

Plant-based green synthesis of metallic nanoparticles: scientific curiosity or a realistic alternative to chemical synthesis?

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Abstract Currently, thousands of tons of metallic nanoparticles (MNPs) are produced and utilized in nano-enabled devices, personal care, medicinal, food and agricultural products. It is generally accepted that the reaction compounds and the techniques used in industrial production of MNPs are not environmentally friendly. The green synthesis has been proposed as an alternative to reduce the use of hazardous compounds and harsh reaction conditions in the production of MNPs. In this endeavor, investigators have used organic compounds, microbes, plants and plant-derived materials as reducing agents. Research papers are published every year, and each one of them stresses the benefits of the green approach and the advantages over the

traditional syntheses. However, after almost two decades since the explosion of the reports about the new approach, the commercial production of green-synthesized nanoparticles does not seem to find a way to scale up commercial production. This review includes descriptions of the traditional and green synthesis and applications of MNPs and highlights the factors limiting the use of plant-based synthesis as a real alternative to the traditional synthesis of MNPs.

Keywords Nanoparticles · Chemical synthesis · Biogenic synthesis · Plants · Applications

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Introduction

In the first three decades of the twenty-first century, society has been exposed to a large amount of nano-enabled products. The Nanotechnology Consumer Products Inventory currently lists 622 companies in 32 countries, which together produce 1814 nano-enabled consumer products [210]. Despite the progress in the use of tiny materials cataloged as “nano,” there is still a debate in some aspects of the terminology associated with this new technological revolution. There are several expressions associated with nanotechnology, but two of the most frequently used terms are “nanomaterial” and “nanoparticle.” Although sometimes both terms are used as synonymous, the American Society for Testing and Materials (ASTM) [8] has stated that a “nanoparticle (NP) is a sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 μm (1 nm) and smaller than about 0.1 μm (100 nm) and which may or may not exhibit a size-related intensive property.” On the other hand, the European Union has defined nanomaterial as: “Nanomaterial means a

natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions are in the size range 1–100 nm” [35].

It is well known that metallic nanoparticles (MNPs) possess unique properties, different from the micro-sized materials, which allow multiple industrial, agricultural, and household applications. As a result, there has been an accelerated development and massive production of new MNPs to supply the ever-increasing demand for nanotechnology-based goods and devices. The estimated global production of MNPs for 2010 was of 260,000–309,000 metric tons. At the top of the list are: silica, titania, alumina, iron, and zinc oxides [85].

Several publications describe the traditional methods used to produce MNPs for industrial applications. Detailed examples can be found in a publication by The Royal Society [197] and in the review by Charitidis et al. [29]. To briefly summarize, the variety of techniques used for the mass production of MNPs have been grouped into two categories: “top-down” and “bottom-up” techniques. In top-down techniques, the process starts with a block of material that is crushed to the desired shape. Nano-enabled devices like computer chips and high-quality optical mirrors are produced using top-down techniques. In the bottom-up technique, small units (atoms or molecules) are assembled to make a larger structure. This technique is used to produce cosmetics, fuel additives, and molecular devices [197]. Further details will be presented in this review.

Important characteristics of MNPs for industrial and medical applications include type of material, size, shape, composition, and surface charge, among others. The purity and uniformity of the nanomaterial is particularly important in many applications, like in cosmetics, where impurities may have serious effects in users [57]. Similarly, the high-quality performance of electronics devices relies on the high purity of components [55]. In biological sciences, MNPs have gained a preponderant place in multiple applications. Essentially, each application requires particles with unique characteristics. For example, double-stranded DNA separation has shown to be size dependent [77]. Adams et al. [1] reported a size-dependent toxicity of Pd NPs to *Escherichia coli* and *Staphylococcus aureus*. In a literature review, Fröhlich [58] analyzed the effects of particle surface charge on its interaction with the cell and subsequent cellular response. The literature on characteristics of drug nanocarriers for cancer treatment was analyzed by Pérez-Herrero and Fernández-Medarde [149]. These authors highlight the importance of the size of carrier particles for their movement within the body, avoiding the action of the defensive body cells and the

reticuloendothelial system. The current review includes descriptions of traditional techniques as well as green approaches by using plants/plant-derived materials for the synthesis of MNPs using plants/plant-derived materials. We analyze aspects concerning the most produced and used NPs including Au, Ag, Cu, CeO₂, TiO₂, ZnO, and Fe NPs. We discuss some of the reasons why the green synthesis approaches have not been used for the mass production of widely applied MNPs.

Chemical synthesis and applications of MNPs

Engineered nanomaterials are designed with a specific purpose or for a specific process. The applications of MNPs are various and include, but are not limited, to the following: catalysis, biomedical, biosensing, environmental remediation/reclamation, pest control, and water treatment. In general, the synthesis of metallic MNPs is achieved through the reduction of the parent ion in different ways. The synthesis of MNPs varies depending on the desired product, and there are numerous methods for their production. Figure 1 shows a summary of methods used for the synthesis of MNPs. The following sections contain a brief description of the methods.

Chemical synthesis

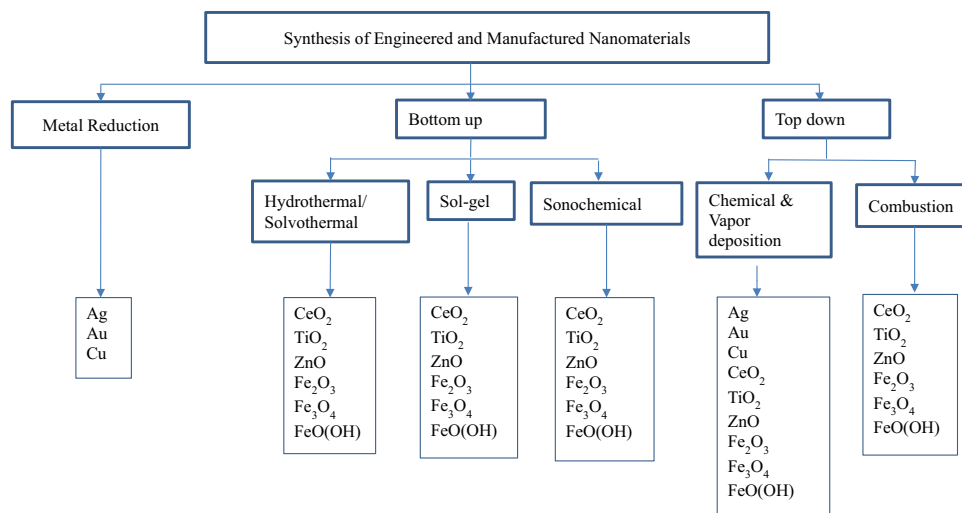
Metal reduction

In a solution containing a metal ion, a reducing agent is added to synthesize the NPs. This method is used for the preparation of copper, gold, and silver NPs. The reduction of the metal ions in solution is achieved with NaBH₄, sodium citrate, ascorbic acid, and hydrazine, which is accompanied by a capping/stabilizing agent [25, 41, 207]. The media for the reaction can also act as the reducing and stabilizing agent, which is referred to as the polyol method, where a polyol is the reducing and capping agent [152]. The size and shape of the nanomaterials show control based on a combination of the metal ion concentration, the reducing agent, and the capping/stabilizing agent.

Bottom-up methods

Hydrothermal/solvothermal synthesis Hydrothermal and solvothermal syntheses are similar techniques; the only difference in the two methods is the solvent system used. In hydrothermal synthesis, water is the medium for the synthesis, whereas any solvent can be used in solvothermal method [32, 86, 91]. The hydrothermal and solvothermal synthesis techniques have generated MNPs with very specific shapes and sizes that enhance the properties of

Fig. 1 Traditional methods for the synthesis of engineered and manufactured metal-based nanomaterials



nanomaterials. In addition, hydrothermal and solvothermal processes can be performed under microwave irradiation, which has been shown to affect the properties of the synthesized MNPs.

Sol-gel method The sol-gel method has been traditionally used for the synthesis of nanomaterials/colloids from solution. In general, the method consists of generating a gel in solution through the hydrolysis of a metal ion; the gel coagulates forming particles [32, 91, 112, 136]. The synthesis can be achieved with different precursors such as the metal ions (from metallic salts) and organo-metal complexes [32]. The MNPs obtained through this process can be tailored to any desired application; in addition, there is good control on the size and morphology of the synthesized NPs.

Sonochemical method In sonochemical synthesis, ultrasound is used as an energy source [32]. The ultrasound waves form cavitation in the solvent that produces intense energy, causing local heating and high pressures [32]. The local energy results in fast reactions and rapid synthesis of MNPs with controlled sizes and shapes [32, 91, 136]. It is worth mentioning the tutorial developed by Xu et al. [223] where phenomena occurring in sonochemistry were highlighted.

Top-down methods

Chemical and vapor deposition In chemical and vapor deposition techniques, the materials are first placed into the gas phase and into the solid phase [32] and are performed under vacuum. If a chemical reaction occurs during the deposition, then the process is called chemical vapor deposition (CVD); if no reaction is observed, then the process is called physical vapor deposition (PVD) [32].

The material is heated to its vaporization point and then condensed onto a target or substrate. In general, CVD and PVD techniques are used to make thin films and nanofilms of materials for specific applications such as optical coatings and photovoltaic applications.

Combustion Combustion synthesis consists of two sub techniques: solid-state combustion and solution combustion syntheses [146, 147]. In solid-state combustion synthesis, both the starting materials and final products are in the solid phase [146, 147]. The reactants are pressed into a pellet and combusted by an external source. The ignition of the pellet starts an exothermic reaction that is self-propagating and synthesizes the NPs [146, 147]. The solution combustion synthesis consists of rapidly heating a solution containing metal nitrate and a fuel source such as urea/hydrazides [146, 147]. Combustion synthesis techniques have been successfully employed to synthesize metal oxide NPs and composite nanomaterials such as Au on CeO₂ and Ag on CeO₂ [146, 147]. In addition, Eu³⁺-activated red phosphors LnMAlO₄, where “Ln = La or Y and M = Ca or Sr, having K₂Ni₄” structure and lamp phosphorus have been prepared using aqueous combustion synthesis and solid-state methods [50, 51].

