

Review

Synergetic Green Synthesis of Silver Nanoparticles Using DES-Based Plant Extracts

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Abstract

Green synthesis methods offer an environmentally friendly and alternative approach for the development of silver nanoparticles (AgNPs). These methods utilize natural and renewable resources such as plant extracts or deep eutectic solvents (DESs) while minimizing the use of hazardous chemicals. Nanoparticles, characterized by their dimensions within the 1–100 nm range, exhibit unique properties that enable their diverse applications in medicine, diagnostics, drug delivery systems, cosmetics, sensing, catalysis, food and agricultural technologies. This review summarizes recent advancements in the biogenic synthesis of AgNPs using plant extracts prepared via deep eutectic solvents (DESs) or natural deep eutectic solvents (NaDESs), as well as individual plant extracts or DESs/NaDESs. The research highlights the strategic synergy in which DES-based media and their different bioactive compounds of plant extracts play a crucial role as both reducing and stabilizing agents. Furthermore, the physicochemical properties of the synthesized AgNPs, including core diameter, morphology, and long-term stability, are critically evaluated in relation to eutectic composition, and plant species utilized. This review demonstrates that DESs actively modulate the biosynthesis of AgNPs: functioning as green extraction media and steric/electrostatic stabilizing agents, while selectively serving as direct reducing agents in compositions containing reducing sugars, polyols, organic acids, and bioactive plant compounds.

Keywords: silver nanoparticles (AgNPs); biogenic synthesis; synergetic green synthesis; deep eutectic solvents (DESs); natural deep eutectic solvents; plant extracts



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1. Introduction

Silver nanoparticles (AgNPs) represent one of the most widely utilized classes of nanomaterials, recognized for their unique optical, electrical, and catalytic properties [1], as well as their wide range of biological activities including antimicrobial [1], antifungal [2], anticancer [3] and antiviral effects [4]. Consequently, they present extensive applications across medicine, drug delivery, cosmetics, sensing, catalysis [5], wastewater treatment, food technologies, and agriculture [3]. AgNPs can be synthesized through various physical, chemical, biological, and hybrid methods [6]. Physical methods utilize mechanical, thermal, or electrical energy rather than chemical reagents, including both top–down breaking of bulk silver and bottom–up vapor-phase condensation (e.g., physical vapor deposition) [7]. In contrast, chemical methods rely on bottom–up molecular reactions, where silver ions

(Ag⁺) are reduced to metallic silver (Ag⁰) in solution, regulated by reducing agents and capping ligands [2]. However, conventional physical methods often require high energy input, while chemical methods present significant environmental and toxicological hazards due to toxic reducing agents and organic solvents [8,9]. As a safer alternative, green biogenic synthesis has gained wide attention [10,11]. These eco-friendly approaches harness naturally derived biomass, such as plant extracts and microorganisms, to serve as dual reducing and capping agents. In biogenic synthesis, the reduction of silver precursor ions (Ag⁺ to Ag⁰) is driven by secondary plant metabolites, collectively known as phytochemicals, including flavonoids, phenolics, tannins, terpenoids, and proteins [12]. These bioactive compounds possess a high density of functional hydroxyl and carboxyl groups, which facilitate sacrificial electron donation to Ag⁺ under ambient conditions, while simultaneously forming a protective phytochemical capping agent that prevents nanoparticle accumulation through steric and electrostatic repulsion [13]. Despite these advantages of biogenic synthesis, conventional extraction protocols relying on conventional aqueous or organic solvents, such as methanol, ethanol, acetone for phytochemical extraction often limits the yield of poorly water-soluble bioactive compounds [14,15]. To overcome these extraction limitations, the application of Deep Eutectic Solvents (DESs) and Natural Deep Eutectic Solvents (NaDESs) in biogenic synthesis has attracted particular research interest. DESs are mixtures of two or more components, a hydrogen bond acceptor (HBA), like choline chloride or betaine and a hydrogen bond donor (HBD), like glycerol, organic acids, or sugars. DESs exhibit highly tunable physicochemical properties and are characterized by their efficiency, low toxicity, and biodegradability [16,17]. Their unique hydrogen-bonded architecture not only enables the highly efficient extraction of bioactive phytochemicals from raw biomass but also directly modulates nanoparticle crystallization [18]. Specifically, the high viscosity and ionic strength of the eutectic system impose strong mass-transfer and diffusion-controlled limitations that regulate nucleation and growth kinetics, thereby yielding highly uniform, monodisperse nanoparticles with long-term stability. While the individual applications of plant extracts [19,20] and DESs in nanotechnology have been reported [21,22], their strategic synergy in fabricating functional AgNPs remains a rapidly evolving field of research. Hence, this review evaluates the synergetic mechanisms operating at the interface of green biosynthesis and next-generation green solvents. We explore how DES-based plant extracts serve as a multi-functional reagent, simultaneously as the extraction solvent, the primary reducing and capping agent, and the electrostatic stabilizer of AgNPs. Particular emphasis is placed on the mechanisms by which phytochemicals mediate AgNP formation, DES-mediated mixture effects, and the efficacy that this technology offers for a fully green approach to nanomaterials manufacture.

2. Aim, Scope and Overview of the Review

This review provides a critical overview of the synergistic green synthesis of silver nanoparticles (AgNPs) mediated by Deep Eutectic Solvents (DESs) and Natural Deep Eutectic Solvents (NaDESs) combined with plants extracts. While existing literature has largely examined plants extracts or green solvents independently, this work specifically highlights the integrated framework in which DES-based plant extracts serve as multi-functional systems: acting as extraction media, stabilizing agents, and reaction modulators, while functioning as direct reducing agents in specific formulations. The scope includes a comparative classification of biogenic synergistic synthesis, against conventional methods. Next, the fundamental supramolecular chemistry of eutectic mixtures is evaluated to explain its role in regulating mass transfer and crystallization kinetics. In this context, the discussion addresses how key operational parameters such as pH, temperature, precursor concentration, and hydration, on particle size and stability is systematically analyzed.

