispersity, and other characteristics of biosynthesized NPs. The review concludes with an analysis of the current landscape and future prospects for nanoparticle production through various green methods.

In summary, the demand for nanomaterials in a wide range of applications, from biomedicine to bioenergy, is rapidly increasing. This is due to their nanoscale size, which is associated with a high surface area that facilitates the loading of molecules for diverse scientific uses, such as drug delivery systems for treating conditions like cancer. When employing nanomaterials as drug carriers, assessing their toxicity is crucial.

This consideration has led to the adoption of green synthesis methods, which offer a safer alternative to chemical processes that create toxic nanocarriers. A metal oxide that responds to various stimuli could serve as an effective approach to targeted drug delivery. Beyond drug delivery, these nanomaterials are also highly effective in bioremediation, as they can break down pollutants without harming ecosystems, due to their synthesis from natural substances. This study primarily highlights advanced green synthesis techniques for metal oxide nanoparticles that respond to multiple stimuli, leading to cost-effective and versatile nanomaterials suitable for a range of applications. Their biodegradability, a key feature of this work, enhances their environmental sustainability. This green approach not only produces highly efficient nanocarriers but also ensures that their function does not negatively impact living organisms or the environment.

The three primary factors for nanoparticle synthesis are the choice of eco-friendly solvent, an effective reducing agent, and a safe material for stabilization. A wide range of synthetic methods have been utilized for nanoparticle production, with physical, chemical, and biosynthetic routes being the most common. However, chemical methods are often costly and involve the use of hazardous and toxic chemicals, which pose environmental risks. In contrast, the biosynthetic route is a safe, biocompatible, and environmentally friendly method for synthesizing nanoparticles, utilizing plants and microorganisms for biomedical applications. This approach can involve fungi, algae, bacteria, and plants. Various plant parts, including leaves, fruits, roots, stems, and seeds, have been used to synthesize nanoparticles.

due to the presence of phytochemicals in their extracts, which act as reducing and stabilizing agents. Nanoparticle synthesis through biological and physicochemical methods can be classified into two main categories: bottom-up and top-down approaches.

Bottomupapproach

The bottom-up approach refers to the creation of nanoparticles from smaller units such as atoms and molecules, or through the self-assembly of atoms into new nuclei. These nuclei then grow into particles with nanoscale dimensions, utilizing various chemical and biological methods.

Top down approach

In this approach, nanoparticles are formed through a size reduction method, where a suitable bulk material is broken down into smaller units using techniques such as crushing, splitting, and milling.

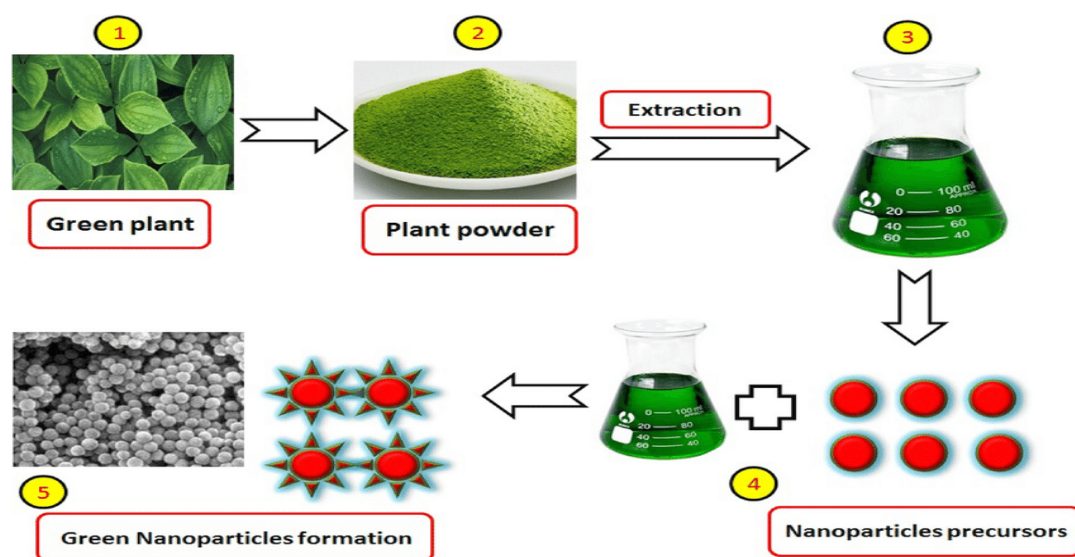


Figure -1 synthesis of green nanoparticles.

