Review Article

Plant-Extract-Mediated Synthesis of Metal Nanoparticles

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Metal nanoparticles (MNPs) have been widely used in several fields including catalysis, bioengineering, photoelectricity, antibacterial, anticancer, and medical imaging due to their unique physical and chemical properties. In the traditional synthesis method of MNPs, toxic chemicals are generally used as reducing agents and stabilizing agents, which is fussy to operate and extremely environment unfriendly. Based on this, the development of an environment-friendly synthesis method of MNPs has recently attracted great attention. The use of plant extracts as reductants and stabilizers to synthesize MNPs has the advantages of low cost, environmental friendliness, sustainability, and ease of operation. Besides, the as-synthesized MNPs are nontoxic, more stable, and more uniform in size than the counterparts prepared by the traditional method. Thus, green preparation methods have become a research hotspot in the field of MNPs synthesis. In this review, recent advances in green synthesis of MNPs using plant extracts as reductants and stabilizers have been systematically summarized. In addition, the insights into the potential applications and future development for MNPs prepared by using plant extracts have been provided.

1. Introduction

Many areas of research including medicine, catalysis, photoelectricity, and industrial manufacture have been revolutionized by nanotechnology. It is estimated that the industrial production of nanomaterials had reached 58,000 tons per year in 2020 [1]. Metal nanoparticles (MNPs) have been widely used in catalysis, bioengineering, electronics, optoelectronics, medicine, sensing, and information storage [2, 3] due to unique physicochemical and biological properties of MNPs such as high electrical conductivity, thermal conductivity, chemical stability, high catalytic activity, and medically related antimicrobial and anticancer activities [4, 5]. The synthesis of MNPs usually includes "Top-down" and "Bottom-up" approaches (Figure 1(a)). The “Top-down” approach fabricates MNPs from the corresponding bulk metallic materials by various physical or chemical methods (e.g., mechanical grinding, laser ablation, and thermal decomposition) to achieve size reduction [6]. The “Top-down” preparation method often requires high pressure, temperature, and expensive specialized equipment, as well as usually introduces defects in the surface structure of MNPs. Since the physicochemical properties of nanoparticles are highly dependent on their surface structure [7], the application of MNPs prepared by the “Top-down” method is greatly limited.

In the “Bottom-up” synthesis, MNPs are formed by stacking the corresponding metal atoms [8], which mainly includes chemical synthesis and biosynthesis. Generally, chemical synthesis uses polyvinylpyrrolidone, alkyl mercaptan, thioantracenol, dimethylformamide, or Tween 80 as the stabilizer and sodium borohydride, hydrazine hydrate, or formaldehyde as the reducing agent to synthesize MNPs [9]. This route inevitably uses toxic chemicals and is, therefore, extremely environment unfriendly. In the process of preparing MNPs with traditional chemical reducing agents, some stabilizers are usually added to maintain the stability of MNPs due to the fierce reduction reaction. The chemical reducing agents used in this process are generally expensive, toxic, and dangerous, which can bring a variety of hazards to the experimenters and the environment [10]. Thus, a green reducing agent featured with mild reaction, low cost, and easy operation and acting as a stabilizer agent is highly desirable. The biosynthesis method mainly uses...
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2.1. Synthesis of Gold Nanoparticles. In the field of nanomaterial research, gold nanoparticles (AuNPs) are of great interest due to their stability, size controllability, biocompatibility, high adsorption capacity, and high catalytic activity [16]. AuNPs have a wide range of applications in medicine [17], drug and gene delivery [18], biosensors [19], tomography [20], photocatalysis [21], environmental sensing [22] and water purification [23]. Among the most commonly used “Bottom-up” synthesis strategies (Figure 1(a)), the metal ions are firstly reduced to metal atoms, the metal atoms are then self-assembled to form nuclei, and subsequently, the metal nuclei continue to grow to form MNPs, which includes the processes of coprecipitation, sol-gel, and atomic condensation [24, 25]. The currently used chemical synthesis of AuNPs usually involves toxic chemicals that adsorb on the surface of AuNPs, limiting their applications in fields such as biology and medicine. Therefore, there is an urgent need for novel green and efficient synthetic methods to replace toxic chemical synthesis. In this context, plant-extract-mediated AuNP synthesis has aroused numerous interests since it can produce AuNPs efficiently and the as-prepared AuNPs have better biocompatibility without carrying toxic chemicals [26].