Furthermore, downstream biomedical and environmental applications are systematically evaluated alongside current engineering challenges regarding industrial scalability and solvent recovery. A systematic literature review was performed across Web of Science, Scopus, PubMed, and Google Scholar. Foundational studies were used to the introduction of DES and provide the theoretical background (2003), whereas the quantitative analysis emphasizes recent advances published between 2018 and 2026. The search utilized targeted keyword combinations, including *Silver Nanoparticles*, *AgNPs*, *Deep Eutectic Solvents*, *NaDES*, *Plant Extracts*, and *Green Biosynthesis*.

3. Classification of Silver Nanoparticle (AgNP) Synthesis Approaches

There are three main approaches for developing silver nanoparticles (AgNPs): physical, chemical, and green methods [5,7,23]. The choice of reducing and capping agents governs the mechanism of silver ion reduction, directly influencing colloidal stability, production costs, and suitability for specific downstream applications. As one of the foundational approaches for silver nanoparticle synthesis, the physical method relies on high-energy inputs to top-down reduce bulk metal into nanoscale structures [5]. Because these techniques operate without chemical reducing agents, they yield ultra-pure nanoparticles free from residual contaminants [24]. Chemical synthesis is a well-known method for developing AgNPs, because of its ease, scalability, and precise control over particle size, shape, and distribution. This method involves the chemical reduction of silver ions (Ag^+) to elemental silver (Ag^0) with potent reducing agents in either an aqueous or organic medium [2,25]. The nucleation of AgNPs is typically initiated through electrons on Ag^+ ions in solution, utilizing reducing agents such as sodium borohydride (NaBH_4) [5], alanine/sodium hydroxide [26], trisodium citrate, and hydrazine. Stabilizing or capping agents, including polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), and different surfactants, are frequently employed to inhibit nanoparticle aggregation, alter growth kinetics, and control shape and surface characteristics [5]. However, these conventional protocols frequently require stringent purification steps to eliminate unreacted reagents and secondary byproducts, which significantly escalates both the duration and capital expenditure of production [17]. In contrast, green synthesis avoids these hazardous chemicals by utilizing biological extracts, thereby streamlining the process and minimizing environmental toxicity [4,27].

The adoption of green synthesis as a method in nanotechnology has become rapid due to its compatibility with sustainability and biomedical safety requirements. Green methods utilize biological systems, such as plant extracts, microorganisms, green solvents as both reducing and capping agents. Unlike chemical methods, this approach eliminates the need for toxic chemicals and offers a natural method for producing AgNPs that are environmentally friendly [5,28]. These biological frameworks effectively stabilize nanoparticles against aggregation while maintaining a high yield, thereby addressing the limitations often observed in conventional physical and chemical methods [24]. Furthermore, the incorporation of plant-based secondary metabolites, such as flavonoids, proteins, and phenolic compounds, serves to enhance the long-term stability of the resulting particles, frequently yielding AgNPs with superior biological activity compared to those generated through conventional synthetic routes [19,29]. The primary benefits of green synthesis are that it is simple, cost-effective, and environmentally friendly [28,29]. Moreover, the bioactive compounds involved, such as polyphenols, proteins, enzymes, sugars reduce the silver ions Ag^+ to Ag^0 and maintain their stability for nanoparticles interaction. There are two main types of green synthesis, each categorized by the source of the green solvents or biological reducing agents, as illustrated in Figure 1. These categories are primarily distinguished by the utilization of plant-based extracts versus microbial fermentation processes, both of

which harness intrinsic metabolites to facilitate rapid bio-reduction under ambient conditions. While microbial-mediated routes often benefit from the precise enzymatic control of metabolite secretion, plant-based methods are frequently prioritized for their superior cost-effectiveness and ease of material preparation [30,31]. In addition, plant-derived synthesis eliminates the requirement for specialized infrastructure or complex culture media, significantly reducing the overall cost of large-scale production [32].

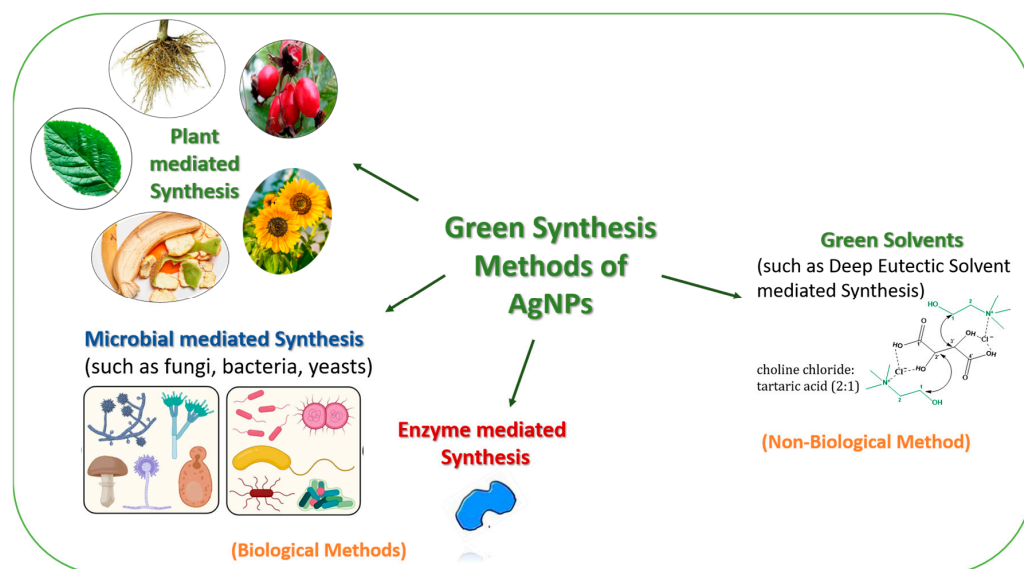


Figure 1. Classification of green synthesis methods for silver nanoparticles (AgNPs).

