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Review

Green synthesis of metal nanoparticles: A Review

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Abstract

Nanoparticles have unique properties due to their small size and large surface area, leading to various applications in medicine, electronics, and environmental science. Traditional synthesis methods often involve harmful chemicals and high energy requirements. Green synthesis offers a sustainable and eco-friendly alternative. Metal nanoparticles are categorized based on size, shape, and properties, with gold nanoparticles, silver nanoparticles, zinc oxide nanoparticles and copper nanoparticles. Plant extracts rich in biomolecules like polyphenols and flavonoids act as reducing agents for gold ions, resulting in varying properties and potential applications. This review provides an overview of green synthesis of various metal nanoparticles.

Keywords: metal nanoparticles, green synthesis, gold nanoparticles.

INTRODUCTION

Nanoparticles are incredibly small materials ranging in size from 1 to 100 nm. Based on their size, shape and material properties, nanoparticles can be classified into several categories. Fullerenes, metal nanoparticles, ceramic nanoparticles, and polymer nanoparticles are some of the groups. Due to their large surface area and nanoscale, nanoparticles have different physical and chemical properties[1,2]. Metallic nanoparticles have taken an intrigued researchers for more than a century, and they are presently broadly utilized in building and the organic sciences[3]. In recent decades, the biosynthesis of metal nanoparticles has increased significantly. As a result, many methods have been developed to produce metallic nanomaterials using various physical and chemical methods. However, the limitations of these current technologies make their large-scale application difficult. These disadvantages include the high energy required for production, the high cost of the synthesis process and the introduction of harmful substances[4]. Green synthesis aims to reduce the use of harmful chemicals. There are many potentials uses for the production of green nanoparticles in medicine and environmental science. Nanoparticles include gold, silver, copper, palladium, platinum, zinc oxide, and titanium dioxide, which can be synthesized using green synthesis methods[5]. The steps involved in green synthesis of nanoparticle is given in figure1.

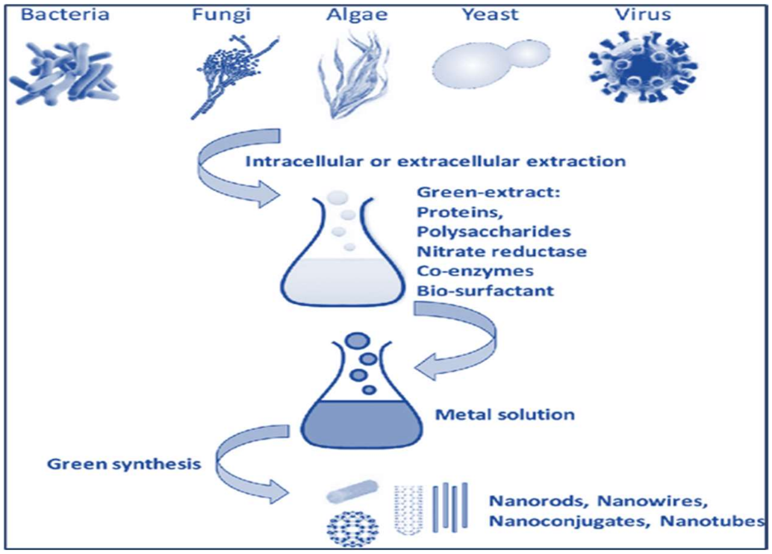

Fig 1: steps involved in green nanoparticle synthesis

Types of metal nanoparticles
Metallic nanoparticles are nanomaterials that consist of only one element. Single atoms or groups of several atoms may be present. Au, Ag, Pt, Cu, Pd, Re, Zn, Ru, Co, Cd, Al, Ni and Fe are some of the most commonly produced nanoparticles. Simple approaches such as bio assisted method, hydrothermal method and microwave method are used to prepare metal nanoparticles in the form of colloidal liquids or solid nanoparticles.[6] Metal nanoparticles (MNPs) are a leading class of nanoparticles due to their unique properties and wide applications [7]. The utility of MNPs is a function of size, shape, degree of dispersion, and physical and chemical properties, which are determined by how the MNPs are synthesized.[8]