AuNPs were synthesized using leaf extracts; Guo et al. [27] prepared AuNPs by reducing chlorauric acid (HAuCl₄) using ethanol extracts of dried powder of vine tea leaves. They also studied the effects of reaction conditions such as temperature, pH, and extract dosage on the physicochemical properties of AuNPs and found that alkaline conditions or excess vine tea extracts led to agglomeration of AuNPs; higher temperature was more favorable for the synthesis of small-sized AuNPs, and AuNPs were more stable at low temperature. Tao et al. [28] reported that spherical and highly crystalline AuNPs with particle size between 20–60 nm were prepared by reducing HAuCl₄ using aqueous extracts of aloe vera leaves, and under the protection of the extracts, the AuNPs were less prone to agglomeration and oxidation and had good stability.

AuNPs were synthesized using flower extracts; Ghosh et al. [29] found that the aqueous extracts of Gnidia glauca flowers could reduce HAuCl₄ and synthesize AuNPs within 20 min. The resulting AuNPs contained spherical, triangular, and hexagonal shapes, with sizes mainly around 10 nm. It was also found that the AuNPs had a significant catalytic effect on the synthesis of 4-amino phenol by reduction of 4-nitrophenol with NaBH₄. Zangeneh and Zangeneh [30] reduced HAuCl₄·3H₂O with water extracts from Hibiscus sabdariffa flowers and obtained spherical AuNPs with a particle size of 15–45 nm. Interestingly, the as-synthesized AuNPs could significantly reduce proinflammatory...
cytokines and enhance anti-inflammatory cytokines. In addition, AuNPs showed no significant cytotoxicity to endothelial cells, which was similar to daunorubicin.

AuNPs were synthesized using extracts of fruits or fruit shells; Baldea et al. [31] studied the feasibility of AuNPs synthesis using the water extracts from *Cornus mas* fruit and the biological effects of the as-obtained AuNPs. It was found that HAuCl₄ could be reduced to AuNPs at pH ≈ 7.5 and AuNPs had selective toxicity to hypertrophic keratinocytes and could induce their death. The AuNPs showed good biocompatibility to normal gingival fibroblasts and had the potential to be used in the treatment of diseases related to oral dysplasia. Sathishkumar et al. [32] reported that nanogold was prepared by reduction of HAuCl₄ using aqueous extracts of *Cordyceps sinensis* at pH ≈ 7, at 70°C, with 1 mM substrate and 5 mL of fruit extracts when reacting for 60 min. The AuNPs obtained had an average size of 26 ± 11 nm, was negatively charged, nonagglomerated, and covered by a layer of polyphenolic substances. In addition, it was found that the as-prepared AuNPs have good antioxidant and hemocompatibility properties. Chen [33] prepared hydrophilic AuNPs with sizes of 9–23 nm using mangosteen polyphenols from the aqueous extracts of *Garcinia mangostana* L. pericarp as reducing and stabilizing agents, respectively, and found that decreasing the concentration of the extracts resulted in various forms of AuNPs.

AuNPs were synthesized using root extracts; Sutan et al. [45] showed that ethanol extracts of *Aconitum toxicum* Reichenb roots reduced with HAuCl₄ for three hours at room temperature could be used to prepare AuNPs with a size of 9–15 nm. Meanwhile, the total polyphenol content of the extracts was measured to be 1.49%, and the aconitine content was measured to be 4.891 mg/mL. The antioxidant activity of the AuNPs was measured to be between 78% and 84.32%. Gonzalez-Ballesteros et al. [46] found when the water extracts of an *Ulva intestinalis* L. was used to reduce chlorauric acid for 4 hours under the condition of pH = 6.65, AuNPs were synthesized. The average diameter and the average zeta potential of AuNPs were 17.8 ± 2.7 nm and −22.30 ± 0.24 mV, respectively. The biocompatibility of AuNPs was systematically studied, and the results showed that AuNPs had good biocompatibility and low hemolytic toxicity and could induce cell proliferation. Similarly, Jacob et al. [47] showed that water extracts from *Brassica oleracea* var. *capitata* plants could reduce HAuCl₄ to prepare AuNPs, and the diameter of AuNPs was related to the pH value of the reaction medium, reaction time, and initial reactant concentration.

The AuNPs were synthesized using extracts from whole plants; Lee et al. [48] extracted the active ingredient in *Ocimum sanctum* with four solvents of different polarities, namely, water, n-butanol, chloroform, and n-hexane, and used the extracts to reduce HAuCl₄ to produce AuNPs. They found that the AuNPs synthesized from the water extracts were mainly thin flakes with various shapes and sizes along with neat edges, while the AuNPs synthesized from n-butanol extracts were mainly spherical small particles of about 20 nm in size and nanosheets of about 1 μm in size; the AuNPs synthesized from chloroform extracts were mainly nanosheets with rough edges; the AuNPs synthesized from hexane extracts were mainly nanospheres of less than 10 nm.