Among green synthesis approaches, plant-mediated synthesis has gained significant attention due to scalability and versatility. It harnesses plant extracts rich in bioactive phytochemicals, including flavonoids, polyphenols, alkaloids, terpenoids, and tannins which act synergistically to reduce silver ions and form a protective “phytochemical surface” around the nanoparticles. This capping layer prevents aggregation, optimizing the stability of the colloids and enhancing their biological efficacy. Nevertheless, parameters such as extraction protocols and conditions significantly affect the concentration of phytochemicals, often introducing inconsistencies in the morphological characteristics and stability of the nanoparticles [26]. In addition to plant-assisted methods, microorganisms such as bacteria (like *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus thermophilus*), fungi (like *Aspergillus fumigatus*, *Aspergillus flavus*, and *Fusarium oxysporum*) and yeast (like *Saccharomyces cerevisiae*, *Candida* sp., and *Meyerozyma guilliermondii*) can facilitate the development of silver nanoparticles [26]. This biogenic process is driven by metabolic and enzymatic complexes, which actively reduce silver ions into stable Ag^0 nanoparticles [5,26]. In recent years, in addition to biological methods, the green synthesis of silver nanoparticles has also involved the use of green solvents, such as deep eutectic solvents, acting as reducing and stabilizing/capping agents [21,22,33], which are analyzed in the following section.

3.1. Synthesis of AgNPs Using Deep Eutectic Solvents (DESs)

Deep eutectic solvents (DESs) are gaining significant traction as eco-friendly alternative solvents due to their biodegradability, low volatility, non-flammability, and high thermal stability, presenting characteristics similar to those of ionic liquids (ILs) [34]. DESs are generally preferred over traditional ionic liquids because of their capacity to be derived from a variety of available components [35]. Generally, DESs are defined as mixtures that can be prepared from at least two components, one as a hydrogen bond donor (HBD), including urea, carboxylic acids, amino acids, polyols, and sugars, and another one as a hydrogen bond acceptor (HBA), including ammonium salts (such as choline chloride),

amphoteric ions (such as betaine), or their hydrochloride salts [16,35]. The versatility of DESs has been demonstrated across a wide range of advanced applications, including the extraction of bioactive compounds from plants sources [16], targeted drug delivery systems, metal recovery [36], synthesis of nanoparticles, and electro-chemistry [35].

The foundational principles of DESs in biogenic nanomaterial synthesis are schematically summarized in Figure 2. As illustrated, DESs are formed by tailoring the molar ratios of hydrogen bond donors (HBDs), such as lactic acid, and hydrogen bond acceptors (HBAs), like choline chloride. Beyond serving as sustainable reaction media, DESs exhibit a dual functionality: they act as highly efficient media for solubilizing and extracting bioactive plant metabolites including polyphenols, flavonoids, alkaloids, while simultaneously modulating Ag^+ reduction kinetics, nucleation, and steric/electrostatic stabilization during nanoparticle growth.

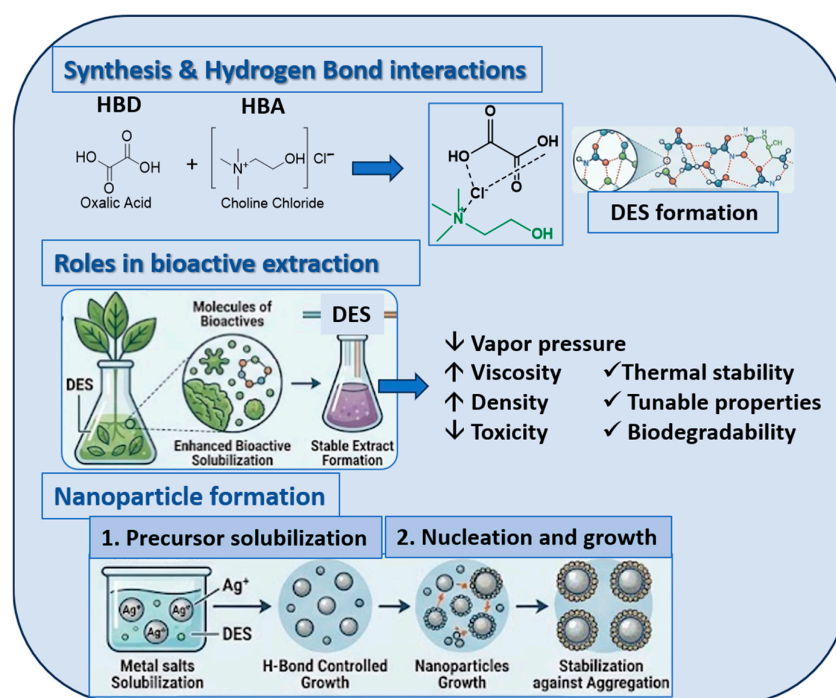


Figure 2. Fundamental principles of Deep Eutectic Solvents (DESs), including (1) synthesis via hydrogen bond donor (HBD) and acceptor (HBA), (2) key physicochemical properties, (3) roles in the extraction and stabilization of plant bioactive compounds, and (4) facilitation of silver nanoparticle nucleation, growth, and stabilization, where downward and upward arrows indicate decrease and increase, respectively, and check marks denote favorable properties.