Gold nanoparticles
Gold nanoparticles (AuNPs) are a unique class of nanoparticles that exhibit chemical stability, water solubility. They are present in various sizes (1–800 mm) and shapes (spherical, spherical, circle-shaped, or open). AuNPs can be synthesized by various methods such as chemical deposition, lithography, biosynthesis etc. [9]

Green synthesis of gold nanoparticles
The foundation of all gold NP preparation techniques is the reduction of gold ions, typically in $HAuCl_4$ solution. Sodium borohydride and sodium citrate are the two most significant reducing agents that have been reported in the literature. A protective agent is also needed for GNP synthesis, as it adsorbs to the surface of freshly created nanoparticles (NPs) to stop more protection from occurring particle formation and assembly. Thus, by selecting the proper preservation type, concentration, and agitation and reduction techniques as well as by adjusting the synthesis conditions (temperature, pH, agitation), GNP size and shape can be regulated. [10,11]. Many articles proposing new synthetic approaches to AuNPs employing reducing agents and green protection have been prompted by these ideas. The majority of these approach are stabilisation and reduction are derived from plants, including algae, bacteria, and fungi. [12,13]

A study by Aljabali AA et al 2018[14] developed a simple and greener method for synthesizing gold nanoparticles using a plant extract and aqueous $HAuCl_4$ solution. The process involves reducing Au^{3+} ions to Au0, purifying the Ennab leaf extract and dialyzing samples. The plant extract contains biomolecules like polyphenols, flavonoids, and proteins that act as reductants for metal ions. The AuNPs exhibit excellent colloidal stability and showed no antimicrobial or antifungal activity, making them suitable for drug delivery without interfering with human microbiota.

Ahmad S et al 2022 [15] demonstrates a cost-effective and safe method for green synthesis of Au nanoparticles which show potential anticholinesterase activities. Delphinium chitralense was extracted from Kumrat valley, Pakistan, and the alkaloids were synthesised using a traditional acid-base method. The resulting solution was then dried and morphologically analyzed. The NPs were found to have a cubic morphology, with a size range of 100-300 nm. The synthesis was confirmed through TEM, FTIR, and UV-Visible spectroscopy.

Fouda A et al 2022 [16] produced AuNPs from zingiber officinale rhizome extract by utilizing chloroauric acid as the metal precursor in the study. The rhizome underwent washing, was then cut into small pieces, and subsequently combined with distilled H_2O. The resultant nanoparticles had a spherical shape and exhibited a size range of 5-55 nm, appearing in a purple color. Furthermore, the plant extract displayed high stability and demonstrated efficacy in antimicrobial, antioxidant, and cytotoxic properties.

The study by Geetha R et al 2013[17] aimed to explore the potential of C. guianensis as a potential therapeutic agent by synthesizing gold nanoparticles from a flower extract. The extract was subjected to different reaction concentrations and characterized by using UV-visible spectrum, FTIR, XRD, and TEM studies. The resulting nanoparticles were dried and analyzed using a Thermo Nicolet Quator instrument. The study revealed the anticancer activity of the nanoparticles, demonstrating their pharmacological properties and functionalization without molecule doping.

Elia P et al 2014 [18] synthesized using plant extracts from Salvia officinalis, Lippia citriodora, Pelargonium graveolens, and Punica granatum. The size distributions were measured using various methods, and the AuNPs showed good biocompatibility and stability over three weeks. High-resolution transmission electron microscopy and infrared spectroscopy were used to study the shapes of larger AuNPs. An organic protective layer was observed around the AuNPs. The study identified active ingredients in the plant extracts responsible for GNP formation, highlighting their potential for green AuNP synthesis.

