



# Synthesis of Metallic Nanomaterials Using Green Chemistry Approaches

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## Authors' contributions

This work was carried out in collaboration among all authors. Authors CTA, SB, MK, IK, JS and IK participated in writing the main manuscript and discussed the previous findings. All authors read and approved the final manuscript.

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## ABSTRACT

Herein, we reviewed metallic nanomaterials (MNMs), which have gained significant attention due to their unique properties and diverse applications across various fields. However, traditional methods for MNM synthesis often involve toxic chemicals and harsh conditions, raising environmental concerns. However, green synthesis approaches have emerged as promising alternatives. This

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review explores the various green methods employed for MNM synthesis, including using biological agents like plants, fungi, and bacteria. It further goes deeper into the mechanisms of these methods and discusses the factors influencing the shape, size, and physical properties of the synthesized MNMs. Additionally, the potential applications of green-synthesized MNMs in fields such as catalysis, biomedical sciences, and environmental remediation are discussed. This review aims to examine the synthesis of metallic nanomaterials using green approaches.

*Keywords: Nanomaterials; green synthesis; biological agents; sustainability; remediation.*

## 1. INTRODUCTION

Nanotechnology is a developing and burgeoning technology with a plethora of applications. Nanotechnology encompasses the creation and utilization of materials with at least one dimension of between 1 and 100 nanometers [1,2]. Currently, a diverse range of physio-chemical methods are being employed for the production of nanoparticles (NPs) [3]. The growing need for eco-friendly and sustainable synthesis techniques has led to the investigation of green pathways for the manufacturing of silver nanoparticles [4]. Biogenic reduction of metal precursors to make nanoparticles is a cost-effective and environmentally friendly method. It is particularly suitable for biological and medicinal purposes where the purity of nanoparticles is a significant consideration, as it does not include any chemical impurities. Biogenic reduction is a method that involves using natural extracts with inherent stabilizing, growth terminating, and capping qualities as a replacement for a reducing agent in a chemical reduction process. This technique is known as a "Bottom Up" approach. In addition, the presence of varying concentrations of living entities, together with the presence of reducing organic agents, affects the size and form of nanoparticles [3].

## 2. METAL NANOPARTICLES

Nanometallic materials consist of metals and alloys characterized by nanocrystalline grains ranging in size from approximately 5 to 100 nm [3]. Compared to their non-nano or bulk counterparts, nanoscale metals have a relatively large surface area. Moreover, because of their quantum effects, small dimensions, surface area, and interface, nanometals display unique chemical and physical properties that are not seen in non-nano crystals. Metals at the nanoscale find several applications in the fields of biology, medicine, and engineering [5].

Specifically, Gold nanoparticles (Au NPs) have biological characteristics that render them appropriate for the regulation of enzymes, antimicrobial capabilities, and muscle-relaxing activities [6]. Nanoparticles of silver (Ag NPs) hinder the growth rates of both gram-negative and positive bacteria [7]. Studies have demonstrated that iron nanoparticles (Fe NPs) effectively prevent bacteria life and efficiently eliminate organic materials, metal pollutants, non-metal ions, and dyes from polluted matrices [10-12]. Palladium nanoparticles (Pd NPs) are used in several applications, including the breakdown of dyes [14,15], antimicrobial properties [16], and catalytic processes [17]. Presently, several research studies are dedicated towards the synthesis of metals in the nanoscale via chemical, physical, and ecologically-friendly manufacturing methods [18,19]. In response to concerns about excessive energy consumption, the release of dangerous and poisonous compounds, and the usage of sophisticated instruments and synthesis conditions, green synthesis methods are progressively supplanting physical and chemical approaches [20,19,21,22,23]. Physical approaches include aerosols, UV radiation, and thermal breakdown, all of which need high temperature and pressure conditions. The aerosol approach requires a temperature of around 2400 K to produce atomized aerosol droplets and form metallic nanoparticles. Production of Palladium Oxide nanoparticles by plasma-assisted physical vapour deposition necessitates three heat cycles within the temperature range of 250 °C to 800 °C, leading to substantial energy usage. Chemical methods frequently include the utilization of sodium borohydride, a compound that is both expensive and toxic, in conjunction with supplementary dispersion stabilizers and organic solvents [2]. Conversely, green synthesis employs natural and environmentally favourable compounds, such as reducing agents. Select ecologically friendly compounds can function as both end-capping agents and dispersants concurrently [28]. This dual functionality not only reduces energy usage