Solvents for green synthesis

"Nanoparticle (NP) production typically involves solvents constituting over 80% of the reaction mixture. Given their substantial environmental impact, selecting sustainable solvents is crucial for green chemistry. While organic solvents are often used to dissolve precursors and facilitate NP synthesis, their toxicity necessitates careful handling. Green synthesis prioritizes alternatives, especially water, which is non-toxic, non-flammable, and abundant.^[1] However, water's high heat capacity can lead to energy-intensive processes.^[2] Consequently,

research has explored alternative solvents like supercritical (SC) fluids (e.g., SC CO₂) and ionic liquids (ILs) to mitigate environmental concerns.^[3] SC fluids, formed by heating ordinary solvents above their critical temperature, offer increased free space and compressibility."

Systems for green synthesis of NPs

Green synthesis from enzymes

The well-defined structure and high purity of enzymes make them ideal for green synthesis methods. For instance, silver nanoparticles (Ag NPs) were synthesized through an enzyme-induced growth process on solid substrates. Enzymes were incorporated into polymer multilayer-assembled membranes via electrostatic interactions to facilitate the direct, "green" synthesis of bimetallic Fe/Pd particles in a membrane environment.^[4] The generation of gold nanoparticles (Au NPs) using extracellular amylase to reduce AuCl₄ while preserving enzymatic activity in the complex has been documented. Additionally, a reaction surface approach combined with central composite rotary design (CCRD) was employed to optimize a fermentation medium for α -amylase production by *Bacillus licheniformis* at pH 8.^[5] A sulfite reductase enzyme, purified from *E. coli* via ion-exchange chromatography, was utilized to create a cell-free extract for Au NPs synthesis, exhibiting antifungal activity against human pathogenic fungi.^[6] Nanoparticles (NPs) can also be synthesized from agro-wastes such as *Cocos nucifera* coir, corn cob, fruit seeds and peels, wheat and rice bran, and palm oil. These materials, rich in biomolecules like flavonoids, phenolic compounds, and proteins, can act as reducing agents for NP synthesis. In one method involving beet juice, it was found that reducing the quantity of beet juice resulted in the formation of larger Ag NPs, which demonstrated significantly higher catalytic activity and stability compared to those produced with NaBH₄ in the transformation of 4-nitrophenol to 4-aminophenol.^[7] Green tea extracts were used to produce bimetallic Fe/Pd NPs for the first time, as these extracts function both as reducing and capping agents.^[8] Au NPs, functionalized with a redox enzyme, can act as electron transmitters between a biocatalyst and an electrode, thus creating a hybrid electrically active biomaterial for various sensor applications.^[9]

Green synthesis from vitamins

A green approach involving the combination of silver (Ag) and palladium nano-spheres, nanowires, and nano-rods has been reported, utilizing vitamin B2 as both a reducing and capping agent. Vitamin B2 serves as the reducing agent in the synthesis of nanowires and

nanorods. This unique method in green nanotechnology highlights the use of natural agents to advance the field, such as their effects on various tumor cells.^[10] Ascorbic acid is employed as both a capping and reducing agent, with chitosan used as a stabilizing agent due to its ability to bind with metal ions. The concentration of nanoparticles is directly influenced by the amount of chitosan used.^[11] A straightforward method for producing uniform-sized nanoparticles using ascorbic acid as the reducing and capping material has been reported.^[12] Additionally, water-soluble antioxidants like ascorbic acid play a crucial role in reducing silver nanoparticles (Ag NPs) in *Desmodium triflorum*. During glycolysis, plants generate significant amounts of H⁺ ions along with NAD, acting as potent reducing agents, which aids in the formation of Ag NPs.^[13]