Sliver nanoparticles

Silver nanoparticles (AgNPs) are tiny specks of silver, ranging in size from 1 to 100 nanometers. Due to their small size and large surface area relative to their volume, silver nanoparticles have unique physical, chemical, and biological properties that differ significantly from those of bulk silver. These distinctive properties make them highly valuable in various fields such as medicine, electronics, and environmental science. Silver nanoparticles possess strong antibacterial and antiviral properties, inhibiting the growth of a wide range of microorganisms. Consequently, they are used in medical applications such as wound dressings, coatings for medical devices, and water treatment. Furthermore, the high surface area and active surface sites of AgNPs make them excellent catalysts for chemical reactions, rendering them valuable in industrial processes and environmental applications such as pollution control.[19,20]

Silver nanoparticles can be synthesized using physical, chemical, and biological methods. Physical methods involve breaking down bulk materials, chemical methods reduce silver salts with reducing agents, and biological methods use microorganisms or plant extracts for environmentally friendly and sustainable synthesis. [21,22]

Green synthesis of sliver nanoparticles

The green synthesis of AgNPs involves a silver metal ion solution and a biological reducing agent. Ag^+ ions can be obtained from various water-soluble silver salts, with aqueous $AgNO_3$ solution being the most commonly used. Biological reducing agents are abundant in biological systems, and AgNPs have been synthesized using various organisms. Green syntheses have been performed using plant extracts, microbial cell biomass, cell-free growth medium, and biopolymers. Angiosperm plants, especially parts like leaves, bark, roots, and stems, are the most suitable choice for AgNP synthesis. [23]

The study by Padilla-Cruz et al. 2021 [24] focuses on preparing an extract from Gardenia jasminoides leaves for nanoparticle synthesis. The extract was mixed with $AgNO_3$ and heated at 80°C for 1 hour, resulting in the formation of silver and iron nanoparticles. The nanoparticles were characterized using UV spectra, FT-IR spectroscopy, TEM, HR-TEM, dark-field microscopy, and EDX analysis. The interaction between the nanoparticles and the plant extract was measured using a Raman spectrum.

In 2021, Amrutha DS et al. [25] used a bio reduction method with cuminum cyminum to create a phyto-nanocomposite that exhibits antioxidant properties and is non-cytotoxic. This innovation showed the potential for the treatment of tendon injuries and for providing cost-effective healthcare solutions. The process involved washing, shade-drying, and powdering the seeds, followed by the green synthesis of Cuminum cyminum silver nanoparticles. The bio reduction method entailed adding pale yellow colored CCE to a 0.1 M aqueous silver nitrate solution. The reaction occurred under dark conditions, as indicated by the color change and UV visible spectroscopy. The resulting precipitate was centrifuged, washed, dried, and powdered for further studies. The successful synthesis was confirmed through observable color change and UV-visible spectroscopy.

The study by Ahmed S et al. 2016 [26] showed A. indica leaf extract can be used to prepare silver nanoparticles. The extract was made by cleaning and drying fresh leaves, boiling them for 30 minutes, and then filtering. Silver nanoparticles were synthesized using a solution of silver nitrate GR from Merck, India. The extract was added to the silver nitrate solution, and the formation of silver nanoparticles was confirmed using UV-visible spectroscopy. This method was cost-effective, easy to obtain, and demonstrated medicinal properties. The synthesized silver nanoparticles were characterized using UV, DLC, FTIR, TEM, and photoluminescence studies. The analysis was performed using a Shimadzu UV-visible absorption spectrophotometer, dynamic light scattering, and FTIR spectra.

Kouvaris P et al.2012 [27] used Arbutus Unedo leaf extract prepared by boiling the leaves with distilled water, filtered, and stored. Silver nanoparticles were synthesized by adding $AgNO_3$ to distilled water and mixed with leaf extracts. The rapid biological synthesis of silver nanoparticles using Arbutus Unedo leaf broth offers an environmentally friendly, simple, and efficient method for producing benign nanoparticles. These nanoparticles, sized between 3-20 nm, have potential applications in biomedical fields, medical and pharmaceutical applications, and large-scale commercial products.