In 2003, Abbott et al. introduced DESs as a novel class of green solvents, offering a sustainable alternative to conventional ionic liquids (ILs) [37]. Their pioneering research demonstrated that choline chloride, as HBA, and urea, as HBD, could be mixed in a 1:2 molar ratio to form a stable eutectic mixture [35]. Between 2010 and 2015, DESs were recognized for their immense capacity in noble metal nanoparticle synthesis, acting as reducing agents and stabilizers for noble metal nanoparticles like AuNPs, AgNPs [38,39]. By 2016, the research focus shifted toward controlling the morphology and size of AgNPs by manipulating the specific composition of DESs. Physicochemical properties of DESs, such as viscosity, polarity, and ionic strength, can be precisely tuned to directly influence nucleation and growth kinetics, offering fine control of nanoparticle characteristics and optimizing their performance in catalysis and biomedicine [38]. In 2018 and 2019, DES integrated with extracts of plants opened a new area to green nanotechnology [40,41]. The combination of DESs and phytochemicals enhanced both the biocompatibility and antioxidant properties

of the resulting AgNPs. This approach merely made the sustainable synthesis of AgNPs more robust and widened their applications in pharmaceutical and cosmetic formulations. During 2020, AgNPs synthesized via DESs were applied in antimicrobial coatings for medical devices, textiles, and filtration systems [14,38,42], establishing a synergistic interrelationship between DES and AgNPs to ensure long-lasting antimicrobial activity. In 2022, the area of application of the DES–AgNPs technology was extended to environmental sensing incorporating DES-mediated AgNPs into sensor systems designed to detect heavy metals and pharmaceutical residues in water and biological samples [33,43,44]. Recently, DESs have been explored as carriers for AgNPs in targeted drug delivery, wound healing, and skin-rejuvenating cosmetic formulations, leveraging the controlled release profiles and the inherent antimicrobial and anticancer properties of the nano-silver complexes. The milestones observed in using these green solvents for silver nanoparticle synthesis and their subsequent use in next-generation technologies and environmental remediation are schematically represented in Figure 3, which provides insight into the chronology of DES-based milestones and advancements in an ever-evolving research field. Several barriers still exist and overcoming them will be critical to effectively using the potential within these systems. Primary challenges involve optimizing the long-term stability of DES-based metallic nanostructures and ensuring their regulatory compliance for large-scale industrial manufacturing [42]. Furthermore, current research is actively focusing on the development of novel three-component deep eutectic solvents with inherent antimicrobial properties that can simultaneously act as both reducing and capping agents to further streamline the synthesis process.

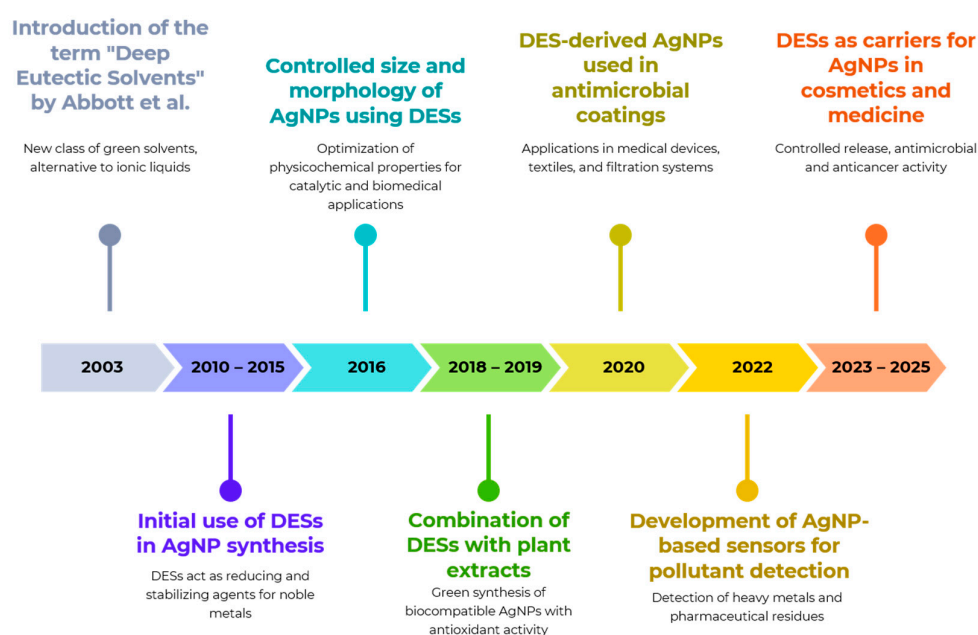


Figure 3. Milestones in the green synthesis of silver nanoparticles (AgNPs) using Deep Eutectic Solvents (DESs): introduction of DESs by Abbott et al. [37]; initial use in AgNPs synthesis [38,39]; controlled size and morphology [38]; combination with plant extracts [40,41]; antimicrobial coatings [14,38,42]; sensor development for pollutant detection [33,43,44]; and applications as carriers in cosmetics and medicine.

The general mechanism governing the DES-mediated synthesis of AgNPs is schematically illustrated in Figure 4. In DES-mediated systems, the eutectic mixture exhibits dual or singular functional behavior depending on its constituents. When composed of non-reducing HBAs and HBDs (such as choline chloride: urea), the DES acts primarily as a structured reaction medium, shape-directing agent, and electrostatic capping matrix [21,35]. Conversely, when functionalized with intrinsically reducing HBDs (like D-glucose, fruc-

tose, ascorbic acid), the eutectic matrix directly participates in the reduction of Ag^+ to Ag^0 , precluding the need for exogenous reducing additives [45,46].