In conclusion, researchers have prepared AuNPs using flavonoids, polyphenols and amino acids from leaves, flowers, seeds, roots, and fruits of plants as reducing and stabilizing agents and HAuCl₄ as the precursor (Table 1) to achieve the green synthesis of AuNPs. Many researchers also investigated the effects of extracts concentration, reaction temperature, pH, and reaction time on the morphology of AuNPs. The applications of AuNPs prepared via green synthesis mainly focused on detection and antibacterial and catalytic degradation of certain colored dyes. In the future, the synthesis of AuNPs using plant extracts has great potential, and it is worthwhile to further explore the synthesis mechanism to achieve precise and controllable AuNPs morphology or to synthesize AuNPs on the surface of other materials by in situ reduction to form multifaceted composites, which are all research directions worthy of investment.

### 2.2. Synthesis of Silver Nanoparticles

Silver nanoparticles (AgNPs), an important product in the field of nanotechnology, are one of the most widely used nanoparticles in the biomedical field [49]. Owing to their unique chemical stability, good electrical conductivity and catalytic properties, and particularly outstanding antimicrobial properties [50], AgNPs have been used in a large number of applications including biomolecular detection, drug delivery, food production, antimicrobial, and agricultural fields [51]. In particular, AgNPs have become one of the most promising materials for fighting the threat of drug-resistant bacteria due to their excellent antimicrobial properties [52]. The use of AgNPs synthesized from plant extracts is more beneficial for AgNPs to exploit their value in biomedical and other fields thanks to their low toxicity and biocompatibility [5, 53].

AgNPs were synthesized using leaf extracts; Pang et al. [54] found that AgNPs could be prepared from the extracts of *Youngia japonica* leaves, and the suitable reaction conditions were 60 mL of yellow quail leaf extracts (material ratio 15 g/L), 10 mL of AgNO₃ (0.005 mol/L), a reaction temperature of 60°C, and a reaction time for 40 min; the average particle size of the resulting AgNPs was 20 nm, and most of them were spherical; they had a significant suppressing effect on the bacteria isolated from the stem ends of cut lilies and are expected to be applied to the freshness treatment of cut flowers after the reaction. Wang et al. [55] obtained AgNPs by reducing silver nitrate with the aqueous extracts of green tea, and the obtained AgNPs were spherical with a particle size of 30–40 nm. Meanwhile, the optimal conditions for the preparation of AgNPs by this system were determined by orthogonal experiments: AgNO₃ concentration 0.08 mol/L, green tea extracts 0.0125 g/mL, reaction temperature 40°C, and time 2 h.

AgNPs were synthesized using extracts of the fruits; Jiang et al. [67] prepared AgNPs by reducing silver nitrate using aqueous and ethanolic extracts of hawthorn fruits as
reducing and stabilizing agents, respectively. A comparative study revealed that the AgNPs synthesized from the aqueous extracts were smaller and more homogeneous and had higher antibacterial activity. Kumar et al. [62] examined the feasibility of synthesizing AgNPs from extracts of Eugenia stipitata McVaugh fruits, and the results proved feasible. The as-prepared AgNPs were spherical in shape and 15–45 nm in size and had good antioxidant effects; furthermore, infrared spectroscopy demonstrated that the synthesis of AgNPs was associated with malic acid, citric acid, and carotenoids in the extracts.

AgNPs were synthesized using extracts of the bark or tubers. Rohaizad et al. [64] used aqueous extracts of the Catharanthus roseus bark as the raw material to reduce silver nitrate via green synthesis and produced AgNPs in situ on the surface of graphene oxide (GO). The resulting AgNPs were mostly spherical with particle sizes ranging from 1 to 26 nm, and the AgNPs-GO composites showed good adsorption effect on methylene blue dye. Liu et al. [68] used 70% ethanol extracts of ginger as a reducing agent for the green synthesis of AgNPs, and the AgNPs obtained were face-centered cubic structures with spherical shape and a particle size of 5–30 nm and had good thermal stability and antibacterial effect.

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In summary, similar to the commonly used synthesis methods of MNPs and their application (Figure 2), when using plant extracts to produce AgNPs, water was mainly used as the extraction solvent, partly ethanol or methanol solution, all silver salts used were silver nitrate (Table 2), and the reaction time was mostly longer than 1 h. The resulting AgNPs were mainly used in the antibacterial field. Therefore, it is of great importance to explore to further shorten the reaction time for synthesizing AgNPs in subsequent studies and to investigate the in vivo and in vitro toxicity of such AgNPs more systematically in order to better exploit their antibacterial properties, especially anti-drug-resistant bacteria, which is of great significance.