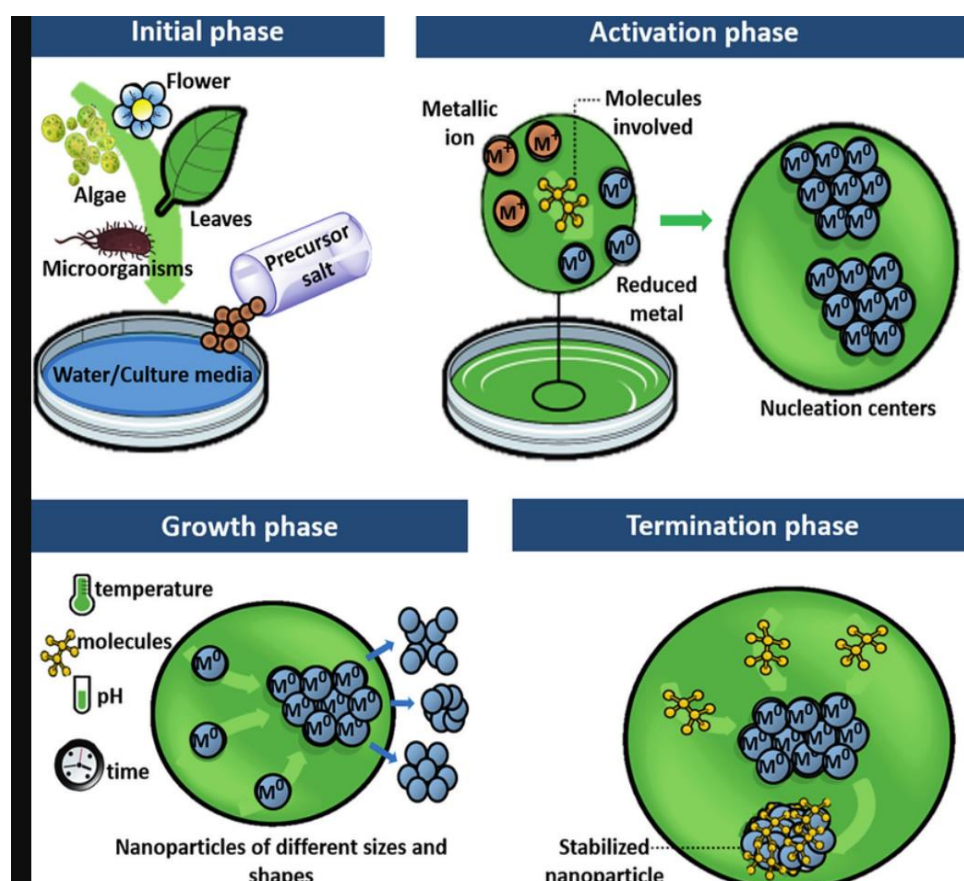


Figure -2 phases of nanoparticles.

Types of nanoparticles

Silver nanoparticles

Silver nanoparticles (AgNPs) are commonly utilized nanoparticles and have attracted much study interest due to their distinctive properties. They are widely used in emerging

biomedical and industrial applications.^[14] AgNPs exhibit completely different characteristics from bulk materials derived from the same material due to their elevated surface/volume ratio.^[15] In recent times, the synthesis of silver NPs by bio-organisms containing phytochemical agents has become an important goal for workers. Various unique secondary metabolites derived from plant extracts such as sugars, alkaloids, phenolic acids, flavonoids and terpenoids are responsible for bio-reducing ionic silver metal into nanoparticle.^[15]

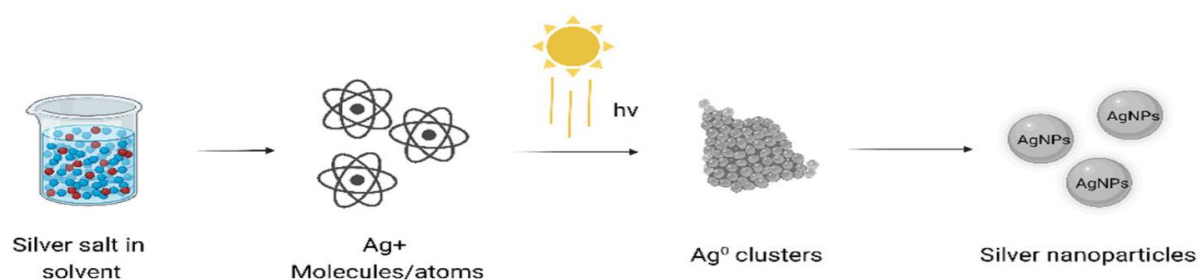


Figure -3 Formation of silver nanoparticles.

Gold nanoparticles

The synthesis of gold [Grab your reader's attention with a great quote from the document or use this space to emphasize a key point. To place this text box anywhere on the page, just drag it.] nanoparticles (AuNPs) using plant extracts offers a green and sustainable alternative. These AuNPs possess remarkable applications across various fields. While the stability of biogenically synthesized AuNPs can be limited, numerous studies have demonstrated successful synthesis using diverse plant sources. Specifically, tea leaf extract, *Morinda citrifolia* root extract (8-17nm), *Nyctanthes arbortristis* alcoholic extract (19.8 ± 5.0 nm, spherical), *Aegle marmelos* leaf extract (4-10 nm, spherical), *Garcinia mangostana* peel aqueous extract (32.96 ± 5.25 nm, spherical), and *Mimosa tenuiflora* bark extract have been utilized. The reduction of gold ions to form AuNPs is often facilitated by phytochemicals such as anthocyanins, benzophenones, flavonoids, and phenols, as evidenced by FTIR analysis in the *G. mangostana* synthesis. TEM analysis confirms the size and morphology of the synthesized AuNPs.^[17]