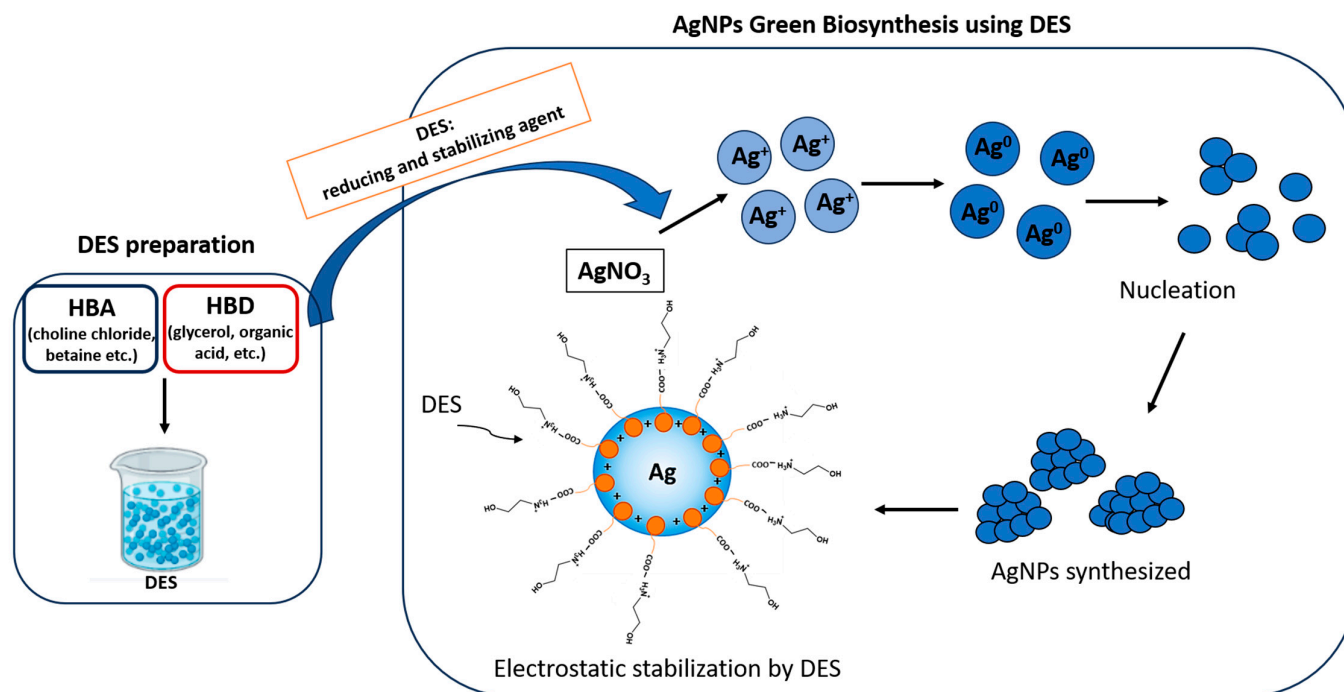


Figure 4. Green synthesis of silver nanoparticles (AgNPs) from AgNO_3 as the silver ion precursor, illustrating the dual role of the deep eutectic solvent (DES) as both a reducing and stabilizing agent leading to electrostatic stabilization.

Gold nanoparticles (AuNPs) were the earliest noble metals synthesized using NaDESs; for instance, Liao et al. (2008) reported a simple synthesis route using choline chloride-urea ($\text{ChCl}:\text{Urea}$) as a stabilizing agent [47]. Table 1 provides a selected overview of green synthesis of silver nanoparticles using Deep Eutectic Solvents, highlighting how their unique physicochemical profiles yield distinct nanostructures.

Table 1. Selected examples of green synthesis of silver nanoparticles using Deep Eutectic Solvents (DESs).

DES Composition	AgNPs Synthesis/ Conditions	AgNP Size/Shape	Applications	Ref.
Choline nitrate–glycerol (1:2) Choline chloride–glycerol (1:2) Choline acetate–glycerol (1:2)	AgNO_3 precursor with oleylamine (OAm) acting as a dual reducing /capping agent. Conventional heating in 60–70 °C, microwave-assisted heating at 100–230 °C for 30–240 s (P_{max} : 200 W).	7.6–11.5 nm (reaches 9.1 ± 2.9 nm under strictly dry conditions with 333 ppm water). Monodisperse spherical nanostructures. Stability: Soluble in toluene; stable for 30–40 days.	High-throughput continuous fabrication formatted for process intensification and structural scale-up loops.	[41]
Silver triflate–acetamide (1:4)	Conventional heating in 70 °C, rapid one-pot microwave-mediated reduction at 200 °C for 2 min (P_{max} : 200 W).	9–16 nm, highly monodisperse spherical nanocrystals. Stability: Attains high colloidal concentration of 54 mg mL^{-1} ; stable for over 82 days in toluene.	High-volume nanomanufacturing and process intensification for colloidal nanocrystals. Pushes batch output parameters to industrial scales (~58 g of AgNCs per kilogram of DES), effectively bypassing the mass bottlenecks of traditional microfluidic or highly diluted solution methods.	[40]

Table 1. Cont.