Applications of engineered and manufactured nanomaterials

For the most part, applications of MNPs are very similar to the application of parent metal ions or the bulk materials. Gold and silver MNPs have numerous applications and are perhaps among the most studied NPs. In the last decade, other MNPs such as CeO₂, Cu/CuO, TiO₂, ZnO, and Fe/Fe oxide have gained attention due to their application in goods, consumer products, and environmental remediation. Table 1 shows a detailed list of applications of some of the

Table 1 Main applications of engineered and manufactured nanomaterials

ENM	Uses	References
Gold ENPs	Cellular distribution studies, RNA technology, targeting cellular/intracellular, bioimaging, gene delivery and detection, drug delivery, immune assays, and electrochemical sensing of toxic chemicals	Saha et al. [166], Tiwari et al. [203]
	Catalytic in chemical reactions such as the oxidation of CO to CO ₂ , the reduction of p-nitrophenol to aminophenol using NaBH ₄ , alcohol oxidation, carbon-carbon coupling reactions (Suzuki type cross coupling), and benzannulations, among other reactions	Corma and Garcia [37], Lin et al. [108], Mikami et al. [123], Li and Jin [106]
Silver ENPs	Antimicrobial/antibacterial activities	Lin et al. [107]
	Diagnosis and therapeutic	
	Catalysis of organic reactions: Diels-Alder reactions and oxidation of phenylsilanes to silanols	Cong et al. [36], Mitsudome et al. [125]
	Catalytic in Michael addition, Friedel-Crafts reactions, reduction reactions, cross-coupling reaction, oxidation reactions, alkynylation and alkylation reactions	Dong et al. [48]
	Surface-enhanced Raman spectroscopy (SERS) combined with membrane electrophoresis for cancer determination	Lin et al. [107]
Copper-based ENPs	Optical, thermal, electrical properties, catalytic applications, and antibacterial properties	Tamilvanan et al. [195], Soomro et al. [183]
	Catalysis for the formation of carbon-carbon bonds from C(aryl)-C(aryl/alkynyl) C(aryl)-N, C(aryl)-O, C(aryl)-S and C(aryl)-Se	Ranu et al. [161]
	Catalysis in cyclization of Schiff bases	Kidwai et al. [88]
	Oxidation of CO to CO ₂	Tu et al. [206]
	Hydrogenolysis of glycerol	Huang et al. [78]
	Catalysis in "click" reaction between terminal alkynes and azides	Sarkar et al. [173]
	Reduction of aromatic nitrocompounds in the presence of NaBH ₄	Duan et al. [49]
Zinc oxide ENPs	Used in UV lasers, field effect transistors, photodetectors, gas sensors, solar cells, piezoelectric generators, and photocatalysts	Kolodziejczak-Radzimska and Jesionowski [91, 148], Keller et al. [85]
	Antimicrobial activity in food packaging	
	Added to textiles as UV-absorbing agents as well as antimicrobial agents	
	Used in personal care products	
	Photochemical destruction of methyl orange, degradation of rhodamines, stearic acids, and many other organic chemicals	Kolodziejczak-Radzimska and Jesionowski [91]
	Used in methanol synthesis	Strunk et al. [186]
	Used as antibacterial agent against <i>Bacillus subtilis</i> , <i>Staphylococcus aureus</i> , <i>Pseudomonas aeruginosa</i> , <i>Campylobacter jejuni</i> , and <i>Escherichia coli</i>	Perez Espitia et al. [148]
Successful in reducing cell viability of colon cancer cells (LoVo). Drug transporter for the targeted treatment of different cancers such as leukemia and hepatocarcinoma cells	Perez Espitia et al. [148]	
Titanium dioxide ENPs	Photovoltaic and photochemical applications	Chen and Mao [32], Macwan et al. [112]
	Photocatalytic degradation of organic acids, inorganic ions such as nitrate, nitrite, ammonia, and sulfate	Mital and Manoj [124]
	Destruction of dyes in solution by absorption and oxidation	Macwan et al. [112], Bradley [23], Keller et al. [85]
	Additive to medical and food products	
	Personal care products	
Cerium dioxide ENPs	Catalysis, fuel cells, microelectronics, luminescence, ceramic applications, sunscreens for UV absorbers, oxygen storage, H ₂ S removal, and hybrid solar cells	Dahle and Arai [40]
	Abrasives for grinding and polishing applications	Dahle and Arai [40]
	Effective photocatalysis in degradation of organic compounds such as amido black and acridine orange, toluene, and catalysis for the ozonation of organic compounds	Khan et al. [86], Dahle and Arai [40]
	Removal of congo-red from solution	Li et al. [105]
	Sensing of chemicals such as ethanol	Khan et al. [86]

Table 1 continued

ENM	Uses	References
	Effective as an electrocatalytic oxidizing agent for the oxidation of ethanol Antibacterial effects	Zhang et al. [227], Dahle and Arai [40],
Iron-based ENPs	Reduction of subsurface contaminants such as PCBs and chlorinated solvents Removal of dyes, removal of heavy metals	O'Carroll et al. [141] Trujillo-reyes et al. [205]

most produced MNPs. As seen in this table, Au, Ag, Cu, and ZnO NPs have biomedical applications [107, 148, 164, 166, 203]. Silver and Au NPs have also been used as sensors and catalysts [36, 37, 48, 88, 106, 108, 123, 125, 161, 166]. Zinc Oxide NPs are used in food packaging [91] and personal care products [85]. Titanium dioxide NPs are used in personal care products [85]; catalysis [124], and solar cells [112, 124]. Iron-based NPs are used in many applications including environmental remediation [205]. More details are shown in Table 1.

Green synthesis and applications of metal-based nanomaterials

According to Cheviron et al. [34], there are three general aspects that need to be considered in green synthesis: solvent medium, non-toxic reducing agents, and environmentally safe nanoparticle stabilizers. Cruz et al. [39] stated that green synthesis by plant extracts can be comparable to some conventional methods; however, they did not give details about nanoparticle yields, stability, and ions reduction mechanisms. The mass production of atomically precise MNPs requires highly reactive substances and/or energy consuming procedures, which are not considered environmentally friendly [144, 216]. To overcome this problem, researchers began to use more environmentally benign methods that are collectively called green synthesis. A simple search using ScienceDirect.com and the keywords “green synthesis of metal nanoparticles” showed 21,488 results, while SciFinder Scholar showed 1326 results (January 11, 2016). Figure 2 shows the annual publications about the green synthesis of MNPs since 2000–2016. As seen in this figure, there has been a constant increase in publications since 2006. The biological synthesis has been accomplished using viruses, bacteria, fungi, and plants [19, 89, 128, 129]. For a complete review on the synthesis of MNPs by microbes, the reader is directed to Narayanan and Sakthivel [137], Hulkoti and Taranath [79], and Virkutyte and Varma [216].

Reports of the reduction of precious metals by inactivated plant materials date back almost 100 years. Molisch [126] and Iwase [81] studied the reduction of Ag by plant

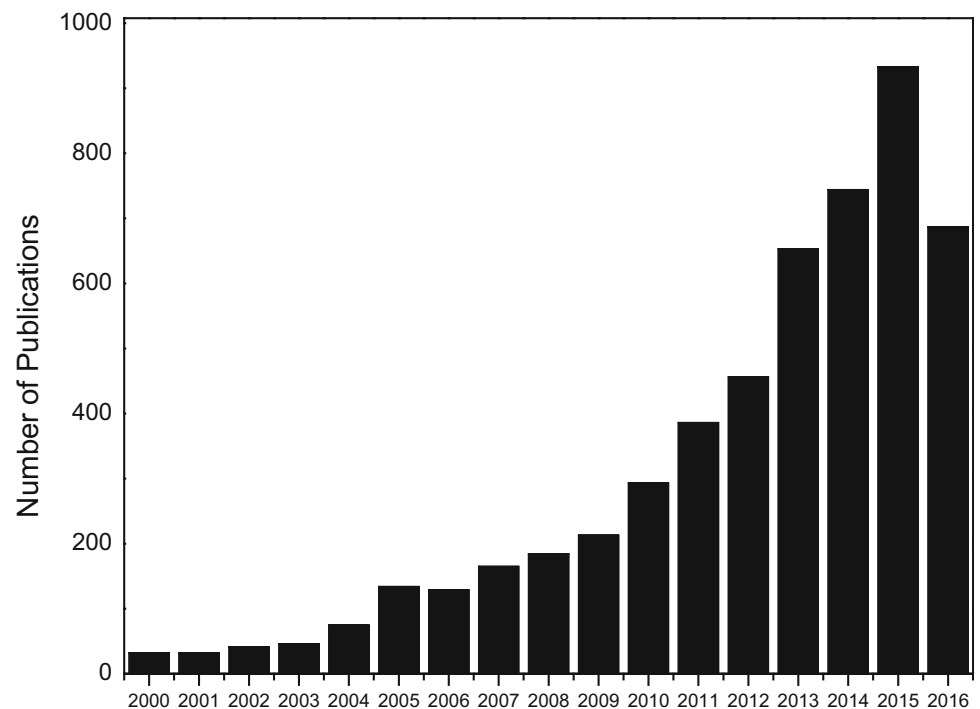
chlorophyll and the reduction of Au by extract of fresh leaves, respectively. About 66 years ago, Nagai [133] reported the reduction of $\text{Ag}(\text{NO}_3)_3$ by plant cells. A decade ago, Armendariz et al. [10, 11] reported the bioreduction of KAuCl_4 by powdered wheat (*Triticum aestivum*) and oat (*Avena sativa*) biomasses and the subsequent formation of Au NPs. These researchers reported that the solution pH is a key variable to control the size and to reduce the polydispersity of the biogenic Au NPs. More recently, Montes et al. [127] reported that the biomass solvent extract determined the type of biogenic Au NPs. Water extracts of alfalfa (*Medicago sativa*) biomass led to the formation of triangular nanoplates, while isopropyl alcohol extract rendered decahedra and icosahedra NPs [127]. Besides biomass, living plants can also reduce KAuCl_4 and form metal NPs. Gardea-Torresdey et al. [61, 62] reported, for the first time, the formation of metal NPs by living plants exposed to AuCl_4^- solution. Alfalfa plants were grown in an agar medium spiked with AuCl_4^- and formed crystalline pure Au NPs, confirming that the NPs grew within the plant [61]. A year later, these researchers reported the formation of silver nanowires inside stems of alfalfa plants exposed to silver chloride [62]. Since then, thousands of papers have reported the formation of MNPs by plant or plant-derived materials. Extensive details can be found in Hong et al. [76] and Virkutyte and Varma [216].

Green synthesis of gold nanoparticles

Gold NPs have been synthesized using different green approaches that include biologically based chemicals, plants/plant-derived materials, algae, bacteria, and microbes. The green-synthesized Au NPs have similar physical characteristics as chemically synthesized nanomaterials (Table 2). Numerous chemicals have been extracted from living systems, which have shown much promise in the reduction of Au ions to Au NPs. These biologically relevant materials include simple organic chemicals such as citric acid and ascorbic acid [207].

Perhaps one of the best known reduction techniques for the synthesis of Au NPs is the Turkevich method, where Au(III) ions are reacted with citric acid/sodium citrate at elevated temperatures, causing the reduction of ions to Au

Fig. 2 Annual publications showcasing the green synthesis of metal nanoparticles.



NPs [207, 208]. The reduction technique using citric acid/sodium citrate has shown that the synthesized NPs' size and shape is depend on the concentration of the citrate. The average particle size of the NPs also depends on the time and the chemicals used [207, 208]. Furthermore, in the synthesis of the Au NPs through the Turkevich method, the oxidized citric acid becomes the stabilizing agent for the produced NPs [207]. Similarly, ascorbic acid and tannic acid have been shown to reduce Au(III) ions to produce Au NPs [2, 175]. Additionally, different polysaccharides and phytochemicals have been used for the synthesis of Au NPs [143]. Studies have shown that gum Arabic, a polysaccharide extracted from *Acacia* trees, has been successfully used as a reducing agent for the synthesis of Au NPs. Wu and Chen [221] showed that at a temperature of 50 °C, the reduction of the Au ions occurs within the first 15 min of reaction time.