but also obviates the necessity for toxic and hazardous chemicals. At present, green synthesis predominantly employs microorganisms, including fungus, bacteria, and algae [27,29,30], along with extracts obtained from leaves [28,31,32], flowers [33,34,35], roots, peels [36], fruits [37], and seeds [38,39] of different plant species. Green materials, as defined by Can [40], are composed of polyphenols and proteins that can function as alternative reducing agents in place of chemical reagents. Synthesis of metal nanoparticles can occur in the presence of green materials under favourable conditions, including concentration, ambient air and temperature. The quality of MNPs produced by green technologies can surpass that of nanoparticles formed by chemical procedures under certain conditions. For example, the  $\text{Fe}_3\text{O}_4$  nanoparticles generated by the green synthesis method have a particle size between 2 and 80 nm, which is much smaller than the particles produced by the wet chemical procedure, which range in size from 87 to 400 nm [41]. Prior research has described the advantages of green synthesis over chemical approaches and outlined the potential and prospects of green synthesis in the future [42]. In comparison to chemical and physical methods, green synthesis offers various advantages. Its distinguishing features include its non-toxic properties [28], lack of pollution [20], environmental compatibility, cost-efficiency [43], and improved sustainability [44]. However, significant obstacles exist regarding the extraction of raw materials, the length of chemical reactions, and the general quality of the products. For example, the supply of raw ingredients is restricted [45]; thus, the synthesis process is time-consuming [29].

### 3. CHEMICAL SYNTHESIS

Chemical reduction is a very efficient wet-chemical technique used to produce zero-valent nanoparticles. This approach involves using metal salts as chemical reductants, such as silver nitrate ( $\text{AgNO}_3$ ), to synthesize silver nanoparticles. To decrease the metal salt used as the precursor, a minimum of one reductant is employed to generate electrons for metal ions, which then reduce them to a zero-valent state. Borohydride, citrate, and ascorbate are frequently employed as reductants. Nanoparticles that have decreased in size are kept stable by the presence of a stabilizing agent. A commonly used stabilizing agent in gold

nanoparticle manufacturing is cetyltrimethylammonium bromide ( $(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3\text{Br}$ ). The stabilizing chemicals used in the production of silver nanoparticles, such as sodium citrate, can also act as reducing agents [46]. Synthesis of Ag NPs via chemical treatment is the predominant approach, according to Tran et al. [47]. This technique involves reduction using either organic or inorganic reducing agents [48]. Silver ions can be reduced by many agents, including sodium citrate, ascorbic acid, Tollen's reagent, polyol process, N-dimethylformamide, and poly(ethylene glycol) block copolymers, in both aqueous and nonaqueous solutions. The reactions result in the creation of metallic silver, which then forms into oligometric clusters and subsequently transforms into metallic colloidal silver particles [48]. To prevent the clumping together of silver nanoparticles during their manufacture, protective chemicals are employed to stabilize and safeguard them [48]. The microemulsion technique is a chemical approach employed to synthesize silver nanoparticles with consistent and controllable sizes. This production method utilizes Ag NPs in two different states: the reducing agent and metal precursor [49]. The transport level and the interface across them influence the interactions between the reducing agent and metal precursor. Stabilizer molecules cover the surface of stabilized metal clusters, resulting in their formation on the interface. An inherent drawback of this approach is the substantial quantities of surfactant and organic solvent employed, necessitating their subsequent elimination from the ultimate sample. A significant benefit is the lack of clumping when colloidal nanoparticles are produced in nonaqueous solvents and evenly spread across a moist polymeric surface substrate [49]. UV-induced photoreduction is a straightforward and efficient technique used to produce silver nanoparticles in the presence of collagen, citrate, poly(acrylic acid), or polyvinylpyrrolidone. Huang and Yang [50] utilized inorganic laponite clay suspensions as a stabilizing agent to avoid the clumping of nanoparticles. The underlying concept of this technique is exposing silver nitrate to ultraviolet (UV) light. The size of the nanoparticles is directly proportional to the duration of irradiation: as the irradiation period increases, the nanoparticles decrease in size. The operation is halted after a consistent size is achieved. An alternative method for acquiring nanoparticles involves employing a sono electrochemistry process that employs ultrasonic power to control the creation of their shape. To

prevent the formation of clumps, some complexing agents, such as nitrilotriacetate, are employed [50]. An electrochemical approach can also be utilized to get silver nanoparticles. Silver nanoparticles ranging in size from 3 to 20 nm were produced using electrochemical reduction at the interface between two liquids. Ma et al. [51] produced silver nanoparticles ranging from 10 to 20 nm in size using an electrochemical technique in a water-based solution. Poly N-vinylpyrrolidone was employed as a stabilizer to safeguard silver from clumping together and settling while also facilitating the initiation of silver nuclei and the creation of particles. Laser irradiation of an aqueous solution containing silver salt and surfactants can be utilized to create silver nanoparticles with certain shapes and sizes. Additionally, it is possible to carry out the synthesis using microwave assistance. The production of silver nano spheroids used the combination of microwave polyol methods, utilizing ethylene glycol and poly N-vinylpyrrolidone as the reducing and stabilizing agents, respectively [49]. The polyol process is a production technique for silver nanoparticles in which silver nitrate is reduced by ethylene glycol. Ethylene glycol serves as both a reactant and solvent in a solution that contains a high concentration of polyvinylpyrrolidone [47]. Typically, physical synthesis processes are used, including evaporation, condensation, and laser ablation. These techniques necessitate the use of a tube furnace and the maintenance of air pressure [49].