DES Composition	AgNPs Synthesis/ Conditions	AgNP Size/Shape	Applications	Ref.
D-glucose–urea–glycerol (1:1:2)	AgNO ₃ precursor (0.006 g) mixed with L-ascorbic acid (0.025 g) in DES (10.195 g). Stirred for 30 min at RT, centrifuged (7000 rpm, 10 min), and deposited on APTES-functionalized glass substrate.	Rod-like nanostructures with an average length of 122.6 nm. Stability: Colloidal shelf-life was not evaluated in liquid suspension (rapidly immobilized onto APTES-glass substrates); exhibited high thin-film substrate signal stability and reproducibility (SERS signal RSD: 4.69–11.95%)	High-performance SERS sensor substrate for detecting toxic antibiotic residues (NFTNitrofurantoin and SDZSulfadiazine) down to 10 ^{−8} M (<i>EF</i> = 6.29 × 10 ⁷ for NFT, 1.69 × 10 ⁷ for SDZ).	[48]
Betaine-glucose-ethylene glycol (1:1:3)	Silver salts (AgNO ₃ , AgC ₂ H ₃ O ₂ , or AgF). Stirring of the full mixture at 40 °C for 30 min under ambient pressure.	2.5 to 24.3 nm, granular, monodisperse spherical supramolecular assemblies. Stability: Superior colloidal longevity exceeding 180 to 500 days.	Highly suited for water-free industrial upcycling, plastics formulation, cosmetic matrices, and functional construction nanomaterials where standard water content would completely destroy the base material structure.	[49]
Betaine-glucose-ethylene glycol (2:1:3)		28 nm to 230 nm *, granular, monodisperse spherical supramolecular assemblies. Stability: Superior colloidal longevity exceeding 180 to 500 days.		
Betaine-ascorbic acid-ethylene glycol (2:1:3)				
Betaine-ascorbic acid-ethylene glycol (3:1:4)				
Betaine: D-Glucose (1:1)	AgNO ₃ precursor dissolved in glycerol and mixed directly into the glucose-based DES (DES-BG). Rapid mixing and heating for 5 min in an oil bath at 150 °C.	32–56 nm, spherical. Stability: Colloidal shelf-life was not evaluated in suspension (nanoparticles were directly incorporated into a carbon black composite electrochemical sensor).	Antibacterial activity, strong broad-spectrum action against Gram-negative <i>E. coli</i> and Gram-positive <i>B. natto</i> (ZOI: 11.3–13.4 mm). Efficacy at 50 µg/mL significantly outperforms standard penicillin controls at 60 µg/mL (<i>E. coli</i>) and 90 µg/mL (<i>B. natto</i>).	[50]
Choline chloride (ChCl): Diethanolamine (DEA) (1:3)	AgNO ₃ precursor mixed with sodium citrate/citric acid as protective/reducing agents within the DES matrix. Controlled heating at 80 °C for 30 min.	15.8–81.3 nm (TEM average: 51.7 nm; XRD crystallite size: 22.5 ± 2.1 nm; ~75% crystallinity; cubic crystallographic planes). Polycrystalline nanostructures with varied geometric shapes. Stability: Long-term liquid suspension shelf-life/zeta potential not quantitatively reported (nanoparticles were directly formulated into a CB composite electrochemical sensor exhibiting high repeatability, with RSD: 2.7–5.0%).	Fabrication of a nanostructured composite electrochemical sensor modified with carbon black (CB/GCE). Enhanced voltammetric detection of famotidine (FMT) in pharmaceutical formulations and synthetic urine.	[43]

* Ascorbic acid-driven DES formulations yield much broader distributions up to 230 nm due to aggressive reduction kinetics.

In 2025, Dlugosz et al. demonstrated that in glucose-betaine-ethylene glycol mixtures, AgNPs ranging from 2.5 to 24.3 nm are achievable, whereas betaine-ascorbic acid-ethylene glycol systems result in larger particle sizes ranging from 28 nm up to 230 nm. Betaine-glucose-glycol DES yields AgNPs of 3–10 nm with >180 days of stability. The use of glucose-betaine-ethylene glycol yields highly stable nanoparticles [49]. The gradual reduction of silver ions with glucose, which acts as a reducing agent, is performed with a highly favorable stabilization rate relative to the newly formed nanoparticles, resulting in an average diameter of 3–10 nm [49]. Depending on the specific compounds included in their composition, NaDESs allow the morphology of the produced nanomaterials to be directed [21,49]. In particular, the selected glucose serves a dual functional role, it actively participates in the development of the eutectic system with betaine, while simultaneously acting as a reducing agent for the synthesis of AgNPs [50]. This controlled reaction kinetics prevents rapid, uncontrolled crystal growth, thereby favoring the formation of numerous small nuclei over crystal growth. Furthermore, owing to the abundant hydroxyl groups in its chemical structure, glucose acts as a capping agent that forms a protective steric barrier around the nanoparticles, effectively suppressing agglomeration [45,46]. Crucially, NaDES parameters such as viscosity, conductivity and surface tension prevent aggregation and agglomeration of the nanoparticles, ensuring that their stability within the NaDES system is maintained over time [21,51]. The chemical reduction of Ag⁺ within DES media

produces distinct reaction by-products governed by the specific hydrogen bond donor (HBD) oxidized during nucleation. When reducing sugars such as D-glucose serve as the functional HBD, the reduction of Ag^+ to Ag^0 is coupled with the selective two-electron oxidation of the aldehyde moiety to carboxylate species, primarily yielding gluconic acid along with its corresponding lactone forms [45,52]. In polyol-based systems, including glycerol, and ethylene glycol operating under elevated thermal or microwave conditions, partial sacrificial oxidation generates trace aldehydes and ketones, such as glyceraldehyde and dihydroxyacetone [49,50]. Concurrently, the nitrate ions (NO_3^-) originating from standard AgNO_3 precursors remain solubilized within the ionic matrix or undergo minor thermal dissociation.