Plant extracts have shown to be effective in the reduction of Au ions to Au NPs [138]. Table 2 shows a summary of the synthesis of Au NPs using plants/plant extracts. As seen in this table, tetrachloroaurate has been used as precursor in all the cases. Although the forms and applications are similar to those observed in chemically synthesized NPs, the size of the green-synthesized NPs, with the exception of those synthesized using honey and banana peel, shows higher variability. This might be one of the reasons that have prevented the massive production of Au NPs using plants/plants extracts.

Green synthesis of silver nanoparticles

Silver nanoparticles (Ag NPs) have been extensively synthesized and studied because of their unique physical, chemical, and biological properties [17, 212]. Global synthesis of Ag NPs has been estimated to be 55 tons per year [22]. The synthesis process of these NPs involves reduction of the silver ions, nucleation, and growth of the particles [38]. A summary of the methods is shown in Fig. 1. One of the main challenges using traditional methods to synthesize Ag NPs is the high cost of equipment. Moreover, sometimes the addition of surfactants or stabilizers is needed during the synthesis to avoid nanoparticle aggregation [140]. Hart et al. [72] stated that size and monodispersity of the particles define their chemical, optical, and physical properties. Smaller particles are desirable because they have lesser Van der Waals interactions, which avoid aggregation and precipitation.

Lately, researchers have been looking for greener technologies to manufacture NPs [92]. Green technologies to produce Ag NPs are described in Table 3. As indicated in Table 3, Ag(NO)₃ has been used as precursor and extracts from different plant parts have been used as reducers. Researchers reported that main compounds involved in Ag(NO)₃ reduction can be proteins, carbohydrates, flavonoids, phenols, vitamins, and capsaicinoids [17, 110]. David et al. [43] synthesized Ag NPs from the European black elderberry fruit extract mixed with 1 % of Ag(NO)₃. These authors suggest that fruit polyphenols are the

Table 2 Summary of the biogenic synthesis of gold nanoparticles using plant extracts and principal applications

Gold material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
HAuCl ₄	<i>Cymbopogon citratus</i>	0.1–1.9-mL in 5 mL of 10 ⁻³ M HAuCl ₄	50–1800	Triangular nanoplatelets	IR radiation blocker	Shankar et al. [176]
HAuCl ₄	<i>Menta piperita</i>	1.5 mL of plant extract in 30 mL of HAuCl ₄ solution (1 mM/mL) and incubated at 28 °C for 24 h	Up to 150	Spherical	Antibacterial	Ali et al. [6]
HAuCl ₄	<i>Cinnamomum zeylanicum</i>	30 mL 2 × 10 ⁻⁴ M aqueous HAuCl ₄ solution, 4 mL in <i>C. zeylanicum</i> leaf broth	25	Spherical	Cell labeling and bio sensors	Smitha et al. [181]
HAuCl ₄	<i>Musa paradisiaca</i> Peel	10 mg of BPE powder in 2 mL of chloroauric acid solution (1 mM)	~300	N/A	Antibacterial/antifungal	Bankar et al. [16]
HAuCl ₄	<i>Maduca longifolia</i>	1 mL of 10 mM HAuCl ₄ mixed with 9 mL plant extract; pH 2–10	7–3000	Platelets	IR coatings for glass	Fayaz et al. [54]
HAuCl ₄	Honey	10 mL of ~300 mg/mL honey added to 30 mL of HAuCl ₄	15	Spherical and platelets	Application in the therapeutics	Philip [151]
HAuCl ₄	<i>Scutellaria barbata</i>	0.2–2.0 mL HAuCl ₄ solution (0.01 M) mixed with solution at ~33 mg/mL	20–35	Spherical and triangular	Electro catalytic reduction of p-nitrophenol	Wang et al. [219]
KAuCl ₄	<i>Sesbania drummondii</i>	3 week old seedlings exposed to 0–200 mg/L of Au solution	6–20	Spherical	Reduction of 4-nitrophenol	Sharma et al. [178]
HAuCl ₄	<i>Breynia rhamnoides</i>	1 mM aqueous HAuCl ₄ mixed with 0.5–3.5 mL of biomass solution at 150 mg/mL	5–60	Spherical	Reduction of 4-nitrophenol	Gangula et al. [60]
HAuCl ₄	<i>Sapindus Mukorossi</i> fruit pericarp	1 mL 10 mM HAuCl ₄ added to 10 mL of 30 % w/v shell extract	9–19	Spherical, triangular, and decahedral	Reduction of p-nitroaniline	Reddy et al. [162]
HAuCl ₄	<i>Acalypha indica</i>	0.5–4 mL of extract 930 g/100 mL) mixed with 6 mL solutions of 10 ⁻³ M aqueous HAuCl ₄	20–30	Spherical	Human breast cancer cells	Krishnaraj et al. [93]

reducers, while polyphenols act as capping agents. However, the Ag reduction mechanism was not elucidated in this study. David et al. [43] also tested the anti-inflammatory effects of the green-synthesized Ag NPs but did not compare the effects with those of NPs synthesized by other methods. Cruz et al. [39] reported that the glycoside verbascoside is the major reducing component in the extract of *Lippia citrodora* and they suggested that this compound acted as reducer and capping agent, promoting the stability of Ag NPs. Kouvaris et al. [92] also synthesized Ag NPs from *Arbutus unedo* leaf extract and stated that organic compounds are responsible for reduction and stabilization of NPs. Several researchers suggest that green-synthesized Ag NPs can be used for drug delivery due to the compatibility of some pharmaceutical drugs with natural capping agents; however, the feasibility of their use in biomedical areas has not been tested. Most of the studies reported in

the literature confirmed the synthesis of Ag NPs by plant extracts as a single step; nonetheless, organic compounds responsible for the Ag ion reduction have not been clearly identified.

Barbinta-Patrascu et al. [17] suggested that alkaloids and flavonoids from *Chelidonium majus* L. are responsible for the reduction Ag ions and capping agents for the NPs. These authors compared the antimicrobial activity of green-synthesized Ag NPs against *E. coli* ATCC8738 strain with that synthesized by classical methods. They observed that alkaloids or phenolic compounds present in plant extracts, which have antibacterial activity, increased the inhibition zone diameter of the green-synthesized NPs. Coseri et al. [38] used the polysaccharide pullulan and oxidized pullulan to synthesize and stabilize Ag NPs. They reported that the size of the NPs varied depending upon the concentration of Ag(NO)₃ and pullulan used (from 30 to

Table 3 Summary of the biogenic synthesis of silver nanoparticles using plant extracts and principal applications

Silver material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Silver nitrate	<i>Chelidonium majus</i> L. plant extract	1:1 ratio plant extract/1 mM silver nitrate	90 nm	Spherical	Antioxidant and antimicrobial activities	Barbinta-Patrascu et al. [17]
Silver nitrate	<i>Prunus serotina</i> Ehrh. var. Capuli	1 mL extract in 10 mL 1 mM silver nitrate	20–100 nm	Spherical	Antioxidant activity	Kumar et al. [96, 98, 99]
Silver nitrate	Potato (<i>Solanum tuberosum</i>) starch	85 mg of soluble starch and 15 mL of a glucose solution (0.06 or 0.12 M) in 10 mL 60 mM silver nitrate	20–50 nm	Spherical	Antimicrobial activity, biomedicine and sensors	Cheviron et al. [34]
Silver nitrate	<i>Sambucus nigra</i> fruit extract	16.6 mL fruit extract in 6.6 mL 1 % silver nitrate	20–80 nm	Spherical	Anti-inflammatory activity	David et al. [43]
Silver nitrate	Casein hydrolytic peptides (CHP)	CHP, NaOH, and AgNO ₃ concentrations ranging from 0.075 to 0.3 %, 2.5 to 80 mM, and 0.75 to 13 mM, respectively	10–15 nm	Spherical and hexagonal	Antimicrobial activity	Ghodake et al. [66]
Silver nitrate	Peanut (<i>Arachis hypogaea</i>) shell extract	5 mL extract in 45 mL of 10 mM silver nitrate	10–50 nm	Spherical	Antifungal activity	Velmurugan et al. [212]
Silver nitrate	Ascorbic acid, glucose, glycerol, NADH, and uric acid	Different concentrations in 5 mM silver nitrate	7–20 nm	Spherical	–	Passos et al. [145]
Silver nitrate	<i>Anacardium othonianum</i> Rizz nutshell extract	50 µL extract in 4950 µL of 1 mM silver nitrate	4–13 nm	Spherical	Optoelectrical and antifungal properties	Bonatto and Silva [21]
Silver nitrate	Pullulan and 2,2,6,6-tetramethylpiperidin-1-yl	Different concentrations of pullulan and oxidized pullulan in silver nitrate	50–55 nm for unmodified pullulan and 8–25 nm for oxidized pullulan	Spherical	Antimicrobial activity	Coseri et al. [38]
Silver nitrate	<i>Lippia citriodora</i> leaf extract	A range between 5 and 10 mL of leaf extract in 5 mL of 1 mM silver nitrate	16 ± 5 nm	Spherical	–	Cruz et al. [39]
Silver nitrate	α-D-Glucose, sucralose, triethylamine	2 g of α-D-glucose and 2 g of sucralose in 100 mL of ultrapure water and 2.5 mL of 0.1 M silver nitrate	4–10 nm	Spherical	Environmental applications (sensing)	Filippo et al. [56]
Silver nitrate	Natural rubber latex (NRL) extracted from <i>Hevea brasiliensis</i>	Different volumes of the latex solution and the concentration of silver nitrate	2–100 nm depending on silver nitrate/NRL ratio	Spherical	–	Guidelli et al. [71]
Silver nitrate	<i>Arbutus unedo</i> leaf extract	50 mL of leaf extracts in 50 mL 1 mM silver nitrate	3–20 nm	Spherical	Biotechnology applications	Kouvaris et al. [92]
Silver nitrate	<i>Illicium verum</i> (star anise) seed extract	10 mL of extract and 10 mL of 0.5, 0.05 or 0.01 M silver nitrate	19–32 nm	Spherical	Molecular sensors and nanophotonic devices	Luna et al. [110]
Silver nitrate	<i>Cassia tora</i> leaf extract	50 mL of diluted extract into 100 mL of 0.1 M silver nitrate	400–450 nm	Spherical	Antibacterial activity	Saravanakumar et al. [172]
Silver nitrate	<i>Picrasma quassioides</i> bark extract	5 mL of extract in 95 mL of 1 mM silver nitrate	17.5–66.5 nm	Spherical	Catalytic activity	Sreekanth et al. [184]
Silver nitrate	Rosa 'Andeli' petals extract	1.6 mL of petals extract and 20 mL 1 mM silver nitrate	0.5–1.4 nm	Spherical	Photocatalytic activity	Suarez-Cerda et al. [187]