### Table 1: Representative examples for the use of plant extracts for AuNP synthesis.

| Plant                  | Part          | Extractant | Precursor | Size (nm) | Reference |
|------------------------|---------------|------------|-----------|-----------|-----------|
| Butea monosperma       | Leaf          | Water      | HAuCl₄    | 10–100    | [34]      |
| Pelargonium graveolens | Leaf          | Water      | HAuCl₄    | 20–40     | [35]      |
| Salix alba             | Leaf          | Water      | HAuCl₄+H₂O| 50–80     | [36]      |
| Guazuma ulmifolia L.   | Bark          | Water      | HAuCl₄+H₂O| 20–25     | [37]      |
| Mimulus elengi         | Bark          | Ethanol    | HAuCl₄    | 9–14      | [38]      |
| Nerium oleander        | Bark          | Methanol   | HAuCl₄    | 20–40     | [39]      |
| Rubia cordifolia       | Fruit         | Ethanol    | HAuCl₄    | 5–20      | [40]      |
| Litsea cubeba          | Fruit         | Water      | HAuCl₄+H₂O| 8–18      | [41]      |
| Piper longum           | Fruit         | Water      | HAuCl₄    | 20–200    | [42]      |
| Hibiscus sabdariffa    | Flower        | Water      | HAuCl₄+H₂O| 15–45     | [30]      |
| Coleus forskohlii      | Root          | Water      | HAuCl₄    | 5–18      | [43]      |
| Stachys lavandulifolia | Overground part | Water  | HAuCl₄    | 34–80     | [44]      |
CuNPs were synthesized using flower or bark extracts; Dinesh et al. [77] applied aqueous extracts of *Hibiscus rosa-sinensis* flowers to reduce copper acetate monohydrate and obtained square CuNPs with the size of 0.115–1.1 μm in a 30 min reaction assisted by acoustic waves. Meanwhile, it was found that the CuNPs could generate free radicals to catalyze the degradation of two drugs, 5-fluorouracil and lovastatin. Pinto et al. [78] used different concentrations of aqueous extracts of *Eucalyptus globulus* bark to reduce copper chloride dihydrate in oleamide, oleic acid, and ethanol systems, respectively, for 2 h at 120°C to produce CuNPs. Meanwhile, the phytoactive components of the extracts were attached to CuNPs, rendering CuNPs with better antioxidant and conductive effects. CuNPs showed no sign of copper oxide phase after two weeks of storage.

CuNPs were synthesized using fruit or seed extracts; Khani et al. [86] reported the reduction of copper sulfate using aqueous extracts of dried *Ziziphus spina-christi* (L.) Wild. fruit powder associated with starch as a stabilizer, to produce spherical CuNPs with a particle size of 5–20 nm. The resulting CuNPs showed an inhibitory activity against *Escherichia coli* and *Staphylococcus aureus* in a concentration-dependent manner. In addition, the CuNPs were found to have good adsorption effect on crystalline violet. Sajadi et al. [84] used the aqueous extracts of *Silybum marianum* L. seeds to react with both ferric chloride hexahydrate and copper chloride dihydrate to produce CuNPs-Fe₃O₄ composites at 60°C, which are of sizes 8.5–60 nm and good stability (>2 months). The possible synthesis mechanism is shown in Figure 3. In terms of application, CuNPs-Fe₃O₄ was found to be effective in catalyzing the reduction of nitroaromatics and was recyclable and reusable (more than five times).

Researchers have used plant flower, leaf, seed, fruit, and bark extracts to reduce certain copper salts (e.g., copper acetate monohydrate, copper chloride, copper chloride dihydrate, copper sulfate, copper nitrate trihydrate, and copper sulfate pentahydrate) to prepare CuNPs. The resulting CuNPs are mainly used for detection, antibacterial, antioxidant, degradation of organic dyes, and mitigation of cytotoxicity of certain drugs. In addition, some CuNPs prepared via green synthesis using plant extracts were found to have better antibacterial effects and biocompatibility compared with CuNPs synthesized via traditional methods; since copper itself is a trace element required by the human body, it is of great practical value and significance to broaden the application of green-synthesized CuNPs for antibacterial and drug toxicity mitigation in the human body in future studies.