#### 4. PHYSICAL SYNTHESIS

Evaporation, condensation, and laser ablation are the primary physical synthesis procedures employed to acquire metal nanoparticles. A tube furnace and air pressure are necessary for a physical technique. The benefits of employing a physical method, as opposed to a chemical one, are the lack of solvent pollution and the even dispersion of nanoparticles. Nevertheless, physical synthesis has many drawbacks, including the substantial dimensions of the tube furnace, the considerable energy consumption, and the extended duration required to establish thermal stability (often several tens of minutes to attain a steady operating temperature). The process of cooling evaporated vapors creates small nanoparticles. This occurs because of the difference in temperature between the area near the heater surface and the tube furnace [49]. Utilizing laser ablation in a solution is a physical method employed to produce silver nanoparticles from a metallic portion. The properties of particles are influenced by several parameters, including the wavelength and duration of the laser, the period of ablation, the presence or absence of surfactants in the liquid medium, and the laser influence [49]. The laser ablation approach has a significant advantage over other methods since it does not require the use of chemical reagents in solution. As a result, it produces silver nanoparticles that are pure and uncontaminated [49].

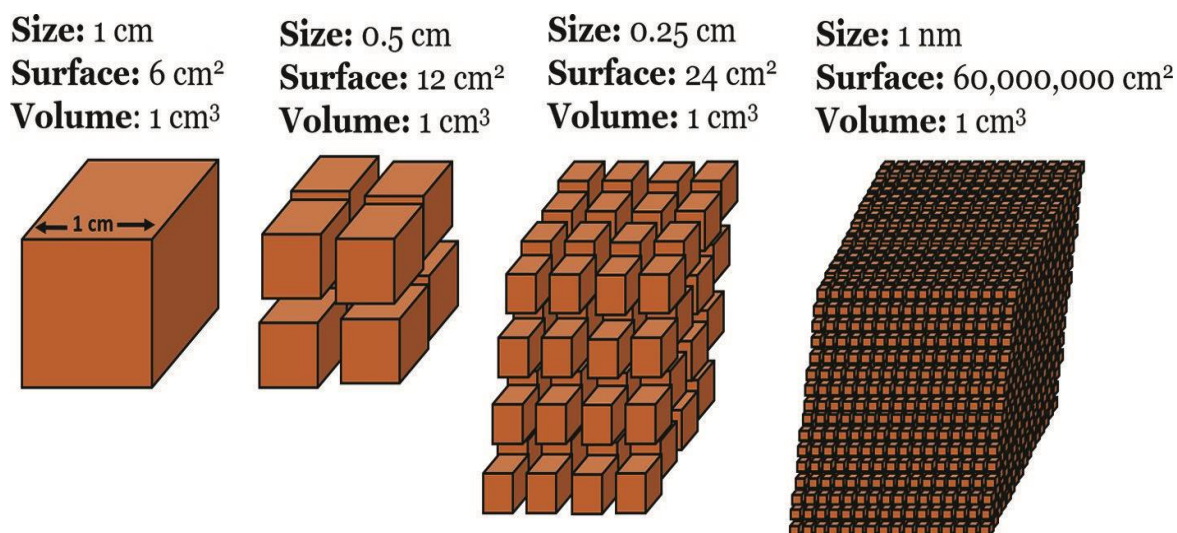


Fig. 1. Surface-to-volume ratio of nanoparticles compared with that of bulk materials [52]

## 5. BIOLOGICAL SYNTHESIS OF NANOPARTICLES

Nanoparticles have garnered significant interest in the domains of biology, medicine, and electronics in recent years due to their notable uses (Fig. 2). Several methods for synthesizing nanoparticles have been devised; however, these methods may require the use of hazardous substances and intense physical procedures. One possible option is to employ biological techniques to overcome these challenges. Bacteria, fungi, algae, and plant species often utilize biological resources to produce eco-friendly nanoparticles (Fig. 2). The biological technique described by [53,54] offers a dependable, easy, harmless, and ecologically advantageous technology.

**Bacteria:** Bacteria-mediated nanoparticle production can occur either extracellularly or intracellularly [55].

**Intracellular** synthesis refers to the process of producing nanoparticles within a live microbe, utilizing its growth circumstances to create favorable conditions for synthesis. This phenomenon is sometimes referred to as "nanoparticle micro-factories." To retrieve nanoparticles, it is necessary to exclude germs [56].

**Extracellular:** The substances discharged by the bacterium upon cell rupture are used. The synthesis is accomplished by introducing a metal salt precursor into the media containing these components. Extracellular synthesis has the benefit of increased speed as it eliminates the need for extra procedures to retrieve nanoparticles from microorganisms [56,58].

**Enzymes:** Enzymes namely reductases, participate in the production process by facilitating the conversion of metal ions into nanoparticles by reduction. Both [59,60] have demonstrated that the various constituents of the genetic material have a role in this phenomenon.