Table 3 continued

Silver material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Silver nitrate	Flavonoids: quercetin, dihydroquercetin, naringenin, morin, chrysin, rutin and naringin	Different amounts of flavonoids, 0.5 mL of ethyl alcohol, 1 mL of 1×10^{-2} mol L ⁻¹ silver nitrate, 0.7 mL of 0.04 % of PVP and 1 mL of 1 mM sodium hydroxide	8–11 nm	Spherical	Analysis of biologically active food additives	Terenteva et al. [196]
Silver nitrate	Corn husk extracts	Different corn husk extract volumes (1, 3, 5, 8 and 12 mL) with 25 mL of 2 mM silver nitrate	20 nm	Spherical	Antibacterial activity	Villanueva-Ibáñez et al. [214]

50 nm for natural pullulan and 8–25 nm for oxidized pullulan). The authors explained the inconsistencies in the results for the NPs' size due to the sample preparation. Kumar et al. [96, 98, 99] synthesized Ag NPs using Capuli cherry extract exposed to white solar and blue light-emitting diode (LED) light. They showed that silver ions were reduced faster (8 h) when blue LED light was applied, compared to those NPs synthesized in white solar light (96 h). The authors reported different methods for Ag NPs characterization; however, they did not give any information related to the role of some components from the extract on the reduction of Ag. Ag NPs also have been synthesized by other plant parts such as shell, seed, or flower petal extracts [21, 110, 187, 212]. As mentioned before, these studies were mainly focused at the characterization of obtained Ag NPs; however, reduction mechanism, yield of NPs, and feasibility to use them in similar way to chemically synthesized Ag NPs have not been demonstrated.

Green synthesis of Cu-based nanoparticles

Copper and CuO NPs are attracting attention due to their wide applications. The variety of applications of Cu and CuO NPs are described in Table 1. As catalytic or antibacterial materials, Cu and CuO NPs have the advantages of lower cost and increased abundance when compared to Ag, Au, and Pt [24]. However, the use of toxic chemicals during synthesis of Cu and CuO NPs limits their application in the clinical field [27]. In addition, their higher dissolution rates and toxicological properties limit the use of Cu-based NPs. Green synthesis of Cu NPs can reduce or eliminate the use and generation of hazardous substances; therefore, the method has received some attention. Xiong et al. [222] used L-ascorbic acid as a reducing agent and successfully synthesized highly stable Cu NPs. They reported there are three key factors in the reduction of Cu ions to Cu

NPs: (1) the solvent medium, (2) the reducing agent, and (3) the capping agent [222]. Plant extracts contain various primary and secondary low molecular weight metabolites, such as amino acid, reducing sugars, and phenolics, which are reported to act as reducing or capping agents during Cu NPs' synthesis. In recent years, several studies using plant extracts as reducing and capping agents to synthesize Cu and CuO NPs have been published.

Table 4 summarizes studies about the green synthesis of Cu-based NPs. As seen in the table, Cu and CuO NPs have been manufactured using various Cu compounds and extracts from different plant parts. The table also shows that plant extract-synthesized Cu NPs are mainly used as antibacterial, and some were tested in photocatalyst, antioxidant, and conductive nanobiocomposites. It is noteworthy that even though there are wide applications of Cu and Cu NPs in various fields, most of the green-synthesized Cu and CuO NPs are primarily used in antibacterial activity. As seen in Table 4, there is high variability in the precursor concentration (1–50 mM). In addition, the ratio of the amount of precursor to the amount of plant extract used in the synthesis varied from 1:1 to 1:10. Although the majority of the reports have shown that most of the particles formed are spherical and the reported sizes vary from 3 to 250 nm. This, coupled with a lack of data on the performance of the techniques, may be limiting the use of green techniques for the production of high volume of Cu/CuO NPs.

Green synthesis of zinc oxide nanoparticles (ZnO)

Zinc oxide NPs (ZnO NPs) have a wide band gap and large binding energy, which made them widely used in photovoltaic and photocatalytic applications. It is one of the metal oxide NPs that are produced in large quantities with an annual global production estimate of 31,000–34,000 metric tons [102]. The methods used in manufacturing ZnO

Table 4 Summary of the biogenic synthesis of Cu-based nanoparticles using plant extracts and principal applications

Copper material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Copper sulfate pentahydrate	<i>Magnolia kobus</i> leaf extract	170 mL of 1 mM CuSO ₄ ·5H ₂ O in 30 mL extract	50–250 nm	Spherical	Antibacterial activity	Lee et al. [103]
Copper sulfate	<i>Vitis vinifera</i> extract	40 mL of 1 mM CuSO ₄ in 10 mL extract	–	–	Antibacterial activity	Mahavinod Angrasan and Subbaiya [115]
Copper sulfate pentahydrate	<i>Lawsonia inermis</i>	100 mL of 10 mM CuSO ₄ ·5H ₂ O in 30 mL extract	20–60 nm	Spherical	Conductive nanobiocomposites	Cheirmadurai et al. [30]
Copper sulfate pentahydrate	<i>Citrus grandis</i> peel extract	0.5 g of CuSO ₄ ·5H ₂ O in 50 mL 10 % of peel extracts	22–27 nm	Spherical	Photocatalytic applications	Sinha and Ahmaruzzaman [180]
Copper sulfate pentahydrate	<i>Syzygium aromaticum</i> extract	5 mL of 1 mM CuSO ₄ in 5 mL extract	40–45 nm	Spherical	–	Subhankari and Nayak [189]
Copper sulfate	<i>Capparis zeylanica</i> leaf extract	100 mL of 1 mM CuSO ₄ in 25 mL extract	60–100 nm	Spherical	Antibacterial activity	Saranyaadevi et al. [171]
Copper nitrate	<i>Hibiscus rosasinensis</i> leaf extract	5 mL of 50 mM CuNO ₃ in 5 mL extract	–	Spherical	Antioxidant activity	Subbaiya and Selvam [188]
Copper sulfate	<i>Eucalyptus</i> sp. leaf extract	100 mL of 1 mM CuSO ₄ in 10 mL extract	28–48 nm	Particle-like	–	Kulkarni et al. [94]
Copper sulfate pentahydrate	<i>Cymbopogon citratus</i> grass extract	70 % of 1 mM CuSO ₄ in 29 % lemongrass tea, and 1 % DI water	2.9 ± 0.64 nm	Spherical	–	Brumbaugh et al. [24]
Copper chloride	Lemon (<i>Citrus</i> sp.) fruit extract	10 mL of 1 mM CuCl ₂ in 10 mL lemon extract	60–100 nm	Spherical	Antibacterial activity	Jayandran et al. [83]
Copper sulfate	<i>Phyllanthus Embilica</i> (Gooseberry) extract	75 mL of 20 mM CuSO ₄ in 25 mL lemon extract	15–30 nm	Flake	Antibacterial activity	Caroling et al. [27]
Copper sulfate	<i>Gymnema sylvestre</i> leaf extract	100 mL of 1 mM CuSO ₄ in 25 mL leaf extract	65–184 nm	Spherical	–	Heera et al. [74]
Copper sulfate	<i>Nerium oleander</i> leaf extract	80 mL of 1 mM CuSO ₄ in 20 mL leaf extract	–	–	Antibacterial activity	Gopinath et al. [69]
<i>CuO NPs</i>						
Copper acetate	<i>Centella asiatica</i> leaf extract	1 g of Cu(CH ₂ COO) ₂ H ₂ O in 10 mL leaf extract	2000–5000 nm	–	Photocatalytic activity	Devi and Singh [45]
Cupric nitrate	<i>G. superba</i> leaf extract	2.32 g cupric nitrate in 1 mL of leaf extract	5–10 nm	Spherical	Antibacterial activity	Naika et al. [135]
Copper nitrate	Tea (<i>Camellia sinensis</i>) and coffee (<i>Coffea arabica</i>) leaf extract	Copper nitrate and tea/coffee extract 1:3	50–100 nm	Spherical	Antibacterial activity	Sutradhar et al. [193]
Copper sulfate	<i>Tridax procumbens</i> leaf extract	10 mL Fehling's solution in 10 mL leaf extract	–	–	Antibacterial activity	Gopalakrishnan et al. [68]
Copper chloride	<i>Gum karaya</i> extract	0.1 mL of 10 mM CuCl ₂ ·2H ₂ O in 10 mL of Gum Karaya solution	4.8–5.5 nm	Spherical	Antibacterial activity	Padil and Cernik [142]

NPs are shown in Fig. 1. The industrial methods for manufacturing ZnO and other MNPs use harsh chemicals and generate toxic wastes and byproducts. Thus, many scientists are exploring alternative, eco-friendly techniques in synthesizing ZnO NPs [80, 87, 165].

There is an increasing number of reports regarding the green biosynthesis of ZnO NPs using plant extracts [15, 26, 46]. Table 5 presents several studies where the green synthesis of ZnO NPs was investigated. As seen in the table, ZnO NPs were manufactured from different zinc compounds (e.g., zinc acetate, zinc nitrate, zinc sulfate) using extracts from different parts (stem, leaf, flower, and fruit) of various plants (e.g., trees, herbs, ornamentals, and seaweeds). Other researchers reported ZnO NP synthesis using *Aloe vera*, palm pollen, and dried leaves of zinc hyperaccumulator plants [14, 100, 156]. It is also apparent from the table that the ratio of the amount of precursor Zn compound to the amount of plant extract has the same problem of variability as other NPs. In addition, green-synthesized ZnO NPs had morphologies of hexagonal, spherical, rod, and crystalline, and particle sizes from 9 to 180 nm. The table also shows that the plant extract-synthesized ZnO NPs were tested for various applications and found to exhibit similar properties as chemically synthesized ZnO NPs. Some researchers noted that the green-synthesized ZnO NPs were clean and free of harsh chemicals that make them suitable for biological, pharmaceutical, and medical applications [15, 26, 165], which could give green synthesis an advantage over traditional synthesis.

The general procedure for biogenic synthesis of ZnO NPs utilizes plant metabolites in a relatively facile and rapid one-pot experiment [20, 165]. However, the mechanisms for the green synthesis of ZnO NPs are not fully understood. A review of the studies presented in Table 5 revealed that few papers (6 out of 21) tried to elucidate the mechanisms involved in plant extract-mediated synthesis of ZnO NPs. For example, researchers who worked on *Azadirachta indica* (L.) leaf extract reported that polyols from water-soluble phenolic, flavonoid, and quinone compounds were the major phytochemicals that elicited the formation of ZnO NPs [20, 52]. Kumar et al. [95] hypothesized that free OH/COOH from flavonoids, limonoids, and carotenoid molecules from *Citrus paradisi* peel extract formed complexes with zinc, which yielded ZnO NPs after oven-drying. In addition, Bala et al. [15] deduced that amino and carboxylic groups in proteins, phenolics, flavonoids, and alkaloids in *Hibiscus subdariffa* leaf extract functioned as reducing agents for ZnO NPs formation, while amide from proteins and carbonyl and alkyl groups in heterocyclic compounds acted as stabilizer. In another study, Davar et al. [42] used citric acid from lemon fruit extract and sucrose for the green synthesis of ZnO NPs.