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**Table 2: Representative examples for the use of plant extracts for AgNP synthesis.**

| Plant                  | Part         | Extractant | Precursor | Size (nm) | Reference |
|------------------------|--------------|------------|-----------|-----------|-----------|
| *Lotus garcinii*       | Leaf         | Water      | AgNO₃     | 7–20      | [56]      |
| *Morinda citrifolia*   | Leaf         | Methanol   | AgNO₃     | 10–100    | [57]      |
| *Allium fistulosum*    | Leaf         | Water      | AgNO₃     | 28.95 ± 10.17 | [58]     |
| *Moringa oleifera*     | Leaf         | Water      | AgNO₃     | 15–25     | [59]      |
| *Ocimum basilicum*     | Seed         | Water      | AgNO₃     | ~13.82    | [60]      |
| *Prunus mume*          | Fruit        | Water      | AgNO₃     | ~30       | [61]      |
| *Eugenia stipitata McVaugh* | Fruit      | Water      | AgNO₃     | 15–45     | [62]      |
| *Garcinia mangostana*  | Fruit        | Water      | AgNO₃     | ~23       | [63]      |
| *Aconitum toxicum*     | Root         | 96% ethanol| AgNO₃     | 53–67     | [45]      |
| *Catharanthus roseus*  | Bark         | Water      | AgNO₃     | 1–26      | [64]      |
| *Ulva armoricana*      | Whole plant  | Water      | AgNO₃     | ~215      | [65]      |
| *Ulva lactuca*         | Whole plant  | Water      | AgNO₃     | 31 ± 8    | [66]      |
2.4. Synthesis of Platinum Nanoparticles. Currently, transition metal nanoparticles, especially platinum nanoparticles (PtNPs), are extensively studied. PtNPs have attracted widespread attention due to their applications in the automotive industry, chemical industry, and biomedicine [89]. Traditional physical and chemical synthesis methods of PtNPs are not only energy intensive and require harsh conditions but also inevitably require the use of toxic solvents or reducing agents, which are highly unfriendly to the environment [90]. PtNPs prepared by biosynthesis are preferred for various applications due to their good biocompatibility and ecofriendliness. Therefore, the development of facile and environment friendly methods for the synthesis of PtNPs is not only important for the development and utilization of PtNPs but also caters to the trend of green chemistry [91].

PtNPs were synthesized using extracts of fruits or peels; Sundar et al. [105] found that PtNPs could be produced by reducing H2PtCl6 using aqueous extracts of Sapindus mukorossi fruits. In addition, it was found that this PtNP-modified electrode could be applied to detect single nanoparticle collision. Sahin et al. [106] fabricated PtNPs by reducing PtCl4 with ethanol extracts of pomegranate peel in particle collision. Sahin et al. [106] fabricated PtNPs by modified electrode could be applied to detect single nano-particles or reducing H2PtCl6 using aqueous extracts of Protoparmeliopsis muralis. It can be seen that the synthesis of PtNPs using plant extracts provides a diversity of precursors of platinum source, mainly including H2PtCl6·6H2O, K2PtCl6, PtCl4, Na2PtC4, H2PtCl6. The temperature of the synthesis reaction is generally high (greater than 80°C), and the resulting PtNPs are small, most of which do not exceed 10 nm. The applications are mainly focused on antibacterial, anticancer, and catalytic degradation of organic dyes. However, there are still many challenges in developing green synthetic PtNPs for nanomedicine applications, and more in vitro and animal experiments are needed to investigate the clearance mechanism, antioxidant activity, and long-term effects of PtNPs on the immune system.

2.5. Synthesis of Palladium Nanoparticles. In recent years, palladium nanoparticles (PdNPs) have been discovered to have numerous applications in organocatalysis, hydrogen production, supercapacitors, and biosensors owing to their high specific surface area and high surface energy [109, 110]. Various traditional methods including sol-gel, rapid precipitation, acoustochemical, electrochemical, solid-phase...
reaction, microwave radiation, and alcohol-thermal synthesis have been developed for synthesizing Pd nanoparticles [111]. However, these methods suffer from some shortcomings such as harsh reaction conditions, high reaction temperature, long reaction time, expensive raw materials, and environmental damage [112]. Therefore, the green synthesis method based on using plant extracts for the synthesis of PdNPs has received much attention and has been widely used for the synthesis of PdNPs.

PdNPs were synthesized using leaf extracts; Kanchana et al. [113] used aqueous extracts of Solanum trilobatum leaves to reduce PdCl₂ at room temperature for 24 h to obtain PdNPs. The particle size of the resulting PdNPs was mainly in the range of 60–70 nm. Nasrollahzadeh et al. [114] found that the aqueous extracts of Hippophae rhamnoides leaves could reduce PdCl₂ to prepare PdNPs with a spherical particle size of 2.5–14 nm. Also, this PdNP has ideal catalytic activity as a multiphase catalyst in the Suzuki–Miyaura coupling reaction. The RGO-T. spicata complex was obtained by attaching the water extracts of Thymbra spicata leaves to the surface of GO, as reported by Veisi et al. [115]. Afterwards, Na₂PdCl₄ was added to the mixture and stirred at 100°C for 12 h, in which Na₂PdCl₄ was reduced to PdNPs to obtain the PdNPs/rGO-T. spicata nanocomposite. At the same time, the as-obtained complex can effectively catalyze the cyanation of halides.