Zinc nanoparticles

Zinc oxide (ZnO) nanoparticles (ZnNPs) are gaining significant attention for their wide range of applications, driven by their unique properties such as low cost, large surface area, UV-filtering capabilities, and antimicrobial activity.^[18] A sustainable approach to ZnNP synthesis involves utilizing plant extracts, which contain phytochemicals (e.g., polyphenols, saponins,

terpenoids) that act as reducing and stabilizing agents. These phytochemicals, present in plant roots, stems, leaves, fruits, and seeds, enable the reduction of zinc ions, followed by complex formation, hydrolysis to Zn(OH)_2 , and ultimately, calcination to form ZnO ^[19] Plants from the Fabaceae, Rutaceae, Apocynaceae, Solanaceae, and Lamiaceae families are commonly employed, with Lamiaceae plants like *Anisochilus carnosus*, *Plectranthus amboinicus*, and *Vitex negundo* yielding ZnNPs with diverse morphologies.

Titanium dioxide nanoparticles

Titanium dioxide nanoparticles (TiNPs) are highly sought after due to their unique properties, including high surface area and stability, enabling applications in dye degradation, pharmaceutical detoxification, and wastewater treatment.^[20] Biogenic synthesis of TiNPs, utilizing microbes, algae, plants, and enzymes, offers a cost-effective and eco-friendly alternative. For example, *Eclipta prostrata* extract yields spherical TiNPs (36-68 nm), while *Albizia saman* leaf extract produces anatase crystals of 41 nm. *Curcuma longa* extract, rich in terpenoids and flavonoids, forms aggregated, circular TiNPs (160-220 nm). *Echinacea purpurea* extract results in TiNPs around 120 nm, and *Psidium guajava* leaf extract^[21], containing alcohols and amines, also facilitates TiNP synthesis.

Palladium nanoparticles

Palladium nanoparticles (PdNPs) are synthesized using plant materials due to the method's cost-effectiveness and environmental advantages. Plant extracts contain primary and secondary metabolites that reduce palladium salts to PdNPs.^[22] The synthesis process is influenced by plant extract concentration, pH, temperature, and incubation time, affecting the resulting PdNP size, shape, and stability. Various plant parts, including leaves, flowers, seeds, fruits, peels, and roots, have been utilized. *Evolvulus alsinoides* extract, containing alkaloids, flavonoids, saponins, tannin, steroids, and phenol, acts as a reducing and capping agent. *Hippophae rhamnoides* leaf extract, rich in polyphenols, yields spherical PdNPs ranging from 2.5 nm to 14 nm, as confirmed by TEM.^[23] *Salvadora persica* root extract, with polyphenols, produces PdNPs with an average size of 10 nm at 90°C. *Pulicaria glutinosa* extract, when reacted with PdCl_2 at 90°C, results in PdNPs ranging from 20 nm to 25 nm. *Glycine max* leaf extract produces uniformly spherical PdNPs with a 15 nm diameter. *Gardenia jasminoides* extract, containing antioxidants like geniposide and crocins, also facilitates PdNP synthesis.

Conditions for green synthesis

The synthesis and stability of biologically derived nanoparticles (NPs) are significantly affected by pH, temperature, and reaction time.

pH

The pH of the reaction medium plays an important role in the synthesis of NPs. The size and shape of the NPs vary due to the different concentrations of hydrogen ions. The larger particles are synthesized at lower pH values than higher pH values. For instance, the maximum number of AuNPs (25–85 nm) were synthesized from *Avena sativa* at pH 2, whereas relatively smaller NPs (5–20 nm) were synthesized at pH 3 and 4. The larger size AgNPs were synthesized at lower pH, whereas dispersed and smaller AgNPs were synthesized at higher pH using *Cinnamomum zeylanicum* bark extract.

Temperature

Temperature is a stimulating factor in the synthesis of metallic NPs, affecting the shapes and sizes of the synthesized NPs. When Au NPs were formed using *Cymbopogon flexuosus* leaf extract, at lower reaction temperatures (25 to 100°C) nano triangles were formed, whereas spherical NPs along with the nano triangles were synthesized at higher reaction (100° C) temperatures.

Pressure

Pressure plays a key role in determining the shape and size of synthesized nanoparticles (NPs). Notably, ambient pressure, within the range of 1-3 megapascals, has been shown to expedite the reduction of metal ions by phytochemical agents.