These researchers indicated that citric acid adsorbed Zn cations that directed the nanostructure formation, while sucrose reduced the crystallization rates, resulting in improved uniformity of ZnO NPs. Similarly, Buazar et al. [26] reported that the long alkyl chain in starch from potato extract served as reducing and capping agents, promoted the monodispersity, and decreased the size of ZnO NPs.

Several reviews have documented the progress in the emerging field of biogenic synthesis of ZnO NPs [80, 87, 165]. Studies presented in Table 5 are focused on demonstrating the feasibility of plant extract-mediated ZnO NPs synthesis. However, questions arise on whether this method can be adopted for massive production of ZnO NPs to meet industrial needs.

Green synthesis of titanium dioxide NPs (TiO₂)

Titanium dioxide (TiO₂) NPs are the most widely produced MNPs in the world, with an annual global production estimate of 83,500–88,000 metric tons [102]. The high prevalence of TiO₂ NPs in the market is due to their many versatile applications originating from the stability of the chemical structure, physical, optical, and electrical properties. TiO₂ exists in three different mineral forms: anatase, rutile, and brookite; usually the former is preferred, due to its increased photocatalytic activity [112]. Several procedures have been developed over the last two decades to synthesize TiO₂ NPs. Although these methods effectively control the desired NP properties, they often use materials with potential hazards such as carcinogenicity and toxicity [4].

Despite the high production and wide use of TiO₂ NPs, very few attempts have been made for the biogenic production. A few plant species have been investigated for the production of TiO₂ NPs (Table 6). Titanium dioxide hydrate has been used as precursor in most of the studies on the green synthesis of TiO₂; spherical NPs have been the most produced NPs. In addition, almost all of them have been reported to have antiparasitic properties. However, there are no studies on the comparison of the green-synthesized TiO₂ NPs with NPs synthesized with other methods. It is possible that the stability of the bulk TiO₂ limits its breakdown by some plant extracts, reducing the availability of Ti ions to form TiO₂ NPs.

Green synthesis of cerium dioxide (CeO₂)

Cerium oxide NPs (CeO₂ NPs) have excellent catalytic properties due to wide band gap energy and large exciton binding energy, showing a wide variety of applications [217]. The CeO₂ NP properties (e.g., catalytic activity) could be significantly affected by their solubility, particle size, surface coating/modification, surface charge, crystal

Table 5 Summary of the biogenic synthesis of zinc oxide nanoparticles using plant extracts and principal applications

Zinc material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Zinc acetate	<i>Hibiscus subdariffa</i> leaf extract	5–15 or 20–25 mL in 1 g zinc acetate	Varies by condition: 16–60 nm; 200–300 nm length, 30–50 nm head, 70–80 nm base	Spherical, crystalline	Antibacterial activity, antidiabetic property	Bala et al. [15]
Zinc acetate	Lemon (<i>Citrus</i> sp.) fruit extract	0.004 mol zinc acetate, 0.002 mol sucrose in 5–70 mL lemon extract	21.5 nm	Hexagonal	Photocatalytic applications	Davar et al. [42]
Zinc acetate dihydrate	<i>Azadirachta indica</i> leaf extract	1 mL 25 % (w/v) extract in 50 mL 2 M zinc acetate	9.6–25.5 nm	Spherical	Antibacterial activity, photocatalytic applications	Bhuyan et al. [20]
Zinc nitrate	<i>Caulerpa peltata</i> , <i>Hypnea valencia</i> , <i>S. myriocystum</i> leaf extract	5 mL extract (10 g leaf in 100 mL water) in 95 mL 1 mM zinc nitrate	76–186 nm	Spherical	Antimicrobial activity	Nagarajan and Kuppusamy [134]
Zinc nitrate	potato (<i>Solanum tuberosum</i>) extract	3 g zinc nitrate in 50 mL extract (13 g potato in 300 mL water)	~20 nm	Hexagonal wurtzite	–	Buazar et al. [26]
Zinc nitrate	<i>Eichhornia crassipes</i> leaf extract	50 % extract	28–36 nm	Crystalline	–	Vanathi et al. [209]
Zinc nitrate	<i>Solanum nigrum</i> leaf extract	5 g zinc nitrate in 50 mL extract (20 g dried leaves in 100 mL water)	20–30 nm	Hexagonal wurtzite	Antibacterial activity	Ramesh et al. [160]
Zinc nitrate	<i>Lycopersicon esculentum</i> fruit extract	1:3 ratio	60–70 nm	Nanocomposite	Photovoltaic property	Sutradhar and Saha [194]
Zinc nitrate	<i>Ruta graveolens</i> stem extract	10 mL extract (50 g stem in 50 mL water) in 90 mL 0.1 M zinc nitrate	~28 nm	Hexagonal wurtzite	Antibacterial activity, antioxidant activity	Lingaraju et al. [109]
Zinc nitrate hexahydrate	<i>Plectranthus amboinicus</i> leaf extract	10 mL (5 g leaves in 30 mL water) in 30 mL 0.1 M zinc nitrate	50–180 nm	Hexagonal wurtzite	Photocatalytic property	Fu and Fu [59]
Zinc nitrate hexahydrate	<i>Azadirachta indica</i> leaf extract	2 g zinc nitrate in 20 mL extract (20 g leaves in 100 mL water)	40 nm	Hexagonal wurtzite	Antimicrobial activity	Elumalai and Velmurugan [52]
Zinc nitrate hexahydrate	<i>Moringa oleifera</i> leaf extract	2 g zinc nitrate in 20 mL extract (20 g dried leaves in 100 mL water)	16–20 nm	Hexagonal wurtzite	Antimicrobial activity	Elumalai et al. [53]
Zinc nitrate hexahydrate	<i>Vitex negundo</i> L. flower extract	25 mL extract (5 g dried flowers in 50 mL water) in 0.1 M zinc nitrate	10–130 nm	Hexagonal wurtzite	Interaction with human serum albumin	Ambika and Sundrarajan [7]
Zinc sulfate heptahydrate	<i>Citrus paradisi</i> peel extract	3 mL extract in 10 mL 3 mM zinc sulfate	12–72 nm	Spherical	Photocatalytic property, antioxidant activity	Kumar et al. [95]

Table 6 Biogenic synthesis of titanium dioxide nanoparticles using plant extracts

Titanium material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Titanium isopropoxide	<i>Nyctanthes arbor-tristis</i> leaf extract	Unspecified volume of extract in 0.40 M Titanium isopropoxide	100–150 nm	Spherical to agglomerates	–	Sundrarajan and Gowri [191]
Titanium dioxide hydrate	<i>Eclipta prostrata</i> leaf extract	15 mL of extract in 85 mL of $\text{TiO}(\text{OH})_2$ 5 mM	36–68 nm	Spherical to agglomerates	–	Rajakumar et al. [158]
Titanium dioxide hydrate	<i>Annona squamosa</i> peel extract	20 mL of extract in 80 mL of $\text{TiO}(\text{OH})_2$ 5 mM	21–25 nm	Spherical	–	Roopan et al. [163]
Titanium dioxide hydrate	<i>Solanum trilobatum</i> leaf extract	20 mL of extract in 80 mL of $\text{TiO}(\text{OH})_2$ 5 mM	70 nm (average)	Spherical to agglomerates	Antiparasitic	Rajakumar et al. [159]
Titanium dioxide hydrate	<i>Calotropis gigantea</i> flower extract	50 mg of lyophilized extract in 100 mL of $\text{TiO}(\text{OH})_2$ 10 mM	160–220 nm	Spherical to agglomerates	Antiparasitic	Marimuthu et al. [120]
Titanium dioxide	<i>Catharanthus roseus</i> leaf extract	20 mL of extract in 80 mL of 5 mM TiO_2	25–110 nm	Irregular shapes	Antiparasitic	Velayutham et al. [211]
Titanium dioxide hydrate	<i>Morinda citrifolia</i> root extract	20 mL of extract in 80 mL of $\text{TiO}(\text{OH})_2$ 5 mM	20–39 nm	Spherical	Antiparasitic	Suman et al. [190]
Titanium dioxide hydrate	<i>Psidium guajava</i> leaf extract	20 mL of extract in 80 mL of $\text{TiO}(\text{OH})_2$ 0.1 mM	32 nm (average)	Spherical to agglomerates	Antibacterial activity	Santhoshkumar et al. [169]

structure and morphology [224]. These variations might be controlled by adjusting the synthesis routes and tuning their kinetic parameters [73]. Various techniques have been used for the chemical synthesis of CeO_2 NPs [12, 31, 33, 44, 67, 80, 84, 104, 113, 117, 118, 122, 150, 174, 185, 218, 225, 226]. However, conventional techniques used in the synthesis of CeO_2 have shown the same drawbacks as the synthesis of other MNPs. Toxic chemical and multiple process are required [12, 80]. At the end, this means threats to the environment and lower cost effectiveness. For example, in solvothermal synthesis, solvents are used under pressures and temperatures above critical points in order to increase the solubility of solids and to accelerate reactions between solids [70]. All these steps require high consumption of energy and might represent safety threats.

Recently, an increasing number of reports have described the green synthesis of CeO_2 NPs using plant extracts [12, 116–118, 168, 170, 201] (Table 7). Compounds such as cerium acetate, cerium nitrate, and cerium chloride have been used as precursors, and extracts from different plant parts (leaves and flowers) have been used as reducing agents. Most of the green-synthesized CeO_2 NPs are spherical and crystalline, with particle size varying from 4 to 19 nm. The table also shows that plant extract-synthesized CeO_2 NPs have been tested for various applications such as photoluminescence [116] and gamma radiation sensing [117, 118]. They have also shown various

properties such as optical [12], photovoltaic and photocatalytic [117, 118], and antimicrobial [12]. The green-synthesized CeO_2 NPs can also be used in biomedical applications due to their autocatalytic properties and less toxicity. Sankar et al. prepared CeO_2 NPs by using aqueous extract of *Centella asiatica* and compared their superoxide and hydroxyl radical scavenging activities with bulk cerium. The green-synthesized CeO_2 NPs performed better than bulk cerium and had higher cellular uptake and viability in H9c2 rat cardiomyoblasts cell line [168].