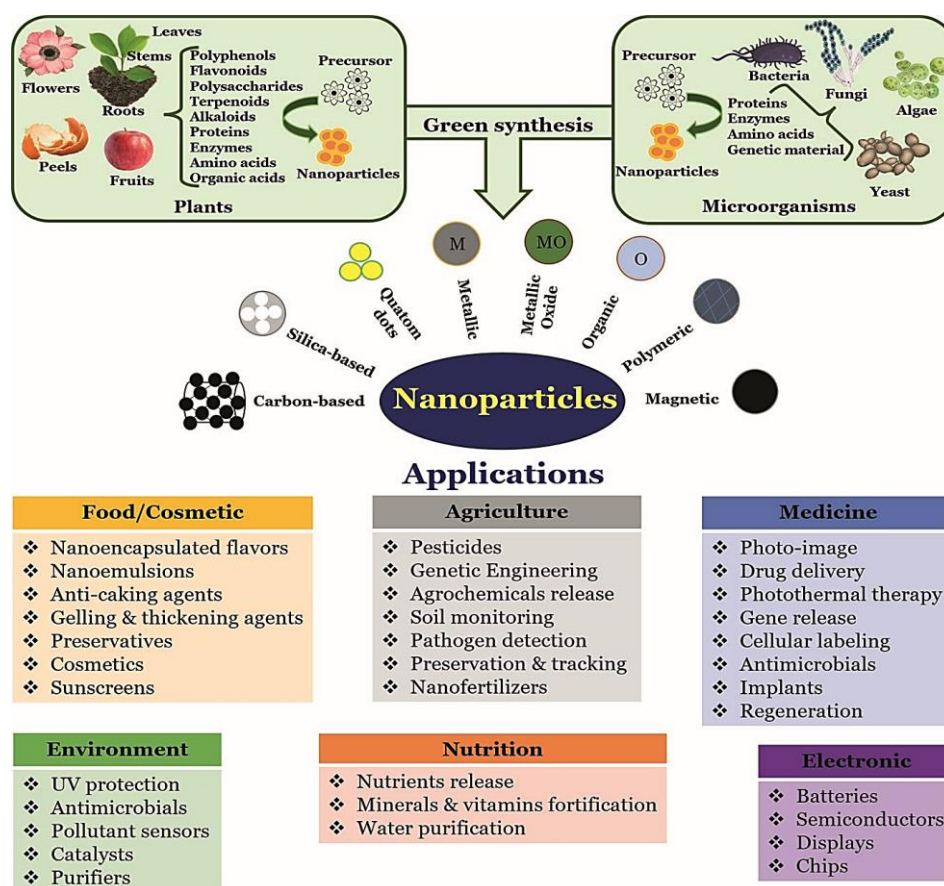


Fig. 2. The utilization of biological resources and chemicals for the environmentally friendly production of nanoparticles, as well as their many applications [57]

**Fungi:** Fungi possess bioactive biomolecules, such as proteins or enzymes, which have a role in the creation of nanoparticles, enhancing their production and durability [61]. Certain fungal species can produce nanoparticles by using amino acids that are located outside of their cells. For instance, the yeast surface contains glutamic and aspartic acids, whereas the cytoplasm of the fungus includes the reductase enzyme. These substances are responsible for reducing metal ions and forming nanoparticles. The presence of hydroxyl groups in the mycelium facilitates this process by donating electrons to the metal ion, resulting in the reduction and formation of nanoparticles. Aliphatic and aromatic amines, as well as some proteins, function as coating agents to provide stability to them [62,63].

**Algae:** Algae are used in nanotechnology because of their minimal toxicity and their capacity to bioaccumulate and diminish metals [64].

Nanoparticle production can occur either intracellularly, where the metal ion penetrates the alga, or extracellularly. This process requires the use of substances such as polysaccharides, proteins, and pigments, which facilitate the reduction of metal ions and provide a coating for the newly created nanoparticles [65].

**Plant species:** The utilization of plants in the synthesis of nanoparticles is a highly prevalent approach due to its eco-friendly characteristics since it circumvents the need for hazardous or detrimental ingredients. Additionally, it is considered one of the most efficient and cost-effective techniques due to its reduced number of processes [66,53]. As a result, it exhibits much greater efficiency in the manufacture of nanoparticles compared to the synthesis involving microbes.

Plants possess many chemicals, such as terpenes, flavonoids, polyphenols, alkaloids, proteins, etc., which can decrease metal ions and stabilize the nanoparticles that are formed as a result [67].

The synthesis can be carried out by intracellular, extracellular, and phytochemical-mediated mechanisms [68]

**Intracellular synthesis:** Intracellular synthesis refers to the process of producing nanoparticles within the plant cell. The nanoparticles are

obtained by breaking down the cell structure, which closely resembles the intracellular technique using microorganisms. Regulation of plant species' growth factors is necessary to prevent interference with synthesis [69]

**The extracellular technique:** The extracellular technique is widely used because of its simplicity and efficiency. The process starts with the acquisition of a plant extract, typically aqueous, to which a metal salt precursor is introduced. Due to the effects of various components in the extract, nanoparticles are formed and maintained in a single process [69,70].

**Phytochemically mediated:** This approach utilizes isolated phytochemical molecules and other stabilizing chemicals to create nanoparticles, following a similar extracellular strategy. The synthesis process offers enhanced control, albeit it requires a higher number of components and stages [68].