3.2. Synthesis of AgNPs Using Plant Extracts

Plant-assisted pathways to AgNPs have been established as sustainable alternatives to conventional physical and chemical synthesis methods [24,25]. Using plant extracts as the reducing, capping and stabilizing agent can minimize energy demand, avoid toxic reagents, and instill a biologically compatible surface corona that often improves colloidal stability and cellular interactions. Phytochemicals play a crucial role in the green synthesis of AgNPs, providing an environmentally friendly alternative to conventional methods. Among the most suitable phenolic compounds for this purpose are polyphenols, most notably flavonoids and tannins. These bioactive compounds found in high yield in many plant sources, with strong antioxidant properties and demonstrate high efficiency as reducing agents [24]. Flavonoids are particularly effective in developing AgNPs while tannins reduce metal ions and facilitate the stabilization of the synthesized nanoparticles [24,53]. Furthermore, another key class includes terpenoids which have demonstrated their ability to facilitate the formation of AgNPs, while alkaloids through nitrogen-containing functional groups provide complementary electron-transfer routes [53,54]. By their amphiphilic structure, saponins act as naturally occurring surface-active agents that reduce surface tension, optimize colloidal dispersibility, and prevent aggregation through steric stabilization. Their integration substantially contributes to colloidal stability and the uniformity of the synthesized nanoparticles. Proteins offer amino, carboxyl, and thiol groups that facilitate metal ion binding, reduction, and strong coordination interactions with nanoparticle surfaces, while polysaccharides act as biocompatible capping agents, forming a hydrophilic protective system that inhibits aggregation and promotes homogeneous dispersion [53]. The overall efficiency of these phytochemicals depends on parameters such as reducing power, stabilizing capability, biocompatibility, and specificity for AgNPs. Often, plant extracts contain a mixture of these compounds which can operate synergistically to develop nanoparticles with tailored physicochemical properties.

Table 2 summarizes the latest literature on AgNPs synthesis using plant extracts, indicating, their role and characteristics in the synthesis. For example, *P. edulis* leaf extracts are rich in phenolic compounds such as C-glycosyl flavones (vitexin, isovitexin, orientin, isoorientin) and other phenolics characterized as reducing agents (donating electrons to convert $\text{Ag}^+ \rightarrow \text{Ag}^0$) and as capping ligands that selectively passivate expanding crystal facets, reflecting core principles established throughout plant-mediated AgNP synthesis. Phenolic compounds accelerate nucleation over crystal growth, thereby producing smaller cores at a given AgNO_3 concentration, whereas polysaccharides provide steric stabilization that slows growth while suppressing agglomeration, often accompanied by more negative zeta potentials and improved shelf stability [12,55]. Reaction pH is also a key point of nanosynthesis: while mildly alkaline conditions (≈ 8 – 10) accelerate reduction to yield small, monodisperse quasi-spherical nanoparticles, acidic conditions retard reduction kinetics and broaden particle size distributions. According to the reaction mechanism, *P. edulis* leaf

extracts are enriched in flavonoids and drive the formation of smaller silver cores, whereas pectin-rich peel extracts furnish a robust protective network that yields slightly larger, highly stable nanostructures. Tural et al. investigated *P. khinjuk* plant extracts for the green synthesis of AgNPs, emphasizing the significant influence of gender-specific phytochemical differences on nanoparticle properties. Female root extracts facilitated the synthesis of smaller and more stable AgNPs with superior antioxidant and antibacterial activities compared to male root extracts. The synthesized AgNPs exhibited distinct properties based on the gender of the root extracts. Female root-derived AgNPs had a more negative zeta potential, smaller particle size, and higher phenolic content, which collectively enhanced their stability and bioactivity. These nanoparticles demonstrated stronger antioxidant and antibacterial activities, as evidenced by superior performance in DPPH, ABTS+, and FRAP assays and larger inhibition zones against bacterial strains. Additionally, the slightly higher yield of AgNPs from female root extracts highlights their efficiency in nanoparticle production. The findings underline the importance of leveraging gender-specific phytochemical differences in plants for sustainable nanoparticle synthesis. The superior properties of female root-derived AgNPs make them promising candidates for biomedical and industrial applications. This research provides a sustainable and eco-friendly alternative to conventional methods while promoting the innovative use of agricultural byproducts [56].

In 2024, Mojela et al. analyzed aqueous extracts derived from Citrus Limon peels, Aloe vera leaves, Capsicum annum fruits, Salix alba bark, Crinum asiaticum Linn leaves, and Crinum macowanii bulbs, which were successfully utilized in a green chemistry procedure to synthesize silver nanoparticles (AgNPs). These local plant components were strategically selected due to their high content of bioactive phytochemicals, including flavonoids, alkaloids (such as rutin and tryptamine), tannins, polyphenols, and amides. Within the water solvent framework, these organic compounds played a dual role, functioning both as reducing and stabilizing/capping agents. Specifically, polyols, phenolic compounds, and amide groups within the extracts facilitated the chemical reduction of silver ions from Ag^+ to Ag^0 . Concurrently, these phytochemicals formed an encapsulating coating layer around the newly developed metallic crystals, effectively stabilizing the AgNPs and preventing undesirable agglomeration and aggregation [57]. Despite the sustainability and simplicity of plant-assisted synthesis, standalone plant-based extracts present notable inherent constraints [24,26]. First, significant batch-to-batch phytochemical variability is driven by temporal, geographic, and climatic factors, as well as plant maturity, which often compromises the reproducibility of nanoparticle size, polydispersity, and batch yield [26,56]. Second, standard aqueous extractions exhibit poor recovery efficiency for hydrophobic and poorly water-soluble secondary metabolites (like specific aglycones, non-polar flavonoids, and terpenoids), consequently limiting the full reducing capacity of the biomass [14,15]. Third, aqueous phyto-synthesized colloidal suspensions frequently suffer from limited long-term shelf stability; the low viscosity of water permits rapid mass transport/diffusion, secondary aggregation, and progressive precipitation over extended storage [18,58].

Table 2. Selected recent examples of synthesis of silver nanoparticles (AgNPs) using plant extracts.