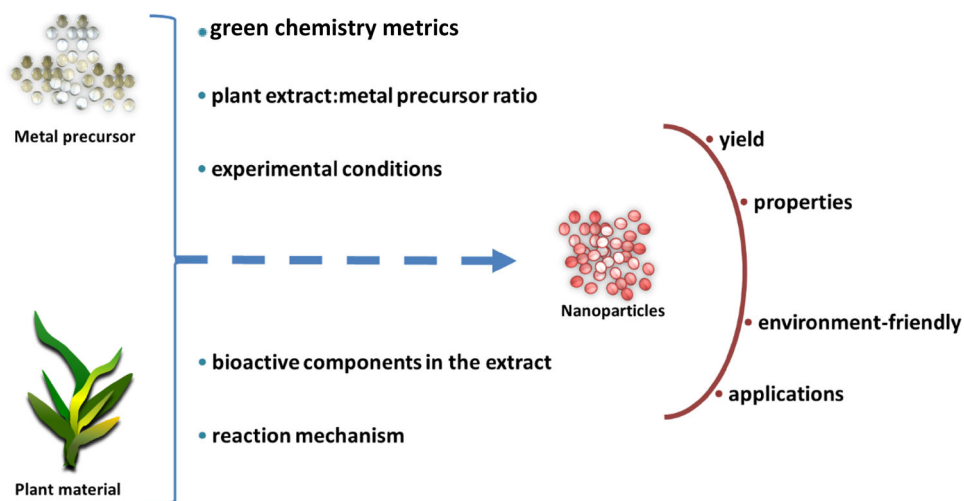
Besides CeO_2 NPs, cerium oxide nanophosphors with the incorporation of rare earth activators, such as Eu^{3+} and Ho^{3+} , have been also synthesized via green route using plant extracts [116–118], showing promising application for efficient display and white light emitting.

Green synthesis of other metal-based nanoparticles

Iron-based NPs have been produced using *Amaranthus spinosus* leaf aqueous extracts. These NPs were spherical with rhombohedral phase structure, smaller size, and large surface with less aggregation than those produced with sodium borohydride (Muthukumar and Matheswaran [130]). Furthermore, these NPs showed better photocatalytic and antioxidant capacity than sodium borohydride-mediated NPs. Similar results were obtained by using tea

Table 7 Summary of the biogenic synthesis of cerium dioxide nanoparticles using plant extracts and principal applications

Cerium material precursor	Plant extract used	Amount of extract	Nanoparticle size (nm)	Morphology	Nanoparticle application	References
Cerium nitrate hexahydrate	<i>Hibiscus sabdariffa</i> flower extract	2.0 g of Ce(NO ₃) ₃ ·6H ₂ O in 100 mL of the red <i>H Sabdariffa</i> flower (2.5 g) water extract solution	~ 3.9	Amorphous and crystalline	Chelating chemical agent	Thovhogi et al. [201]
Cerium nitrate and Holmium nitrate	<i>Aloe vera gel</i> extracted from <i>A. vera</i> leaves	20 mL of <i>A. vera</i> gel	5–10	Highly porous, agglomerates with an irregular morphology, large voids, cracks and shape	Luminescent	Malleshappa et al. [117]
Cerium nitrate and Europium nitrate	Plant latex of <i>E. tirucalli</i>	20 mL of crude latex obtained by cutting green stem of <i>E. tirucalli</i> plant	37–40	Flaky-type morphology with an irregular morphology	Luminescent	Malleshappa et al. [116]
Cerium chloride	<i>Gloriosa superba</i> leaf extract	3.72 g CeCl ₃ salt was added to 100 mL of <i>G. superba</i> leaf extract	5	Spherical	Antibacterial activity	Arumugam et al. [12]
Cerium(III) acetate hydrate	Lemongrass (<i>Cymbopogon flexuosus</i>) plant extract	3 g cerium(III) acetate hydrate was added to 30 mL of lemongrass extract (30 g) solution	10–40	Polycrystalline	Optical	Santi et al. [170]
Ceric nitrate	<i>L. aspera</i> leaf extract	2 g of Ceric nitrate was mixed with 5 mL of leaf extract (0.05 g)	4–13	Relatively uniform microspheres	Photoluminescent, photocatalytic and antibacterial	Malleshappa et al. [118]
Cerium ammonium nitrate	Aqueous extraction of <i>Centella asiatica</i>	1:5 volume ratios of <i>Centella asiatica</i> aqueous extract and an aqueous solution of cerium ammonium nitrate	19.01	Monodispersed particles	Cardiomyoblast hypertrophy	Sankar et al. [168]

Fig. 3 Summary of important issues affecting the technology development of green synthesis of nanoparticles

(*Camellia sinensis*) polyphenols to synthesize iron NPs, and results reveal that the highest rate of bromothymol blue degradation occurs with green synthesized iron NPs, when compared to Fe-ethylenediaminetetraacetic acid (Fe-

EDTA) and Fe-ethylenediamine-dissuccinic acid (Fe-EDDS) (Hoag et al. [75]). This suggests that, for some applications, better results can be obtained with green synthesized NPs.

Besides iron-based NPs, several other metal-based NPs have been synthesized using plant extracts, including Sm_2O_3 NPs (Sone et al. [182]), Co_3O_4 NPs (Diallo et al. [47]), Dy_2O_3 NPs (Chandrasekhar et al. [28]), CdO NPs (Thovhogi et al. [201]), NiO NPs (Thema et al. [200]), In_2O_3 NPs (Maensiri et al. [114]), and hydroxyapatite NPs (Klinkaewnarong et al. [90]). Researches have also investigated the green synthesis of rare earth-doped lanthanide oxides NPs, such as Gd_2O_3 (Vidya et al. [213]) and Y_2O_3 (Prasannakumar et al. [155]; Kumar et al. [96]; Kumar et al. [98]). Magnetic nanocrystalline spinel ferrite, CoFe_2O_4 NPs, MgFe_2O_4 NPs, MnFe_2O_4 NPs, and NiFe_2O_4 NPs were also synthesized by using plant-derived oil (Gherca et al. [65]; Phumying et al. [154]; Gherca et al. [63]) (Table 8).

Factors limiting the development of green synthesis of MNPs

Studies support the feasibility of a facile synthesis of NPs using plant extracts. However, an analysis of the pertinent literature revealed challenging issues and shortcomings limiting the advancement of the green synthesis. Major issues, as depicted in Fig. 3, include: technical, engineering, and economical limitations associated with the source/type and concentration of plant extracts, stoichiometric ratios of the reagents, optimal experimental conditions (temperature, pH, time), yield, and product characterization/application. In addition, process-engineering limitations, operational scalability, and a lack of life cycle assessment are also considered major issues.

Technical factors

Variability in bioactive compounds

Variability in the source/type (i.e., bioactive compounds) of plant extracts is probably the most limiting factor to standardize the green synthesis of metal-based NPs. Most of the reports only show the description of the preparation, collection, washing, and extraction of the plant extract with very little attempt to document which active ingredient triggers the NP formation. For example, Nagarajan and Kuppasamy [134] made comparative studies on the ability of seaweed (*Caulerpa peltata*, *Hypnea valencia*, and *Sargassum myriocystum*) extracts to synthesize ZnO NPs. He found that only *S. myriocystum* extract could trigger the formation of ZnO NPs. The lack of extract characterization seems to be a common element to the most reports. Only 1 out of 21 articles (Table 5) included the characterization of the plant and the extract used in the synthesis [15], while other researchers made the assumption that extracts were rich in plant metabolites. In case of CeO_2 NPs, Thovhogi

et al. [201] found several bioactive compounds (hibiscetin, gossypetine, quercetin, delphinidin, pectin, and cyanidin 3-sambubioside) in *Hibiscus sabdariffa* flower extract, but failed to identify which substance was responsible for the formation of CeO_2 NPs. The antioxidant power of leaf extracts of 26 different plant species was found to have direct effect on their capacity to reduce Fe(III) to form ZVIs NPs; however, authors just characterized the extracts by determining the “ferric reducing antioxidant power” [111]. Most articles on the biogenic synthesis of other NPs have a similar problem, which leave a huge knowledge gap regarding which metabolites in plant extracts are the reducing or capping agents to convert metallic substrates to NPs. Unfortunately, this very broad generalization needs further examination. Obviously, the best source/type of plant extract for the synthesis of each NP has to be identified. Studies cataloging the contribution of the different phytochemicals may be necessary.

A corollary to the lack of knowledge on the bioactive components of plant extracts is the poor understanding on the underlying reaction mechanisms in green synthesis. Despite attempts made by several researchers to unravel the mechanism, it is still a major knowledge gap in green synthesis. Shankar et al. [176, 177] employed IR techniques in deducing the mechanism involved in the green synthesis of Au NPs and concluded that the aldehyde and ketones from sugars in lemon grass extract are involved in the reaction intermediates. IR analyses also suggested that alcohol, amine, and acid groups are responsible for the reduction of the Au(III) ions to form the Au NPs [207, 208]. In another study, Terenteva et al. [196] suggested that flavonoid compounds with lower redox potential facilitate the electron transfer such that flavonoids containing higher hydroxyl groups in their structures are able to produce more Ag NPs. Velmurugan et al. [212] also observed the interaction between Ag ions and hydroxyl groups in phenolic and other compounds from peanut shell extract. It is clear that the existing studies lack description of reaction mechanisms to control the morphology and particle size, which are characteristics inherent to the current physical and chemical synthesis processes. It is understandable that with the difficulty in identifying the active components, it is impossible to comprehend the underlying mechanisms for the green synthesis of NPs. The number of potential reducing agents complicates the investigation of the mechanism. This suggests performing studies using pure solutions of active components found in plant extracts to gain more insights into the efficacy of such compounds in green synthesis.

Variability in experimental conditions

The literature is also lacking analysis of experimental conditions for plant extract-assisted synthesis of NPs. Since

Table 8 Summary of the biogenic synthesis of iron-based and other nanoparticles using plant extracts and principal applications

Material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Sm ₂ O ₃ NPs: Sm(III) acetyl acetate	<i>Callistemon viminalis flower extract</i>	1.625 g of a Sm(III) acetyl acetate in 14 mL of the filtered aqueous extract (0.37 g)	~21.9 ± 5 nm	Polycrystalline	N/A	Sone et al. [182]
Cobalt nitrate hexahydrate	<i>Aspalathus linearis</i> 's natural extract	6.65 g of the <i>A. linearis</i> leaves was added to a 6.0 g of Co(NO ₃) ₃ ·6H ₂ O solution	~3.57 ± 0.05 nm	Non- agglomerated quasi- spherical	N/A	Diallo et al. [47]
Dy(NO ₃) ₃ ·6H ₂ O	Latex of <i>E. tirucalli</i>	1.0 g of Dy(NO ₃) ₃ ·6H ₂ O was added in 1 mL plant latex	~40 nm	Irregular, highly porous and agglomerated	Illumination devices	Chandrasekhar et al. [28]
Cd(NO ₃) ₂ ·4H ₂ O	<i>Hibiscus sabdariffa</i>	2.5 g of clean <i>H Sabdariffa</i> flowers	47–270 nm	Agglomerated grains with quasi- cuboidal form	Illumination devices	Thovhogi et al. [202]
Hydrated cadmium nitrate	<i>Agathosma betulina</i> natural extract	6.0 g Cd(NO ₃) ₂ ·4H ₂ O was mixed with 100 mL of extract	25–50 nm	Clusters formed by smaller agglomerated quasi- spherical nanoparticles	N/A	Thema et al. [198, 199]
Ni(II) nitrate hexahydrate	<i>A. betulina</i>	0.4 g nickel nitrate was mixed with 100 mL of <i>A. betulina</i> reference solution	26.7 ± 0.4 nm	Powder consisting of nanoscaled and slightly agglomerated particles with a certain degree of sharp edges	Photovoltaic/ photodiode	Thema et al. [200]
Gd ₂ O ₃ :Eu ³⁺ nanophosphors: Gd (NO ₃) ₃ and Eu (NO ₃) ₃	Plant Latex of <i>E. tirucalli</i>	1 mL of plant latex	20–30 nm	Nanoflower	Photocatalyst	Vidya et al. [213]
Y ₂ O ₃ :Dy ³⁺ nanophosphor: yttrium nitrate and dysprosium oxide	<i>Aloe vera</i> gel	10 mL of <i>A. vera</i> gel	18–27 nm	Core shell structured microspheres	Photocatalyst	Kumar et al. [96]
Y ₂ O ₃ :Tb ³⁺ nanoparticles: yttrium nitrate and terbium(III) oxide	<i>Aloe vera</i> gel	20 mL of <i>A. vera</i> gel	18–21 nm	Conical, nanoflowers	Antibacterial agents, illumination devices	Prasannakumar et al. [155]
Y ₂ O ₃ :Eu ³⁺ nanophosphor: yttrium nitrate and europium oxide	<i>Aloe vera</i> gel	20 mL of <i>A. vera</i> gel	15–20 nm	Conical, nanoflowers	Illumination devices, photocatalyst	Kumar et al. [98]