## 6. SYNTHESIS OF NANOPARTICLES USING ENVIRONMENTALLY FRIENDLY METHODS

The objective of green synthesis is to advance novel chemical methodologies that minimize or eliminate the utilization and generation of dangerous compounds in the development, manufacturing, and application of chemical goods. This entails the reduction or, ideally, elimination of pollution generated during the synthesis procedures, prevention of the consumption and squandering of nonrenewable resources, utilization of non-hazardous or non-polluting substances in product fabrication, and reduction of the duration of the synthesis process. Paul J. Anastas, widely recognized as the pioneer of green chemistry, has defined it as a professional approach that employs alternative methods and techniques to prevent pollution. This encompasses the design of the synthetic strategy as well as the management of potential byproducts that may arise from that process [71,72].

### 6.1 Gold-Based Nanoparticles (Au NPs)

In the traditional method of environmentally friendly gold nanoparticle (Au NP) synthesis, gold ions are reduced using reducing agents derived from plant extracts or microorganisms. Extracts are obtained by submerging crushed plants in solvents (such as water or ethanol) under suitable environmental conditions (which differ

based on the particular green chemicals being employed). Upon combining the extracts with a solution containing gold ions, Au NPs are formed while the solution undergoes a colour shift to red [73,74,75,76]. The primary morphologies of gold nanoparticles produced by environmentally friendly techniques are spherical, with a lesser distribution showing triangular and hexagonal shapes. To provide an example, the extract of *Pogostemon benghalensis* led to the production of Au NPs with spherical and triangular shapes. The nanoparticles exhibited sizes within the range of 10 to 50 nm, as shown by Paul et al. [77]. However, the application of *Pelargonium* resulted in the formation of precise spherical Au NPs, with diameters varying between 10 and 100 nm [75]. X-ray diffraction (XRD) analysis revealed four well-defined peaks of gold nanoparticles (Au NPs) at about 38°, 44°, 64°, and 77°. This observation suggests that the Au NPs have a face-centered cubic structure, as documented in references [78,79]. By using an aqueous extract of *Elaise guineensis* (palm oil) leaves to reduce the concentration of Au (III) at different levels, the researchers found that the absorption peaks of Au NPs were comparable, but the absorbance values varied. Results indicate that no gold nanoparticles were produced when the gold (III) concentration was less than 1.53 millimolar [24-26]. Due to their large surface area, Aurum nanoparticles are prone to oxidation when exposed to air. Hence, it is important to consider the stability of gold nanoparticles (Au NPs) during their production or storage [80,81,82,83,84]. In their study, Aljabali et al. [85] employed a leaf extract of *Ennab* to quantify absorbance at different reaction durations (0, 0.5, 1, 2, 3, and 10 minutes) using UV-Vis spectroscopy. Previous studies have shown that the zeta potential of Au NPs synthesized by the brown algae *Cystoseira baccata* ( $-30.7 \pm 2.0$  mV) or by the extract of *Cryptolepis buchanani* ( $-30.28$  mV) surpassed 30 mV. This parameter is essential for preserving the stability of gold nanoparticles [83]. Microbial organisms can also be employed to produce Au NPs. For example, the yeast *Magnusiomyces ingens* LH-F1 was grown under aerobic conditions at a room temperature of 30 °C until it reached the logarithmic proliferation stage. The addition of the chemical  $\text{HAuCl}_4$  to the cell solution led to the production of gold nanoparticles [86-88]. HS-11 [89] and mesophilic filamentous fungus [90] were used as supplementary microorganisms in the eco-friendly synthesis of gold nanoparticles (Au NPs). Researchers have thoroughly investigated the

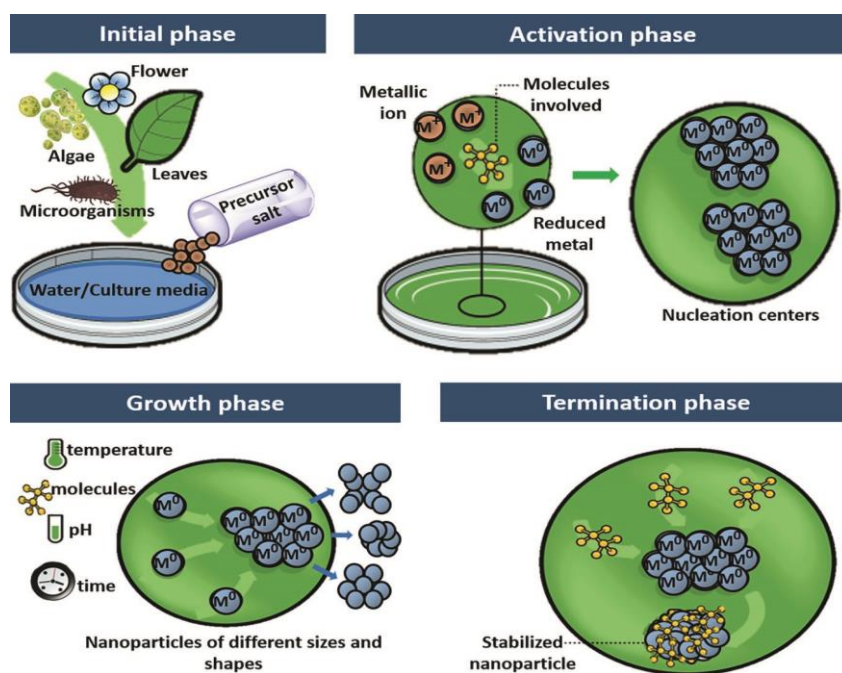
potential of green-synthesized Au NPs as a catalyst for diverse applications. Quercetin-synthesized Au NPs are highly efficient catalysts for breaking down 4-nitrophenol and methyl orange residues [91], as well as for detecting ammonia. Gold nanoparticles are widely employed in the medical industry. Aurum nanoparticles (Au NPs) possess exceptional surface compatibility and facilitate the adsorption of a wide variety of biomolecules. The aforementioned attribute can augment the efficacy of therapeutic therapy [92].

