ACTA BIOLOGY FORUM
Review Article
ISSN: 2583-7419
Journal homepage: biologyforum.actabotanica.org

Green Synthesis of Metal and Metal-Oxide Nanoparticles: Mechanisms, Characterisation and Biomedical, Environmental and Agricultural Applications- A Review

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Citation: Shailendra Madavi, and Poonam Bais (2026). Green Synthesis of Metal and Metal-Oxide Nanoparticles: Mechanisms, Characterisation and Biomedical, Environmental and Agricultural Applications- A Review. *Acta Biology Forum*. **DOI: https://doi.org/10.51470/ABF.2026.5.2.20**

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Received 17 April 2026 | Revised 13 May 2026 | Accepted 09 June 2026 | Available Online 12 July 2026

ABSTRACT

Green synthesis of nanoparticles (NPs) employs biological resources such as plant extracts, microorganisms, and biomolecules as reducing and stabilising agents, offering an environmentally benign alternative to conventional physical and chemical methods. This approach minimises the use of toxic reagents and harsh conditions, reduces energy consumption, and often yields nanomaterials with superior biocompatibility and functional surface chemistry. Plant-mediated and microbe-mediated routes have emerged as the most widely explored green strategies for synthesising metal and metal-oxide nanoparticles including silver, gold, platinum, palladium, zinc oxide, titanium dioxide, and iron oxides. Phytochemicals or microbial metabolites act as electron donors (reducing metal ions) and as capping agents that control nucleation, growth, and stabilization, thereby influencing size, shape, crystallinity, and surface charge. Biogenic nanoparticles exhibit promising applications across biomedicine, catalysis, environmental remediation, food and agriculture, and sensing, frequently matching or surpassing the performance of conventionally produced nanomaterials while offering improved sustainability. Nonetheless, challenges remain, including batch-to-batch variability, incomplete mechanistic understanding, scale-up limitations, and the need for systematic toxicological and life-cycle assessments.

Keywords: *Nanoparticles, green synthesis, metal oxide, phytochemical, nanomaterial.*

INTRODUCTION

Nanotechnology has transformed multiple sectors by enabling control of matter in the 1–100 nm range, where size-dependent properties yield unique optical, electronic, magnetic, and catalytic behaviours. Conventional nanoparticle synthesis typically relies on top-down (e.g., milling, lithography) or bottom-up (e.g., chemical reduction, sol–gel, thermal decomposition) methods that often require hazardous precursors, organic solvents, and high energy input, generating residues that raise environmental and health concerns [1][2][3]. Green synthesis, also called biogenic or bioinspired synthesis, aims to comply with green chemistry principles by using renewable feedstocks, aqueous media, mild temperatures, and non-toxic reagents, while maximizing atom economy and minimizing waste. The use of plant extracts, microbes, and isolated biomolecules offers a simpler and often single-step process where reduction and stabilization occur simultaneously, yielding nanoparticles with bio-derived capping layers that can impart additional functionality (e.g., targeting, antioxidant or antimicrobial activity) [4][5]. This review summarizes recent progress in green synthesis of nanoparticles with emphasis on plant and microbe-mediated approaches, mechanistic aspects, process parameters, characterization methods, and major application domains including biomedicine, catalysis, environmental remediation, and sustainable agriculture [6].

A. Principles and Advantages of Green Nanoparticle Synthesis

1. Green chemistry framework

Green nanoparticle synthesis is grounded in the 12 principles of green chemistry, particularly prevention of waste, safer solvents and auxiliaries, design of less hazardous syntheses, energy efficiency, use of renewable feedstocks, and inherently safer chemistry. In practice, this means avoiding strong chemical reductants such as sodium borohydride or hydrazine, replacing volatile organic solvents with water, and operating near ambient temperature and pressure when possible [7]. Biogenic routes typically employ plant extracts, microbial cell biomass, or extracellular metabolites as multifunctional agents that combine reduction, capping, and sometimes templating or directing roles in nanoparticle nucleation and growth. Because these biomolecules are derived from renewable resources and are biodegradable, the overall process often has a smaller environmental footprint than conventional synthesis, especially when waste biomass or agricultural residues are valorised [8].