Table 8 continued

Material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
MgO:Fe ³⁺ nanoparticles: magnesium nitrate and ferric nitrate	<i>Aloe vera</i> gel	20 mL of <i>A. vera</i> gel	12–20 nm	Nonuniform size with almost spherical shape	Illumination devices, photocatalyst	Anilkumar et al. [9]
Magnetite (Fe ₃ O ₄) nanoparticles: Fe(C ₅ H ₈ O ₂) ₃	<i>Aloe barbadensis</i> (Miller)	Fe(C ₅ H ₈ O ₂) ₃ (10 mmol) was added in 30 mL of aloe vera extract solution	~25–50 nm	Agglomerated nanoparticles	N/A	Phumying et al. [154]
Indium oxide (In ₂ O ₃) nanoparticles: indium(III) acetylacetonate	<i>Aloe barbadensis</i> (Miller)	3 g of indium (III) acetylacetonate was added in 30 mL <i>A. vera</i> extract solution	5–50 nm	Cubic	N/A	Maensiri et al. [114]
Nanocrystalline hydroxyapatite (HAp) powders: calcium nitrate, diammonium hydrogen phosphate	<i>Aloe barbadensis</i> (Miller)	250 mL of the <i>Aloe vera</i> extracted solution	43–171 nm	Spherical shape, a rod-like shape	N/A	Klinkaewnarong et al. [90]
Hydroxyapatite nanoplates: Ca(NO ₃) ₂ ·4H ₂ O and NH ₄ H ₂ PO ₄	<i>Moringa oleifera</i> flower extract	50 mL of <i>M. oleifera</i> extract	80 nm	Plate-like crystalline	N/A	Sundrarajan et al. [192]
NiFe ₂ O ₄ nanoparticles: Ni(NO ₃) ₂ ·6H ₂ O and Fe(NO ₃) ₃ ·9H ₂ O	<i>Aloe vera</i> gel	250 mL <i>A. vera</i> plant extracted solution	~30, 60, and 80 nm	Clusters of agglomerated particles	N/A	Laokul et al. [101]
CoFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and CoCl ₂ ·6H ₂ O	Canola oil	suitable amount of canola oil solution	5–12 nm	Spherical shape and agglomerated	N/A	Gherca et al. [65]
MgFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MgCl ₂ ·6H ₂ O	Canola oil	Suitable amount of canola oil solution	5–12 nm	Spherical shape and agglomerated	N/A	Gherca et al. [65]
MnFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MnCl ₂ ·4H ₂ O	Canola oil	Suitable amount of canola oil solution	5–12 nm	Spherical shape and agglomerated	N/A	Gherca et al. [65]
NiFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and NiCl ₂ ·6H ₂ O	Canola oil	Suitable amount of canola oil solution	5–12 nm	Spherical shape and agglomerated	N/A	Gherca et al. [65]
CoFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and CoCl ₂ ·6H ₂ O	Ricin oil, from the seeds of the castor shrub, <i>R. communis</i>	20 mL of ricin oil solution	10–20 nm	Spherical	N/A	Gherca et al. [63]
MgFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MgCl ₂ ·6H ₂ O	Ricin oil, from the seeds of the castor shrub, <i>R. communis</i>	20 mL of ricin oil solution	~21.75 nm	Polyhedral	N/A	Gherca et al. [63]

Table 8 continued

Material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
MnFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MnCl ₂ ·4H ₂ O	Ricin oil, from the seeds of the castor shrub, <i>R. communis</i>	20 mL of ricin oil solution	28.70 nm	Polyhedral and cubic	N/A	Gherca et al. [63]
NiFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and NiCl ₂ ·6H ₂ O	Ricin oil, from the seeds of the castor shrub, <i>R. communis</i>	20 mL of ricin oil solution	35.64 nm	Polygonal	N/A	Gherca et al. [63]
CoFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and CoCl ₂ ·6H ₂ O	Linseed oil	10 mL of linseed oil solution	10–25 nm	Spherical	N/A	Gherca et al. [64]
MgFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MgCl ₂ ·6H ₂ O	Linseed oil	10 mL of linseed oil solution		Spherical	N/A	Gherca et al. [64]
MnFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and MnCl ₂ ·4H ₂ O	Linseed oil	10 mL of linseed oil solution	33 nm	Spherical	N/A	Gherca et al. [64]
NiFe ₂ O ₄ nanoparticles: FeCl ₃ ·6H ₂ O and NiCl ₂ ·6H ₂ O	linseed oil	10 mL of linseed oil solution	31.5 nm	Spherical	N/A	Gherca et al. [64]
NiFe ₂ O ₄ nanocrystalline spinel: Fe(acac) ₃ and Ni(acac) ₂	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Mill.)	50 mL <i>Aloe vera</i> extract solution	~6–10 nm	Particles	N/A	Phumying et al. [153]
CoFe ₂ O ₄ nanocrystalline spinel: Fe(acac) ₃ and Co(acac) ₂	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Mill.)	50 mL <i>Aloe vera</i> extract solution	~6–10 nm	Particles	N/A	Phumying et al. [153]
MnFe ₂ O ₄ nanocrystalline spinel: Fe(acac) ₃ and Mn(acac) ₂	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Mill.)	50 mL <i>Aloe vera</i> extract solution	~6–40 nm	Platelets and particles	N/A	Phumying et al. [153]
MgFe ₂ O ₄ nanocrystalline spinel: Fe(acac) ₃ and Mg(acac) ₂	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Mill.)	50 mL <i>Aloe vera</i> extract solution	~10–50 nm	Platelets and particles	N/A	Phumying et al. [153]
Nanocrystalline magnetic spinel CoFe ₂ O ₄ ; ferric nitrate and cobalt nitrate	<i>Aloe vera</i> (<i>Aloe barbadensis</i> Mill.)	5 g <i>Aloe vera</i> leaves in 10 mL DI water	~13–17 nm sphere-like nanoparticles; ~24–28 nm flake-like nanoplatelets	Sphere and flake	Catalyst	Manikandan et al. [119]
Nanoscale zerovalent iron particles (NZVI): Fe(NO ₃) ₃	Tea powder (Red label from Tata, India Ltd. 99 %)	1–10 mL tea extract	40–50 nm	Spherical	Borohydride reduction	Nadagouda et al. [132]

Table 8 continued

Material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
nZVIs: iron(II) sulfate heptahydrate	26 different plant species (<i>Apple, Apricot, Avocado, Cherry, Eucalyptus, Kiwi, Lemon, Mandarin, Medlar, Mulberry, Oak, Olive, Orange, Passion fruit, Peach, Pear, Pine, Pomegranate, Plum, Quince, Raspberry, Strawberry, Tea-Black, Tea-Green, Vine, and Walnut</i>)	1 mL of extract was added to 250 μ L of an iron(III) solution	10–30 nm	Spherical and non-agglomerated	N/A	Machado et al. [111]
Fe ₃ O ₄ nanoparticles: ferric chloride hexahydrate	<i>Solanum trilobatum</i> extract	10 wt% <i>Solanum trilobatum</i> extract	18 nm	Spherical	Methylene blue dye degradation	Vinothkannan et al. [215]
Fe ₃ O ₄ nanoparticles: iron(III) oxide	<i>P. frutescens</i> leaf extract	5 mL of <i>P. frutescens</i> extract was added to 50 mL of a prepared 2 mM of iron(III) oxide (Fe ₂ O ₃) solutions	50 nm	Spherical	Catalyst	Basavegowda et al. [18]
α -Fe ₂ O ₃ nanoparticles: ferric chloride	<i>Azadirachta indica</i> leaf extract	<i>A. indica</i> leaf extract was added to 0.1 M FeCl ₃ in a 1:2 ratio	400 nm	Hexagonal cone (HC) like	Thermal catalyst	Sharma et al. [179]
Mesoporous hematite (α -Fe ₂ O ₃) nanoparticles: Fe(NO ₃) ₃ ·9H ₂ O	Green tea (<i>C. sinensis</i>) leaves	30 mL of green tea-extract	40–80 nm	Spherical	Photocatalyst and wet-type solar cell	Ahmmad et al. [3]
FeO nanoparticles: ferric chloride	<i>Amaranthus spinosus</i> Leaf Extract	40 mL of leaf extract	58–530 nm	Spherical like	Photocatalyst decolorizations of MB and MO and antioxidant	Muthukumar and Matheswaran [130]
Iron–polyphenol nanoparticles: FeCl ₃	Extracts obtained from Australian native plant leaves: <i>Eucalyptus tereticornis, Melaleuca nesophila, and Rosemarinus officinalis</i>	0.1 M FeCl ₃ solution was added to the leaves extracts in a 2:1 ratio	40–60 nm	Spherical particles	Catalyst	Wang et al. [220]
α -Fe ₂ O ₃ nanoparticles: iron(III) nitrate	Curcuma and tea leaves extract	10 mL of the extract	4–5 nm	Spherical	Photocatalytic	Alagiri and Hamid [5]
Iron nanoparticles: iron sulfate	Leaves extract of <i>Lawsonia inermis</i> and <i>Gardenia jasminoides</i> plant	50 mL of plant extract	21–32 nm	Hexagonal-like	Antibacterial	Naseem and Farrukh [139]