## 6.2 Silver-Based Nanoparticles (Ag NPS)

A widely employed technique for producing silver nanoparticles requires the combination of silver nitrate with reducing agents obtained from plants. Botanical extracts are obtained using the conventional method described before in relation to Au NPs. These extracts are subsequently mixed with a silver nitrate solution. The formation of silver nanoparticles is indicated by the solution undergoing a colour change to a brownish shade [93,94,95,96]. Ajitha and her colleagues dissolved *Tephrosia purpurea* leaf powder in Milli-Q water and exposed the solution to a heated temperature of 60 °C for 15 minutes. Following filtration, the solution was mixed with silver nitrate and then centrifuged to separate the Ag NPs [7].

In their study, Khatami et al. [93] successfully synthesized Ag NPs utilizing grass waste, namely hay. The experimental protocol involved the systematic washing and sterilization of the hay, followed by the process of boiling and filtration to get the extract. Furthermore, the extract was mixed with different amounts of silver nitrate to generate silver nanoparticles. This presents an environmentally friendly substitute for burning grass waste generated on agricultural landscapes. This technology can produce silver nanoparticles and also has the potential to reduce air pollution resulting from the burning of agricultural leftovers. The antimicrobial properties of silver nanoparticles have been examined [97,98].

Furthermore, it can also influence the growth and development of plants. Previous research has shown that silver nanoparticles significantly affect photosynthetic pigments and hinder the development of the aboveground parts of plants, leading to a considerable 40 % limitation in plant growth [99]. The unique hollow dendritic nanostructure of the Pt-Ag nano catalyst system



**Fig. 3. Phases involved in the green synthesis of nanoparticles [52]**

renders it a very suitable option for a durable and stable photocatalyst [100]. The green synthesis of silver nanoparticles is affected by several factors, such as the plant extract, pH environment, and temperature. Distinct constituents of the same plant produce different effects. For example, Nabikan et al. [101] found that the callus and leaf of *Sesuvium portulacastrum* L. may elicit different effects on the production of silver nanoparticles. The researchers found that the absorption peak of the callus extract and  $AgNO_3$  displayed higher intensity when cultured together compared to the leaf extract. Therefore, it may be inferred that the callus extract, functioning as a reducing agent, produced a greater amount of silver nanoparticles than the leaf extract.

Edison and his colleagues [102] used a pod extract obtained from *Acacia nilotica* to synthesize silver nanoparticles along a pH spectrum of 5 to 9. The shape of silver nanoparticles is unaffected by the pH level, as verified by Surface Plasmon Resonance experiments conducted within the wavelength range of 409 to 430 nm. However, a hypsochromic shift was observed, indicating that the particle size distribution range may be broadened by altering the pH of the reaction between 5 and 9. The inability to synthesize silver nanoparticles at a temperature of 37 °C was reported by Vimala et al. [104]. The silver

nanoparticles produced by environmentally friendly techniques display a variety of shapes and sizes, among which the most commonly seen forms are spherical, triangular, and hexagonal [103,105,106]. In their study, Dhand et al. used *Terminalia cuneata* to produce silver nanoparticles that had a spherical shape and a size range of 25–50 nm. However, certain extracts failed to generate silver nanoparticles at the nanoscale. For example, Vijayaraghavan and colleagues (20) synthesized silver nanoparticles by the use of extracts derived from *Trachyspermum ammi* and *Papaver somniferum*. The size range of the produced Ag NPs varied from 3.2 to 7.6  $\mu m$ . The X-ray diffraction (XRD) analysis revealed that the crystal structure of Ag NPs is face-centred cubic according to the presence of four clearly defined peaks. The observed maxima were at 38.1° for the (1 1 1) cycle, 44.3° for the (2 0 0) cycle, 64.4° for the (220) cycle, and 78.2° for the (3 1 1) cycle. [107]. The durability of silver nanoparticles produced by environmentally friendly technologies is a crucial factor to take into account throughout the chemical synthesis procedure. Conventionally, this is assessed by performing tests with different reaction durations [104,108,109,110]. The investigation undertaken by Palaniappan et al. [111] involved the synthesis of silver nanoparticles using *Cymodocea serrulata*. The UV-Vis absorbance was evaluated at time intervals ranging from 10 to 60 minutes. The