2 Comparative advantages over conventional methods

Green synthesis offers several advantages over traditional physical and chemical routes [9]:

- Environmental friendliness: Avoidance of toxic reducing agents and surfactants decreases risks to workers and ecosystems and simplifies effluent treatment.
- Biocompatibility: Bio-capped nanoparticles often exhibit lower cytotoxicity and better compatibility with biological systems, which is crucial for biomedical and agricultural applications.
- Cost-effectiveness: Plant materials, microbial cultures, and agro-residues are generally inexpensive, and single-pot aqueous processes can reduce processing steps and energy costs.
- Functional surfaces: Biomolecules adsorbed on the nanoparticle surface can enhance colloidal stability and confer additional biological activities such as antioxidant or antimicrobial effects

However, challenges such as limited control over monodispersity, batch variability due to biological source heterogeneity, and sometimes slower kinetics relative to chemical reduction must be carefully managed, especially for scale-up.

B. Biological Resources for Green Synthesis

1. Plant extracts (photosynthesis)

Plant extracts are the most widely used biological resource for green synthesis of metal nanoparticles due to their rich diversity of secondary metabolites (phenolics, flavonoids, terpenoids, alkaloids, sugars, and proteins) [10][11]. These phytochemicals act as electron donors to reduce metal ions (e.g., Ag^{+}, Au^{3+}, Pt^{4+}, Pd^{2+}) and subsequently adsorb on nascent nuclei, preventing aggregation and controlling growth.

A broad range of plant parts leaves, stems, bark, roots, fruits, seeds, flowers, and even whole-plant biomass have been exploited to synthesise gold [12], silver [13], platinum [14], palladium, copper [15], and various metal-oxide nanoparticles [16][17]. Examples include *Rivina Humilis L.*, *Azadirachta indica* (neem), *Nicotiana plumbaginifolia*, *Uraria picta* and many other medicinal and aromatic plants, whose phytochemical richness facilitates efficient reduction and stabilisation of silver nanoparticles.

2. Microorganisms (bacteria, fungi, algae)

Bacteria, fungi, yeasts, and microalgae can synthesise nanoparticles either intracellularly or extracellularly through enzymatic or metabolite-mediated reduction of metal ions. Enzymes such as nitrate reductase, along with cell wall functional groups (e.g., carboxyl, amino, hydroxyl), participate in metal binding and reduction, whereas extracellular polysaccharides and proteins act as stabilizing agents [22]. Bacterial biogenic nanoparticles have attracted attention for agricultural applications such as phytosanitary protection, controlled-release fertilisers, and induction of plant stress resilience, with recent work proposing integrated "bacteria–nanoparticle–plant–microbiome" frameworks for sustainable crop production. Fungal-based synthesis (mycosynthesis) can yield high nanoparticle titters due to robust secretion of extracellular enzymes and metabolites, while algal systems provide additional advantages such as rapid growth and ease of cultivation in wastewater.

3. Isolated biomolecules and biopolymers

Isolated biomolecules (e.g., pure flavonoids, polyphenols, proteins, amino acids) and biopolymers (e.g., chitosan, starch, cellulose, alginate) can also mediate nanoparticle formation, offering more defined composition than crude extracts. Chitosan and plant-derived polysaccharides are particularly attractive as they can serve simultaneously as reducing agents, stabilisers, and functional coatings for metal or metal-oxide nanoparticles, improving colloidal stability and bioactivity [23].

C. Mechanistic Aspects of Biogenic Nanoparticle Formation

1. Reduction, nucleation, and growth

Biogenic nanoparticle formation generally involves three overlapping stages: reduction of metal ions to zero-valent atoms, nucleation of small clusters, and growth/aggregation into larger nanoparticles, all modulated by biomolecules present in the system. Electron-rich groups such as phenolic hydroxyls, aldehydes, and amines donate electrons to reduce metal ions, while simultaneous coordination or adsorption of these molecules on nuclei limits uncontrolled aggregation. Reaction conditions-including pH, temperature, precursor concentration, mixing rate, and extract-to-metal ion ratio-strongly affect nucleation and growth kinetics, thereby determining size distribution, morphology, and crystallinity. Higher temperatures and alkaline pH often accelerate reduction and nucleation, leading to smaller, more uniform particles, whereas higher metal salt concentrations or insufficient capping capacity may promote aggregation and polydispersity [24].

2. Role of phytochemicals and microbial metabolites

Phytochemicals such as flavonoids, tannins, phenolic acids, terpenoids, and sugars exhibit multiple functional groups capable of forming complexes with metal ions and participating in redox reactions. During silver nanoparticle synthesis, for example, carbonyl groups of flavonoids and phenolics can reduce Ag^{+} to Ag^{0} while oxidising themselves, resulting in a surface layer of oxidised metabolites that stabilize the particles in suspension [25]. In microbial systems, enzymes (e.g., reductases, dehydrogenases) and metabolites (e.g., organic acids, peptides, biosurfactants) facilitate electron transfer and template formation. Cell walls of bacteria and fungi, rich in peptidoglycan, chitin, and glucans, provide binding sites that concentrate metal ions and nucleation centres, particularly in intracellular synthesis pathways.