PdNPs were synthesized using extracts of fruits or peels; Nasrollahzadeh et al. [116] used aqueous extracts of barberry fruits as reducing agents to synthesize PdNPs in situ on the surface of reduced graphene oxide (rGO). The PdNP-rGO complexes were produced by vigorous stirring at 75°C for 10 h. When determining its catalytic performance, it is revealed that PdNP-rGO can be used as an efficient multiphase catalyst for the reduction of nitroaromatics by sodium borohydride without significant activity loss and high product yields after 5 cycles. Bankar et al. [117] used aqueous extracts of banana peel at 80°C for 3 min in an aqueous solution to reduce PdCl₂ into PdNPs. The average particle size of the resulting PdNPs was 50 nm. The carboxyl, amino, and hydroxyl groups in the extracts were presumed by infrared spectroscopy to have a possible role in the reduction of PdCl₂.

PdNPs were synthesized using extracts of the bark or whole plant; Mishra et al. [118] used aqueous extracts of the Ulmus davidiana bark as a reducing agent to reduce PdCl₂ at 60°C for 2 h with ultrasonic assistance to synthesize PdNPs. Sathishkumar et al. [119] showed that Cinnamomum zeylanicum bark extracts could reduce PdCl₂ at 30°C for 72 h and, thus, obtain PdNPs. The resulting PdNPs were spherical with particle size ranging from 15 to 20 nm, and it was also found that the pH value of the reaction did not affect the shape of the nanoparticles but affected their size and dispersibility. Momeni et al. [120] used Sargassum bovinum aqueous extracts to reduce PdCl₂. The color of the reaction system changed from yellow to dark brown indicating the formation of PdNPs, which had a particle size of 5–10 nm and good stability (>5 months) and could effectively catalyze the electrochemical reduction of hydrogen peroxide. In the work of Khan et al. [121], using extracts of Pulpicia glutinosa, PdNPs were prepared by reducing PdCl₂ at 90°C with stirring for 2 h. The color of the solution changed from yellow to dark brown indicating the formation of PdNPs, and the particle size of the resulting PdNPs was 20–25 nm. It was found that the PdNPs had good catalytic activity in the Suzuki reaction for the synthesis of biphenyl from bromobenzene.

As reported in the review paper, we can find that the corresponding extracts originate from several parts of plants, such as leaves, fruits, fruit shells, bark, bark, and roots (Table 5). The extraction solvent is mainly water, and the precursor of PdNPs is mainly PdCl₂. The particle size of the resulting PdNPs is generally no more than 50 nm, which is mainly used in the field of catalysis in organic chemistry, especially the Suzuki–Miyaura coupling reaction, and can be reused many times. In future investigation, the synthesis of PdNPs with more homogeneous particle size and controllable shape, as well as the investigation of the specific reaction mechanism and the exact amount of extracts demand, remain scientifically significant and challenging research directions.