Raja S et al 2017 [28] developed a green method for synthesizing silver nanoparticles (SNPs) from C. haematocephala leaves. The resulting aqueous extract was mixed with silver nitrate solution and heated in a water bath. The SNPs showed antibacterial activity against E. coli and a sensing capacity towards H_2O_2, suggesting potential use in drug development. The leaf extract's gallic acid may also play a role.

Zinc Oxide Nanoparticles

Zinc oxide nanoparticles (ZnO NPs) are small, non-toxic particles with unique optical, chemical, and physical properties. They are used in medicine, electronics, and environmental science due to their antimicrobial, UV protection, photocatalytic, semiconductor, and biomedical applications.[29] ZnO NPs are used in sunscreens, cosmetics, water purification, air purification, and drug delivery systems. They also have applications in biomedical research due to their biocompatibility and ability to induce reactive oxygen species.[30]

Zinc oxide nanoparticles can be synthesized using physical, chemical, and biological methods. Physical methods include laser ablation, vapor deposition, and ball milling. Chemical methods involve sol-gel processes, hydrothermal synthesis, precipitation, and microemulsion techniques. Biological synthesis uses microorganisms and plant extracts.[31]

Green synthesis of Zinc Oxide nanoparticles

The microwave heating crystallization technique was utilized by Klink MJ et al. 2021 [32] to produce zinc oxide nanoparticles by heating zinc compounds in a microwave. First, a solution containing specific zinc compounds was prepared. After subjecting this solution to microwave radiation, crystallization occurred, leading to the formation of zinc oxide nanoparticles. The solution was then further heated using microwave radiation to induce crystallization, resulting in the creation of zinc oxide nanoparticles. Following synthesis, the nanoparticles were thoroughly characterized using various methods to understand their properties.

The study by Abdelghani GM et al 2022 [33] focused on the chemical synthesis of ZnO nanoparticles using a sol-gel method. Zinc acetate dihydrate and sodium hydroxide were used as precursors, and the solution was stirred for 4 hours. The precipitate was filtered, washed, dried, and ball milled to produce fine ZnO nanoparticles. X-ray diffraction patterns, surface morphology, and inner structure were analyzed. The efficacy and biological activity of the nanoparticles were tested before and after laser beam irradiation.

Happy et al. 2019 [34] synthesized zinc oxide nanoparticles by using Cassia alata leaves. The resulting white powder was subjected to various characterization techniques. The nanoparticles exhibited excellent antibacterial potential, with an IC_{50} value of 20 μg/mL, indicating their suitability for use in pharmaceuticals, cosmeceuticals, and agricultural industries.

Devi RS et al. 2014 [35] used Hibiscus rosa-sinensis plant leaves to synthesize zinc nanoparticles. The extract was prepared by boiling the leaves, filtering, and storing. The process involved heating the extract to 400 degrees Celsius, resulting in a light-yellow powder. This method offers an environmentally friendly, efficient, and simple method for nanoparticle synthesis.

In 2011, Sangeetha G and colleagues synthesized zinc oxide nanoparticles with adjustable optical properties using Aloe vera leaves from Coimbatore, Tamil Nadu. The nanoparticles, ranging in size from 25 to 45 nm, exhibited noticeable variability and are anticipated to have wide-ranging applications in biomedical and cosmetic industries. This biomimetic approach was developed to make the nanoparticles eco-friendly and efficient.[36]

Copper nanoparticles

Copper nanoparticles (CuNPs) are small copper particles with unique optical, electrical, and thermal properties. They have strong antimicrobial activity, making them useful in medical applications and water treatment. CuNPs are excellent catalysts for chemical reactions, making them useful in industrial processes and environmental remediation. They also possess excellent electrical conductivity, making them suitable for conductive inks, electronic circuits, and printed electronics. Their high thermal conductivity makes them useful in heat transfer applications and biomedical applications, such as drug delivery systems and imaging.[37]