3. Mechanistic challenges and open questions

Despite considerable progress, mechanistic understanding of biogenic nanoparticle synthesis remains incomplete because plant extracts and microbial broths are complex, variable mixtures of many constituents whose individual contributions are difficult to decouple. Identifying specific molecules or pathways responsible for reduction and capping is an active research area that can help rationally optimize yields, size control, and functional properties [26]. Furthermore, there is a need for integrated kinetic and thermodynamic models that incorporate biomolecular interactions, mass transfer, and nucleation/growth dynamics to move beyond empirical optimization towards predictive design of green synthesis processes.

D. Types of Nanoparticles Produced via Green Synthesis

1. Noble metal nanoparticles (Ag, Au, Pt, Pd)

Green routes have been extensively applied to synthesize noble metal nanoparticles such as silver (AgNPs), gold (AuNPs), platinum (PtNPs), and palladium (PdNPs), owing to their strong surface plasmon resonance, catalytic activity, and biomedical relevance. Plant-extract-mediated AgNPs are by far the most widely reported, often yielding spherical or quasi-spherical particles in the 5–100 nm range with strong antimicrobial and anticancer activities [13]. Gold nanoparticles synthesized using plant extracts and microbes are exploited for drug delivery, imaging, and biosensing owing to their inertness, tunable plasmonic properties, and facile bioconjugation with proteins and nucleic acids. PtNPs and PdNPs produced via phytosynthesis or microbial methods show high catalytic efficiency for hydrogenation, carbon–carbon coupling, and environmental catalysis, and efforts are underway to translate these into industrial processes.

2. Base metals and metal-oxide nanoparticles

Green synthesis has also been extended to base metals and metal oxides such as copper, zinc oxide (ZnO), titanium dioxide (TiO_2), iron oxides (Fe_3O_4, γ-Fe_2O_3), and cobalt oxide, which are widely used in antimicrobial coatings, photocatalysis, magnetic separation, and agriculture [15] [16] [18] [20] [21]. Plant-mediated ZnO nanoparticles have been reported as efficient antimicrobial agents and inducers of systemic resistance in plants against viral and bacterial pathogens [20]. Biogenic iron oxide nanoparticles exhibit superparamagnetic behaviour useful for targeted drug delivery, magnetic resonance imaging contrast, and magnetic separation processes. Bioinspired CoO, CuO, and TiO_2 nanoparticles show promise in photocatalytic degradation of dyes and pollutants under visible or UV light, making them attractive for wastewater treatment.

3. Hybrid and composite nanostructures

Emerging work explores hybrid and composite nanostructures where green-synthesised nanoparticles are integrated with biopolymers, carbon-based materials (e.g., graphene, carbon dots), or other inorganic phases to achieve synergistic properties. Examples include chitosan–ZnO nanocomposites for enhanced antibacterial performance and controlled release, as well as polymer-supported biogenic noble metal nanoparticles for recyclable heterogeneous catalysis.

E. Characterisation of Green-Synthesized Nanoparticles

Comprehensive characterization is essential to confirm nanoparticle formation, evaluate stability, and correlate physicochemical parameters with biological or catalytic performance [27].

- **UV–Visible spectroscopy** is routinely used to monitor surface plasmon resonance (SPR) bands characteristic of metallic nanoparticles (e.g., ~400–450 nm for AgNPs, ~520–550 nm for AuNPs) and to follow reaction kinetics.[13]
- **Transmission electron microscopy (TEM) and scanning electron microscopy (SEM)** provide information on particle size, morphology, and aggregation state at high spatial resolution [21].
- **X-ray diffraction (XRD)** reveals crystalline structure and average crystallite size using peak broadening analysis (e.g., Scherrer equation)[15].
- **Dynamic light scattering (DLS)** and zeta potential measurements yield hydrodynamic size distribution and surface charge, reflecting colloidal stability and interaction tendencies.
- **Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy** identify functional groups associated with capping biomolecules and potential interactions between ligand shells and nanoparticle surfaces [18].

Combining multiple techniques is critical for reliable characterisation, especially for complex biological matrices where residual biomolecules or aggregates can complicate interpretation.