| Plant                     | Part      | Extractant | Precursor                | Size (nm) | Reference |
|---------------------------|-----------|------------|--------------------------|-----------|-----------|
| Ocimum sanctum            | Leaf      | Water      | H₂PtCl₆·6H₂O             | ~23       | [92]      |
| Costus speciosus          | Leaf      | 95% ethanol| Platinum 2,4-pentanedion | 10–50     | [93]      |
| Bacopa monnieri           | Leaf      | Water      | H₂PtCl₆                 | 5–20      | [94]      |
| Azadirachta indica        | Leaf      | Water      | H₂PtCl₆·6H₂O            | 5–50      | [95]      |
| Mentha piperita           | Leaf      | Water      | H₂PtCl₆                 | ~54.3     | [96]      |
| Quercus Glauca            | Leaf      | Water      | H₂PtCl₆·6H₂O            | 5–15      | [97]      |
| Coffea Arabica            | Seed      | Water      | H₂PtCl₆                 | ~2        | [98]      |
| Nigella sativa L.         | Seed      | 70% ethanol| PtCl₄                   | 1–6       | [99]      |
| Terminalia chebula        | Fruit     | Water      | H₂PtCl₆                 | <4        | [100]     |
| Garcinia mangostana L.    | Fruit     | Water      | H₂PtCl₆·6H₂O            | 20–25     | [63]      |
| Taraxacum laevigatum      | Whole plant| Water      | H₂PtCl₆                 | 2–7       | [101]     |
| Padina gymnoscopora       | Whole plant| Water      | H₂PtCl₆                 | 5–50      | [102]     |
| Cacumen Platycladi        | Whole plant| Water      | Na₂PtCl₄                | 1.6–3.2   | [103]     |
| Dioscorea bulbifera       | Tuber     | Water      | H₂PtCl₆·6H₂O            | 2–5       | [104]     |
that iron nanoparticles were successfully prepared by reducing ferric chloride using aqueous extracts of *Hizikia fusiformis*, and the resulting iron nanoparticles were spherical in shape with a particle size of about 17–40 nm. In terms of application, the nanoparticles were found to be capable of removing 92.76% of Cr(VI) from water. Ituen et al. [128] used the ethanol extracts of *Allium cepa* to reduce Ni(NO$_3$)$_2$ (50°C, 45 min) to synthesize nanonickel. The obtained nanonickel possessed highly crystalline and spherical appearance with a particle size of 39.5–53.1 nm as well as possessed an average zeta potential of 46.4 mV. It is found that the nanonickel can effectively alleviate the corrosion of steel. Elango et al. [129] used methanolic extracts of *Cocos nucifera* to reduce AgNPs by reducing and stabilizing agents to fabricate nanonickel by reducing nickel acetate at 60°C. The resulting nanonickel was square in shape with an average particle size of 47 nm and had good stability. The nanonickel was also found to have insecticidal activity against the agricultural pest *Callasobruchus maculates*. 98.92% of Cu(II), 98.16% of Cr(III), and 93.39% of Ni(II) in the solution were removed, as reported by Vaseghi et al. [130], by using aqueous extracts of *Eryngium campestre* (wild spurge) leaves to reduce Cu(II) and Ni(II) ions. Veisi et al. [137] found that flavonoids, tannins, and phenolic compounds attached to the surface of AgNPs oxidant properties and serve as a reducing agent to prepare AgNPs by reducing silver ions through carbonyl or carboxyl groups on the linear chain of starch interacted with silver ions and, thus, the hydroxyl groups on nanocellulose. At 80°C, the silver ions were reduced by the hydroxyl groups, which themselves were oxidized to aldehyde groups. Jigyasa and Rajput [136] used polyphenols (rutin/curcumin) to synthesize AgNPs and found that the abundant hydroxyl phenolic hydroxyl groups. Wang et al. [15] used starch to prepare agarose with positively charged silver ions were attracted to negatively charged carboxyl and hydroxyl groups on nanocellulose. At 80°C, the silver ions were reduced by the hydroxyl groups, which themselves were oxidized to aldehyde groups. Jigyasa and Rajput [136] used polyphenols (rutin/curcumin) to synthesize AgNPs and speculated that rutin/curcumin may have obtained AgNPs by reducing silver ions through carbonyl or phenolic hydroxyl groups. Wang et al. [15] used starch to synthesize AgNPs and found that the abundant hydroxyl and carboxyl groups on the linear chain of starch interacted with silver ions and, thus, the hydroxyl groups reduced the silver ions to AgNPs. Moreover, it was found that the prepared AgNPs were stable owing to the passivated surface of AgNPs and surrounded by negatively charged carboxyl groups.

It was found that the preparation of MNPs using plant extracts can be generally divided into the following three phases: the reduction phase, growth phase, and termination phase. In the reduction stage, the reducing phytoactives reduce metal ions to zero-valent metal atoms by electron transfer. Subsequently, the zero-valent metal atoms grow by aggregation into nanometallic particles with various shapes (linear, rod shaped, triangular, hexagonal, or cubic) in the growth stage. Finally, the phytoactive components with antioxidant properties are enriched around the MNPs to maintain the stability of MNPs in the termination stage [77, 134].

Sajadi et al. [84] utilized poly phenolic substances, such as flavonolignans, from *Silybum marianum* L., seed extracts to reduce copper ions to CuNPs and their own structure was transformed from keto to enol, as shown in Figure 3. Yu et al. [135] used nanocellulose to synthesize AgNPs, where positively charged silver ions were attracted to negatively charged carboxyl and hydroxyl groups on nanocellulose. At 80°C, the silver ions were reduced by the hydroxyl groups, which themselves were oxidized to aldehyde groups. Jigyasa and Rajput [136] used polyphenols (rutin/curcumin) to synthesize AgNPs and speculated that rutin/curcumin may have obtained AgNPs by reducing silver ions through carbonyl or phenolic hydroxyl groups. Wang et al. [15] used starch to synthesize AgNPs and found that the abundant hydroxyl and carboxyl groups on the linear chain of starch interacted with silver ions and, thus, the hydroxyl groups reduced the silver ions to AgNPs. Moreover, it was found that the prepared AgNPs were stable owing to the passivated surface of AgNPs and surrounded by negatively charged carboxyl groups.