Copper nanoparticles can be synthesized using physical, chemical, and biological methods. Physical methods involve breaking down bulk copper into nanoparticles, chemical methods involve chemical reduction, electrochemical synthesis, and thermal decomposition, and biological methods use plant extracts and microorganisms.[38]

Green Synthesis of Copper Nanoparticles

In 2021, Liu et al. synthesized copper nanoparticles using green methods. They characterized the nanoparticles, finding that they had a spherical morphology and a size range of 19.55 to 69.70 nm. The nanoparticles demonstrated significant antioxidant and anti-lung carcinoma properties when tested against various cell lines, suggesting their potential use as a chemotherapeutic drug. The study involved using various materials and methods to prepare and extract an aqueous extract of C. zeylanicum, a plant used in the green synthesis of copper nanoparticles. The extract was ground, macerated, and concentrated. The CuNPs were formed by heating and stirring the extract with 0.3 M Cu $(NO_3)_2.3H_2O$. After formation, the CuNPs were washed with water and ethanol, centrifuged, and dried. The antioxidant properties of the CuNPs were determined by adding methanol to the DPPH, and the absorbances were measured at 517 nm. [39]

In 2020, Wu S et al utilized fresh leaves of C. vitiginea, which were boiled in distilled water to create an aqueous extract. This extract was stored for a week before being used to synthesize copper nanoparticles. The extract contained various compounds, which were successfully used to synthesize copper nanoparticles by stirring a copper sulphate solution. The extract was analysed for phytochemicals like carbohydrates, proteins, flavonoids, and tannins. The nanoparticles were confirmed through color change and characterized using techniques like surface plasmon resonance, X-ray diffraction, XPS, TEM, and FT-IR and visual examination confirmed the synthesis. [40]

A study conducted by Nzilu DM et al in 2023 utilized fresh Parthenium hysterophorus plant samples to produce copper oxide nanoparticles. The researchers used an extract from the plant in the synthesis of these nanoparticles, which were then characterized using various analytical techniques. The process involved green synthesis, making use of natural resources for nanoparticle production. The nanoparticles demonstrated efficient degradation of rifampicin antibiotics, achieving a degradation efficiency of over 98% under optimal conditions. This eco-friendly and cost-effective method holds promise for addressing water pollution challenges in wastewater treatment plants. Further research should concentrate on evaluating their usability and potential environmental impacts.[41]

In a study conducted by Sukumar S et al. in 2020, C. Bonducella seed extract, sonication, and copper oxide nanoparticles were utilized to develop a cost-effective method for synthesizing CuO Nps. The solution was optimized for pH and resulted in the formation of a dark brown precipitate. The modified electrode exhibited good stability for 120 days and proved effective in detecting nanomolar concentrations in real samples. This process showcased a cost-effective method for reducing and stabilizing nanoparticles.[42]

Shende S et al. (2015) [43] conducted a study where they used citron fruit juice to synthesize copper nanoparticles (CuNPs). The process involved extracting juice from mature C. medica Linn. fruits and mixing it with a $CuSO_4$ solution. The mixture was then heated to boiling in an aluminum vessel. This novel, eco-friendly, and rapid method of synthesizing CuNPs has proven to be effective against various microorganisms. The CuNPs can be used to develop nano fungicides, nano antimicrobials, and nano fertilizers, which can protect crops from pathogens and provide nutrients. This method is cost-effective due to the use of cheap raw materials.[43].

CONCLUSION

Green synthesis offers an environmentally friendly alternative for producing various metal nanoparticles with diverse applications. Plant extracts play a crucial role in reducing metal ions and shaping the properties of the resulting nanoparticles. This approach holds significant promise for developing sustainable and efficient technologies in various fields, including medicine, electronics, and environmental science. Overall, the review emphasizes the increasing importance of green synthesis methods for metal nanoparticles, offering a promising route for environmentally friendly production while utilizing the unique properties of these nanomaterials for a wide range of applications.

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