Incubation Time

The incubation time affects the quality, shape, and size of the NPs. It has been reported that a long incubation time could have resulted in shrinkage or aggregation of NPs, which can cause a limitation in the NPs' potential.

Applications



Figure -4 Applications of nanoparticles.

Anti inflammatory agents

Nanoparticles (NPs), despite their challenging detection due to weak signals, offer a promising solution for targeted drug delivery, particularly in inflammatory conditions like rheumatoid arthritis (RA). RA, a chronic autoimmune disease, causes joint swelling and destruction, and current treatments often lead to long-term side effects. Delivering drugs directly to inflammation sites could minimize these side effects, but it's technically complex and costly.^[24] NPs, acting as drug carriers, can achieve this targeted delivery. Studies using liposome-encapsulated drugs like glucocorticoids and clodronate have shown significant efficacy in animal RA models. For instance, clodronate liposomes administered intravenously suppressed RA onset by targeting macrophages, and PEG-coated liposomes containing prednisolone achieved tenfold greater effectiveness compared to conventional methods, with rapid symptom remission in rats. These findings suggest NPs are valuable candidates for anti-inflammatory therapies, especially in autoimmune diseases.^[25]

Anti coagulants

Traditional heparin-based anticoagulants, used in surgical procedures and blood clot treatment, pose bleeding risks and require close monitoring. Nanoparticles (NPs), specifically magnetic NPs, are being studied as safer alternatives. Heparin-stabilized ferrimagnetic iron

oxide nanoparticles (Hep-SPIONs) have shown comparable anticoagulant activity to commercial heparin in hemo dialysis, with added magnetic properties and good blood compatibility in animal models.^[26] These findings suggest Hep-SPIONs could be a safe and effective option for future blood purification procedures.

Thrombolytic activity

Cardiovascular disorders, including myocardial infarctions, venous thromboembolisms, and ischemic strokes, are life-threatening conditions primarily caused by blood vessel blockages. Current treatments involve thrombolytic drugs, specifically plasminogen activators (PAs), administered via injection.^[27,28] However, PAs have significant limitations, such as rapid elimination, a narrow therapeutic window, and the risk of bleeding. Nanomedicine, combining medical applications with nanotechnology, offers a promising approach to minimize these adverse effects.

Anticancer therapeutics

Nanoparticles (NPs) have shown promise in cancer treatment, with some exhibiting direct anticancer properties. For example, a 2019 study demonstrated that titanium oxide nanotubes coated with selenium NPs inhibited the growth of MG-63 cancer cells. These coated nanotubes also displayed antibacterial properties.^[29] Current cancer therapies, like chemotherapy, often fall short of optimal effectiveness. Mesoporous silica NPs, however, have emerged as effective drug delivery vectors due to their rapid dissolution rate.

Biosensors

Antimicrobial packaging utilizes organic compounds like essential oils, while nanobiosensors detect pathogens in food processing. Nanoparticles (NPs), including Ag, chitosan, copper, and metal oxides like ZnO and TiO₂, also possess antimicrobial properties.^[30] Traditional infectious disease diagnosis is slow and inefficient, but microbial biosensors offer rapid, cost-effective detection of pathogens, hormones, and DNA. For example, a biosensor using immobilized *Phanerochaete chrysosporium* ME446 detected epinephrine with high sensitivity. Similarly, biosensors using mast cells and *E. coli* SOS-EGFP detect viral antigens and DNA damage, respectively. Lab-on-a-chip devices further enhance detection sensitivity by integrating microbes onto microfluidic chips. Moreover, microbial biosensors are being explored for forensic identification of body fluid traces containing DNA and miRNA.^[31] These portable biosensors hold significant promise for various applications.

Nanoimaging

Nanoparticles (NPs) are increasingly used for diagnostic purposes due to their multimodal imaging capabilities at a molecular level. Their nanoscale size, loading capacity, and controlled release make them particularly effective in cancer diagnosis. Iron oxide magnetic NPs, for example, are used in MRI, drug delivery, and cancer therapy.^[32] Imaging sentinel lymph nodes (SLNs) with NPs allows for detailed monitoring of cancer cell growth. Carbon NPs synthesized from honey offer advantages in SLN imaging due to their optical absorption, small size, and rapid lymphatic transport. Similarly, fluorescent carbon NPs from grape juice provide a non-toxic, stable alternative to quantum dots for cellular imaging. These fluorescent NPs, with their photostability and brightness, are promising for future medical diagnostic tools.

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