Plant extracts possess not only reducing but also antioxidant properties and serve as a reducing agent to prepare MNPs while acting as a stabilizer to protect them from oxidation. Veisi et al. [137] found that flavonoids, tannins, and phenolic compounds attached to the surface of AgNPs to keep them stable through electronic interactions. The presence of active components with antioxidant properties in plant extracts that reduce copper ions and synchronously maintain the stability of copper nanoparticles was reported by Nasrollahzadeh et al. [138].

### 3. Chemical Mechanisms of Metal Nanoparticle Synthesis Using Plant Extracts

Various active ingredients including alkaloids, phenols, terpenoids, quinines, amides, flavonoids, proteins, and alcohols exist in plant extracts, among which reducing active ingredients such as flavonoids and phenols can reduce some metal cations to MNPs and, at the same time, act as stabilizers to prevent the aggregation of MNPs, thus playing a key role in the green synthesis of MNPs [15, 133].

### Table 5: Representative examples for the use of plant extracts for PdNP synthesis.

| Plant                     | Part       | Extractant      | Precursor       | Size (nm) | Reference |
|---------------------------|------------|-----------------|-----------------|-----------|-----------|
| *Artemisia annua*         | Leaf       | Water           | PdCl$_2$        | 20–30     | [122]     |
| *Camellia sinensis*       | Leaf       | Water           | PdCl$_2$        | 5–8       | [123]     |
| *Euphorbia thymifolia L.* | Leaf       | Water           | PdCl$_2$        | 20–30     | [124]     |
| *Euphorbia granulate*     | Leaf       | Water           | PdCl$_2$        | 25–35     | [125]     |
| *Thymbra spicata*         | Leaf       | Water           | Na$_3$PdCl$_4$  | 10–15     | [115]     |
| *Solanum trilobatum*      | Leaf       | Water           | PdCl$_2$        | 60–100    | [113]     |
| *Hippophae rhamnoides*    | Leaf       | Water           | PdCl$_2$        | 2.5–14    | [114]     |
| *Berberis vulgaris*       | Fruit      | Water           | PdCl$_2$        | −18       | [116]     |
| *Ulmus davidiana*         | Bark       | Water           | PdCl$_2$        | −5        | [118]     |
| *Cinnamon zeylanicum*     | Bark       | Water           | PdCl$_2$        | 15–20     | [119]     |
| *Sargassum bovinum*       | Whole plant| 70% ethanol     | PdCl$_2$        | 5–10      | [120]     |
| *Salvia hyrangea*         | Whole plant| 70% ethanol     | Pd(NO$_3$)$_2$  | <10       | [126]     |
4. Conclusions and Prospect

In summary, this review discussed the recent progress on the green synthesis of MNPs using plant extracts, focusing on the synthesis of several commonly used MNPs such as nanogold, silver, copper, platinum, and palladium. The booming development of green chemistry and nanotechnology has promoted the exploitation of green synthetic methods for synthesizing nanomaterials via plants and microorganisms. The green synthesis of MNPs has recently received much attention in sustainable chemistry. The plant-extract-mediated method for the preparation of MNPs has the advantages of low cost, nontoxicity, easy scale-up, and environmental friendliness, which are highly conducive to sustainable nanoscience development. Particularly, the as-synthesized MNPs have a wide range of applications in the fields of catalysis, medicine, water treatment, antibacterial, anticancer, bioengineering, sensors, and medical imaging. Importantly, the synthesis reaction does not involve any toxic chemical reagents and the resulting MNPs are not contaminated with toxic substances, thus being of special value in biomedical applications where nontoxicity is strictly required. In addition, plant extracts contain some unique compounds that help to improve the synthesis efficiency and increase the stability of MNPs.

Despite the significant progress made in this field, there are still a number of issues that need to be addressed. For instance, despite the great potential of MNPs prepared via plant-extract-mediated methods, the specific synthetic process parameters still need to be optimized. Meanwhile, the relevant synthetic mechanisms need to be further elucidated, and the lack of understanding of the chemical components involved in the synthesis and stabilization of MNPs remains a great challenge for researchers. Moreover, the manner in which active molecules in the extracts attach to the surface of MNPs and the determination of the real molecular active groups in the molecules need to be further investigated. Furthermore, with the exponential growth of MNP applications, the accumulation of these nanoparticles in the environment is a concern, and there is a need to focus on the in vivo toxicity of these MNPs and the long-term effects on humans, animals, and the environment. Further investigation of these issues is expected to facilitate us to better utilize this green synthesis method for the development and progress of human society.

Data Availability

No data were used to support the findings of this study.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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