F. Biomedical and Pharmaceutical Applications

1. Antimicrobial and antibiofilm activities

Green-synthesised silver nanoparticles display broad-spectrum antibacterial, antifungal, and antiviral activities at relatively low concentrations, often outperforming bulk silver due to increased surface area and enhanced interaction with microbial membranes. Mechanisms include disruption of cell walls and membranes, generation of reactive oxygen species (ROS), interaction with thiol-containing enzymes, and interference with DNA replication [13]. Biogenic AgNPs, AuNPs, and ZnO NPs have been incorporated into wound dressings, coatings for medical devices, textiles, and packaging to impart durable antimicrobial protection while aiming to reduce toxicity compared to chemically synthesised counterparts. Studies also report effective inhibition of biofilm formation and eradication of preformed biofilms by green AgNPs, which is significant for combating device-associated infections [20].

2. Anticancer and theranostic applications

Biogenic nanoparticles have shown selective cytotoxicity toward cancer cells in vitro, including human breast, lung, prostate, and colon cancer lines, often via ROS generation, mitochondrial damage, and induction of apoptosis pathways. Plant-extract-coated AuNPs have been investigated as photothermal agents and drug carriers due to their tunable optical properties and potential for targeted delivery through ligand conjugation [27]. Some green-synthesized nanoparticles exhibit dual therapeutic and imaging capabilities (theranostics), enabling simultaneous diagnosis and treatment-for example, AuNPs and iron oxide NPs for combined MRI contrast and hyperthermia or photothermal therapy.

3. Drug delivery and nano formulations

Biogenic nanoparticles provide biocompatible platforms for encapsulation or surface adsorption of drugs, phytochemicals, and nucleic acids, improving solubility, stability, and targeted delivery. Plant-derived capping layers can facilitate controlled release and enhance interaction with specific cell types, while biopolymer-based nanocarriers such as chitosan–metal NP systems offer mucoadhesive and penetration-enhancing properties[29].However, translation to clinical applications requires rigorous evaluation of pharmacokinetics, biodistribution, immunogenicity, and long-term safety, as well as scalability and regulatory compliance.

G. Environmental and Catalytic Applications

1. Wastewater treatment and photocatalysis

Green-synthesised metal and metal-oxide nanoparticles are increasingly applied as catalysts and photocatalysts for degradation of dyes, pharmaceuticals, pesticides, and other organic pollutants in water. Plant-mediated AgNPs, AuNPs, and bimetallic systems can catalyse the reduction of nitroaromatics and azo dyes, while ZnO and TiO_2 NPs act as photocatalysts under UV or visible light for mineralisation of diverse contaminants [30]. Recent reviews emphasise the emerging role of plant-mediated metal nanoparticles in wastewater treatment, including adsorption, photocatalytic degradation, and disinfection, with attention to reactor design and recovery/reuse of catalysts. Embedding biogenic nanoparticles into membranes, polymer matrices, or immobilized supports can facilitate separation and reduce nanoparticle release into the environment.

H. Agricultural Applications

1. Nano fertilizers and nutrient management

Biogenic nanoparticles produced using plant growth-promoting rhizobacteria (PGPRs), fungi, or plant extracts are being explored as nano fertilizers to improve nutrient use efficiency and crop productivity. Nanostructured formulations of essential micronutrients (e.g., Zn, Fe, Mn) can provide controlled release, enhanced root uptake, and lower application doses compared to conventional fertilizers. Microbial synthesis of nanoparticles is regarded as eco-friendly and compatible with integrated nutrient management, offering the possibility of combining biofertilization, phytostimulation, and biocontrol in a single platform. Recent work demonstrates that bacterial and fungal biogenic nanoparticles can modulate plant hormone levels, stimulate root growth, and mitigate abiotic stress, although mechanisms remain under active investigation [31].

2. Control of plant pathogens and pests

Biogenic nanoparticles exhibit strong antimicrobial activity against a wide range of plant pathogenic bacteria, fungi, and viruses, opening opportunities for their use as nano-pesticides and phytosanitary agents. Green-synthesised ZnO and AgNPs have been shown to suppress diseases such as bacterial blight, fungal wilt, and viral infections by directly inhibiting pathogens and/or inducing systemic acquired resistance in plants. Reviews highlight that biogenic nanoparticles can be integrated into sustainable plant disease management strategies, including seed treatments, foliar sprays, and soil amendments, potentially reducing reliance on synthetic pesticides. However, careful assessment of non-target effects on beneficial microbes, pollinators, and soil health is essential [32].

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