presence of a single peak with the highest wavelength ( $\lambda_{\text{max}}$ ) at around 420 nm indicates the production of silver nanoparticles. The ultraviolet-visible (UV-Vis) absorbance of silver nanoparticles synthesized from *Couroupita guianensis* Aubl was measured at 5, 10, 20, 30, 40, 50, and 60 minutes. The results were similar to those published by Vimala et al. [104] for the silver nanoparticles generated by *Cymodocea serrulate*. In their investigation, Nakkala et al. employed *Acorouscalamus* rhizome extract to evaluate the absorbance of silver nanoparticles at different time intervals of 4, 8, 12, 16, 20, and 24 hours. A solitary peak with a maximum wavelength ( $\lambda_{\text{max}}$ ) of 420 nm was detected by the researchers, indicating the stability of silver nanoparticles over 24 hours [110]. However, gold nanoparticles did not exhibit the same phenomenon [112]. Moreover, silver nanoparticles can function as photocatalysts in the domain of medical and equipment technology, as shown by Kareem et al. [113].

### 6.3 Palladium Based Nanoparticles (Pd NPs)

Palladium is a highly dense and precious metal. It functions as a catalyst and biosensor and is widely used in medical diagnostics [44]. It can efficiently speed up a variety of chemical reactions and increase the yield of finished goods. Due to its distinct ligand-free catalysis, the generation of Pd NPs has been extensively studied [114]. Pd NPs were produced by Turunc et al. [45] using carboxymethyl cellulose, and these Pd NPs were subsequently employed to degrade azo-dyes. With the help of black tea leaf extract, the catalyst for the Suzuki-Miyaura coupling reaction was successfully created [15].

In two different investigations [3,35], the ZOI diameter for aureus was measured to be  $28 \pm 2.3$  mm and  $26 \pm 2.3$  mm, respectively. A wide range of plant extracts, including those from leaves, fruits, and roots, are used to make palladium nanoparticles (Pd NPs). Palladium nanoparticles (Pd NPs) created from plant extracts were reported to have smaller sizes than those prepared from other synthetic agents [45]. The authors of Sharmila et al. [117] postulated that the leaf extract's steroid, phenolic, flavonoid, saponin, alkaloids, and tannin content served as both stabilizing and reducing agents. A further study using leaf extract from *Euphorbia granulate* revealed a shorter synthesis time [44]. Moreover, agglomeration was impeded by the presence of polyphenols and other phytochemicals.

According to [17,45,115,118], different materials used in the creation of Pd NPs are black tea leaves, *Lithodor ahispidula* leaf, *Rosa canina* fruit, and *Sapium sebiferum* leaf. The leaves of *Lithodor ahispidula* were ground up and then boiled in extremely clean water by Turunc et al. [45]. The extract from the leaves was chilled and filtered before being mixed with a  $K_2 PdCl_4$  solution. Gum olibanum is a renewable material that Kora and Rastogi [116] selected for their study. The analysis verified that the gum's hydroxyl and carboxylate groups, together with proteins, improved the stability of Pd NPs.

### 6.4 Copper Based Nanoparticles (Cu NPs)

Since copper (Cu) is a light transition metal, it is frequently impractical to produce Cu NPs directly from basic copper salts. As capping agents, surfactants are required to control particle size [119]. Microbial and plant extracts are the two main categories into which Moses divided the biological generation of Cu NPs [120]. Extracellular proteins found in the extract of the white-rot fungus *Stereum hirsutum* can stabilize and generate Cu NPs [121]. Other non-toxic substances have been employed to produce Cu NPs, including L-ascorbic acid [3]. L-ascorbic acid produces Cu NPs that are smaller than 2 nm. *Thymus vulgaris* L., G., and *Eucalyptus* sp. leaves are used to make plant extracts. Cu NPs have been synthesized using the plant species *biloba* Linn [102,44,122]. *Eucalyptus* sp. was utilized to create the Cu NPs. The samples showed good uniformity; however, there was no discussion on the usage of Cu NPs. *Thymus vulgaris* L. was used in the production of the copper nanoparticles. The leaves also used bentonite to achieve a high level of Cu NP dispersion. The creation of Cu NPs was facilitated by the protein present in aloe vera blossoms, which served as a coating on the particle surface [123]. The scientific name for the guava plant is *Psidium guajava* L. Vitamin C, a substance with reducing qualities, is abundant in fruits [124]. When these nanoparticles were tested against gram-positive (*Staphylococcus aureus*) and gram-negative (*E. coli*) bacteria, they demonstrated remarkable antibacterial activity. Black soya bean's abundance of bioactive components, such as protease inhibitors, phenolic compounds (flavonoids, tannins, and anthocyanins), and phytic acids, led Nagajyothi et al. [125] to use it as a synthetic agent in their investigation. A mixture of spherical, hexagonal, and amorphous particles generated the CuO NPs. HeLa cells were

exposed to the CuO NPs in an in vitro experiment. The results of the experiment showed that the CuO NPs disrupted the mitochondrial membrane, which inhibited the development of Hela cells [126]. In a different work, the scientists made monoclinic CuO nanoparticles at various calcination temperatures using coffee powder and the sol-gel method [127]. Extracts from *Callistemon viminalis* flowers and *Azadirachta indica* leaves [128] were also used in the creation of CuO NPs.