Table 8 continued

Material precursor	Plant extract used	Amount of extract	Nanoparticle size	Morphology	Nanoparticle application	References
Iron nanoparticles: FeCl ₃	Tea (<i>C. sinensis</i>) polyphenols	0.1 M FeCl ₃ was added to 20 g/L green tea in a 2:1 volume ratio	5–15 nm	Spherical	Degradation of bromothymol	Hoag et al. [75]
Nanoiron: ferric chloride	Five plant extracts and juices, i.e., extracts of <i>C. sinensis</i> (green tea, GT), <i>Syzygium aromaticum</i> (clove, CL), <i>Mentha spicata</i> (spearmint, SM), <i>Punica granatum</i> juice (pomegranate, PG), and <i>red Wine</i> (RW)	10–20 g/L	50–60 nm	Spherical	Cr(VI) reduction	Mystrioti et al. [131]

Table 9 Summary of the main parameters controlling the plant-based synthesis of metal nanoparticles

Parameter	Effects on properties
Precursor concentration	Number of NPs, morphology
Extract concentration	Size, size distribution
Extract/volume ratio	Size, size distribution
pH	Size, size distribution, morphology
Solvent extract	Morphology
Temperature	Size, size distribution
Reaction time	Size, morphology
Amount of extract	Size, morphology
Plant species	Size, size distribution, morphology

plant extracts have very different properties, it is possible that operational conditions would greatly vary for every procedure. Villanueva-Ibáñez et al. [214] compared the effect of pH on the biogenic synthesis of Ag NPs. They obtained NPs of about 10 nm at neutral pH, while those synthesized at lower pH (4.5) had a size of about 25 nm. Authors stated that alkaline condition of silver nitrate solution prevents Ag reduction, while acidic condition promotes Ag solubility and NPs agglomeration. A study by Terenteva et al. [196] showed an optimum pH range of 8–10 to get the highest yield of Ag NPs. In a separate study, Bonatto and Silva [21] described the influence of temperature on the hydrodynamic diameters of Ag NPs. Suspension incubated at 0 °C revealed three size populations, while those at 50 and 75 °C only had one. More negative zeta potential values for Ag NPs were recorded at 25 and 75 °C. Similarly, plant extract reduction of Au ions to Au NPs is temperature dependent [207, 208].

In a related study, Rafaie et al. [157] reported the synthesis of ZnO NPs using *Citrus aurantifolia* extracts at pH values of 5, 7, and 9. Authors reported that the pH had direct influence on the growth and aspect ratios of ZnO nanorods. These researchers observed that the nanorods' growth was inhibited in acidic conditions, compared to those in neutral and alkaline solutions. The NPs synthesized at pH 5 were smaller and shorter than those formed at pH 7 and 9. Likewise, Nagarajan and Kuppasamy [134] found that formation of ZnO NPs using *S. myriocystum* extract yielded better results at pH 8, compared to other pH values (i.e., 5, 6, 7, 9, and 10) tested. The same researchers also observed that the reaction temperature affects the nanoparticle formation. They found that 80 °C was the optimum condition for the synthesis of ZnO NPs [134]. In contrast, other procedures describe reaction temperatures as low as 50 °C to as high as 300, 400 and 450 °C [7, 13, 15, 157]. The reaction time is another factor that could vary from 1 to 8 h [121, 134]. A review of publications shown in Tables 2, 3, 4, 5, 6, 7 and 8 reveals that the majority of these studies did not explain on the optimization of conditions employed in the synthesis. A more thorough investigation on the experimental conditions is needed to determine how they affect the mechanisms involved in the synthesis of each NP.

Engineering factors

Commercial NPs are produced under rigorous standards that guarantee the quality and performance of the products. This includes uniformity in size and surface composition to assure similar behavior. In fact, there are several parameters controlling the plant-based synthesis of MNPs that

need further studies (Table 9). So far, most of the green-synthesized MNPs have not been characterized for properties like zeta potential, thermal and electrical conductivity, and layer of atoms in the external part. In addition, only a few reports (Tables 2, 3, 4, 5, 6, 7, 8) show monodispersion of the green-synthesized MNPs. Works on the green synthesis of Au NPs suggest that uniform material is not produced due to the diversity in bioactive compounds present in different plant materials [60, 162, 178]. Shankar et al. [176, 177] reported that sugars present in lemon grass extracts induced the production of triangular Au nanoplatelets, whereas Fayaz et al. [54] showed that aqueous extracts of *Madhuca longifolia* leaflets produced Au NPs and Au platelets varying from 7 to 3000 nm. On the other hand, Smitha et al. [181] showed that an aqueous extract from *Cinnamomum zeylanicum* was able to reduce Au ions from HAuCl_4 solution to form Au NPs. The morphology of the smaller NPs was spherical, whereas that of the larger particles had mixed geometries consisting of triangular platelets and spherical particles. The literature on the biogenic synthesis of Au NPs (Table 2) reveals similar problems in Au reduction, which clearly hinders the possibility of mass production of Au NPs via green synthesis. These problems have been present since the very beginning of the green synthesis of MNPs and have been continually reported.

The stoichiometric ratio of the extract and metal precursor is a factor that affects the size, shape, yield, and other characteristics of green-synthesized MNPs. The reduction of Au ions using plant extracts has been shown to produce smaller particles with higher plant extract concentrations [207, 208]. Biogenic synthesis of Ag NPs (Table 3) revealed that silver nitrate/extract ratio is the main parameter controlling the synthesis and stability of Ag NPs. Villanueva-Ibáñez et al. [214] observed that Ag NPs synthesized using 1–5 mL of corn husk extract had smaller particle size than those formed at higher extract volume (8 mL), while [196] reported an optimum silver nitrate concentration ranging between 0.8 and 2 mM to get the highest yield of Ag NPs.

The concentration of plant extract is also a critical factor influencing the shapes and crystallinity MNPs. Davar et al. [42] reported that size distribution of ZnO NPs increased with the volume of lemon extract used in the synthesis. These researchers found a narrower size distribution at 30 mL lemon juice, which increased to submicrometer size at 50 and 70 mL extract. Similarly, Nagarajan and Kuppusamy [134] detected formation of ZnO NPs only at 5 mL of *S. myriocystum* extract, while [121] observed varying degrees of crystallinity at different concentrations of *Sapindus rarak* extracts. Likewise, other reports illustrated the influence of the precursor zinc concentration on the synthesis of ZnO NPs. Nagarajan and Kuppusamy [134]

detected the formation ZnO NPs at 1 mM zinc nitrate but not at other concentrations (0.25–0.75 mM), whereas [167] observed morphological variations at different concentrations of zinc acetate (0.05–0.20 M). In addition, an analysis of the stability of plant-based synthesized NPs has not been included in the particle characterization. Very few reports have mentioned that plant-based synthesized NPs were surface capped, but none of them report characterization of the capping. For example, Jang et al. [82] reported that the extract of *Lonicera hypoglauca* flowers functions as silver nitrate reducer and capping agent of the Ag NPs. They used UV–Vis spectroscopy, FTIR, SEM-ED, TEM, and SAED to characterize the NPs but did not characterize the surface coat. In fact, plant-based synthesized MNPs can be capped with several organic molecules [97]. Therefore, much more data are needed to assess and determine the feasibility of the whole process and to obtain a comprehensive analysis on the direction where the green synthesis is headed.

Economical and environmental factors

Some other factors are overlooked in current studies. Claims that biogenic synthesis of NPs is more environmental friendly and compatible with biological systems, compared with the chemical approach, are not widely supported. There are no clear evidences that green approaches are environmental friendly. Case studies appraising how much energy is saved, how many toxic reagents are avoided in lieu of non-toxic alternatives, and the ecological and economic impacts of using plant materials, among others, might be helpful in understanding the environmental benefits of the green synthesis. The effects of plant material conditions (e.g., fresh or dried), extraction conditions (temperature, contact time, volume/mass ratio), and extract storage, in the efficiency of the process have to be studied. There is also a lack of research demonstrating the feasibility of adopting the process to an industrial and more massive scale. Scaling up the green production will increase tremendously the required volume of plant source and extracts, which may be a limiting factor to achieve the long-term demands. Unfortunately, these factors are not well understood. Other factors to evaluate are the yield and stability of the green-synthesized NPs. Yield is a sound measure in assessing the efficiency, practicality, and profitability of the green synthesis. The amount of starting reagents, both the metal compounds and the extract, is reported in the studies (Tables 2, 3, 4, 5, 6, 7, 8), but the yield efficiency of the process is staggeringly missing in the reports. To authors' knowledge, an economic analysis of plant-based production of MNPs is missing. In addition, nobody has characterized the metrics to evaluate the green synthesis of MNPs. For example, the effective mass yield, mass intensity, and the stoichiometric factor, among others,

are parameters to be calculated for a better assessment of the green synthesis of MNPs [204] (Fig. 3).

Conclusions and future work

From the beginning, the methods for the synthesis of metal-based NMs using green processes have been touted in the last three decades as being “environmentally friendly and cost-effective” alternatives to traditional approaches. There has been an explosion of research publications highlighting the benefits of the green synthesis. In practice, all industrially produced MNPs have also been synthesized using plants/plant extracts or microorganisms. Several species of plants and microbes have shown to be promising sources for the green synthesis of MNPs. State-of-the-art analytical techniques such as transmission electron microscopy, X-ray absorption spectroscopy, and X-ray diffraction, among others, have been used to characterize the different NMs generated by green syntheses. Nanoparticles and nanoplates of different forms and sizes have been reported. More than 50 plant species and several microbial species have been used. Extracts of leaves, flowers, and fruits, as well as several plant-derived materials, have shown to reduce metals, forming nanostructures. The green-synthesized MNPs have shown similar properties as their chemically synthesized counterparts. However, almost all of the reports have shown a lack of regularity in size and forms of the synthesized MNPs and, practically, none of them have quantified the production. Other aspects related to the green synthesis are the variety of plant compounds with potential to reduce the metals. Phenolic, amino, carboxyl and hydroxyl groups, proteins, and aminoacids, among others, have shown reducing capacity, resulting in the production of NPs. Moreover, variations in the production conditions result in differences in the synthesized materials. In most of the reports, there is no clear mention of the reducing factor, and none of them have presented stoichiometric calculations. A clear description of the resulting nanoparticles in each extracts condition may allow to fine tune of nano properties. The problems mentioned above raise questions like: How much reducing agent can be obtained from the target plant? How much biomass will be needed for a sustainable production of the respective NP? The literature shows that in 2010 there was a global production of 260,000–309,000 metric tons of MNPs [85]; how much time will be needed for the production, for example, of one ton of green-synthesized NPs? These queries suggest that the future work has to be focused to answer the following research questions:

1. Quantification of the NP production (ratio of starting material/reducing agent for a specific volume of MNP).

2. Establishment of the production time for a required volume of determined MNPs.
3. Standardization of conditions for the production of monodisperse specific particles.
4. Stability of the green-synthesized MNPs.
5. Identification with no doubt of best plant/plant-derived materials for the synthesis of specific MNPs.
6. Clarification of the biochemical and molecular mechanisms involved in the formation of specific NPs.
7. Definition of costs of production of specific amounts of MNPs.
8. Development of chemistry metrics for the green synthesis of MNPs.

Until these questions are answered, the green synthesis of nanomaterials is a scientific curiosity with no possibilities of scaling up to industrial levels.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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