Copper nanoparticles produced by an environmentally friendly method can attain a zeta potential of -26 mV, suggesting a condition of relative stability [129]. Previous studies have demonstrated that the antibacterial efficacy of Cu NPs surpasses that of silver due to its ability to induce damage to essential proteins [130]. This study indicates that Cu NPs synthesized with extracts from the *Terminalia arjuna* plant exhibit substantial antibacterial activity against *S. aureus* and *Escherichia coli* have been reported. A study conducted by [17] examined the microorganisms *Typhi* and *P. aeruginosa*. Antibacterial studies were conducted utilizing Cu NPs synthesized from leaf extracts of *Vitis vinifera* [130,131] and *Nerium oleander* [123]. Moreover, these Copper nanoparticles were used as a catalyst. This study investigates the catalytic activity of Cu NPs synthesized using an extract obtained from the foliage of *G. biloba* Linn on the Huisgen [3 + 2] cycloaddition process was seen, and the catalyst has the potential for recycling [127]. Copper oxide nanoparticles, synthesized with *Annona muricata* leaf extract, exhibited discoloration rates of approximately 90 and 95 % for Reactive Red 120 and Methyl orange, respectively, at a temperature of 60 °C [129].

## 6.5 Iron Based Nanoparticles (Fe NPs)

Fe NPs have been extensively studied for their potential in environmentally sustainable production. Nanoparticles of iron (Fe) with high antioxidant capacity have been successfully synthesized utilizing extracts derived from mango leaves (*Mangifera indica* L.), eucalyptus leaves, grape seed (*Vitis vinifera* L.), pear tree leaves (*Eleocharis tuberosa*), vine leaves, and *Terminalia chebula* fruit. A specific strain of NZVI demonstrated remarkable stability, as evidenced by a zeta potential of around -82.6 mV. A similar phenomenon was seen in NZVI produced from *Urtica dioica* leaf, as documented by Ebrahiminezhad et al. [137] in 2017. Kuang et al.

[132] performed a comparative investigation on the production of Fe NPs using extracts derived from black tea, oolong tea, and green tea. The efficacy of the green tea extract in synthesizing Fe NPs was demonstrated to be the highest. This phenomenon may be attributed to the abundant presence of polyphenols or caffeine, which function as both reducing and capping agents. Fe NPs derived from green tea have been used as a replacement for Fe<sup>2+</sup> in Fenton reactions [133,134]. Scientists have successfully employed Fe NPs generated by the application of oolong tea extract to degrade color molecules [135]. Naseem et al. [8] used conventional heating techniques to get extracts from the leaves of *Gardenia jasminoides* and *Lawsonia inermis* for the synthesis of iron nanoparticles. Fe NPs synthesized from *Gardenia jasminoides* exhibited strong inhibitory effects on *Staphylococcus aureus* [8]. Similarly, Wei et al. [9] examined the application of extract obtained from *Eichhornia crassipes*, an invasive plant renowned for its fast growth and extensive reproductive capacity, for the production of iron nanoparticles. The nanoparticles were analyzed for their capacity to eradicate chromium, and it was demonstrated that chromium can be neutralized by reduction, immobilization, and coprecipitation. The synthesis of NZVI is a more complex procedure than the manufacturing of other nanoparticles [136]. The effectiveness of grape seed extracts as a stabilizing catalyst was shown in inhibiting the oxidation and aggregation of NZVI. The effective removal of reactive oxygen species, such as peroxy and hydroxyl radicals, was ascribed to the coexistence of polyphenol and proanthocyanidins [39]. By functioning as capping agents, polyphenols can improve the stability of nanoparticles [13]. In their 2015 study, Machado et al. [137] investigated the possibility of synthesizing NZVI using leaf extracts from 26 different plants, such as walnut, vine, tea-green, avocado, apricot, and apple. The resulting NZVI displayed variances in both dimensions and morphology.

## 7. CONCLUSION

The green synthesis of metallic nanomaterials offers a promising alternative to traditional methods, addressing environmental concerns and promoting sustainability. Utilizing natural resources and minimizing the use of hazardous chemicals contributes to a more eco-friendly and responsible production of nanomaterials. While significant progress has been made in developing green synthesis techniques, several

challenges remain, including scalability, reproducibility, and the need for further characterization and standardization. Overcoming these obstacles will be crucial for the widespread adoption of green nanomaterials in various applications. In conclusion, the future of nanotechnology lies in the development and implementation of sustainable practices. The green synthesis of metallic nanomaterials presents a viable path toward achieving this goal, offering a balance between innovation and environmental responsibility. Continued research and development in this area are essential to unlock the full potential of green nanomaterials and their contributions to a more sustainable future.

### DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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