Plant Extracts	Phytochemical Characterization	AgNP Synthesis Conditions	AgNP Size/Shape	Applications	Ref.
<i>Plathymenia reticulata</i> bark extract	TPC: 34.36 mg GAE/g TFC: 7.15 mg CE/g Condensed tannins: 9.58 mg CE/g.	3 mM AgNO_3 (1:10 ratio, 100 mL extract to 1000 mL AgNO_3), stirring at 70 °C for 15 min.	43.6 ± 12.5 nm (DLS)/9–23 nm (SEM), predominantly spherical.	Antioxidant activity, cyto- and phytotoxicity assessment in <i>Allium cepa</i> .	[59]
<i>Galega officinalis</i> leaf extract	Rich in flavonoids, alkaloids, and saponins.	Aqueous leaf extract boiled at 100 °C for 5 min, 1.5 mM AgNO_3 , pH 11, stirring at RT * for 24 h.	43–42.4 nm (TEM)/25.07 nm (DLS), predominantly spherical, polydisperse (PDI: 0.39), Zeta: −22 mV.	Insecticidal/nanopesticide activity against <i>T. confusum</i> , <i>E. kuehniella</i> , <i>S. granarius</i> , and <i>P. interpunctella</i> .	[60]

Table 2. Cont.

Plant Extracts	Phytochemical Characterization	AgNP Synthesis Conditions	AgNP Size/Shape	Applications	Ref.
<i>Cinnamomum zeylanicum</i> Blume post-distillation waste (CDW)	TPC: 560.58 ± 9.49 mg GAE/g extract, Rich in trans-cinnamaldehyde, eugenol, and cinnamic acid.	CDW extract mixed with 1 mM AgNO ₃ (1:50 v/v), pH 11, stirring at 80 °C for 120 min.	13–23 nm (TEM) /57.19 nm (DLS), spherical, crystalline structure.	Antibacterial (<i>S. aureus</i> , <i>E. coli</i>), antioxidant, anti-inflammatory (A5-LOX, NO inhibition), non-toxic to Vero cells.	[61]
<i>C. fistula</i> L. Fruit extract (alginate-encapsulated)	Rich in phenolics, flavonoids, terpenoids, and alkaloids.	0.5 mL aqueous extract mixed with 200 mL of 0.5 M AgNO ₃ at RT * for 24 h. Encapsulated in 3.0% sodium alginate and crosslinked with 2.0% CaCl ₂ .	Average size: 43 nm (SEM), crystallite size: 30 nm (XRD), face-centered cubic structure, spherical.	Anticancer against HCT-116 (IC ₅₀ : 28 µg/mL, induces ROS and G2/M arrest; safe for MCF-10). Antimicrobial against <i>P. aeruginosa</i> , <i>A. baumannii</i> , MRSA, and <i>C. albicans</i> .	[62]
<i>Moringa oleifera</i> leaf extract	Rich in proteins, sugars, and polyphenols (flavonoids/terpenoids).	9 mM Ag ₂ SO ₄ mixed with extract, pH adjusted with 5 mM NaOH, stirred at 25 °C.	80–150 nm (SEM) /118.5 nm (DLS), predominantly spherical, monodisperse (PDI: 0.29), Zeta: −18.6 mV.	Antibacterial and antibiofilm agent against ESKAPE pathogens (MIC: 11–43.8 µg/mL). Additive effects with chlorhexidine against <i>K. pneumoniae</i> . Highly biocompatible (CC ₅₀ > 150 µg/mL).	[63]
<i>Azadirachta indica</i> (neem) leaf extract	Rich in alkaloids, flavonoids, and tannins.	5 mM AgNO ₃ mixed with 10% w/v aqueous extract (2:5 v/v), alkaline pH adjusted with 1% ammonia, incubated at RT for 1 h in the dark.	10–50 nm (SEM) /624.1 nm (DLS), spherical, crystalline FCC structure.	Antibacterial activity against <i>S. typhi</i> , <i>S. aureus</i> , <i>K. pneumoniae</i> , and <i>B. cereus</i> (MIC: 100 µg/mL).	[64]
<i>Clitoria ternatea</i> leaf extract	Rich in alkaloids, glycosides, and flavonoids.	5% extract mixed with 100 mM AgNO ₃ , pH 9.0, reaction temperature 45 °C for 24 h.	(SEM), crystalline size: ~20 nm (XRD), granular and moderately aggregated spherical.	Anticancer activity against breast cancer MDA-MB-231 cells (IC ₅₀ : 79.49 µg/mL). Antimicrobial efficacy against <i>B. subtilis</i> , <i>S. aureus</i> , <i>K. pneumoniae</i> , and <i>E. coli</i> .	[65]
<i>Pistacia khinjuk</i> root extract (Gender-specific: Female vs. Male)	Rich in polyphenols, flavonoids, alkaloids, and terpenoids. Female roots (FRs) exhibit significantly higher total phenolic content (20.56 mg GAE/g) than male roots (MRs).	10 mM AgNO ₃ mixed with aqueous extract (9:1 v/v) at 25 °C. FR-AgNPs achieve optimal SPR in 40 min, while MR-AgNPs require 30 min.	FR-AgNPs: 150.1 nm (DLS)/<50 nm (TEM), spherical, highly stable (Zeta: −32.5 mV). MR-AgNPs: 213.8 nm (DLS), Zeta: −21.36 mV.	Enhanced antioxidant (DPPH IC ₅₀ : 18 µg/mL) and antibacterial (<i>S. aureus</i> , <i>E. coli</i>) activities for female root-derived nanoparticles.	[56]
<i>Passiflora edulis</i> (leaf or peel extract)	Leaf: C-glycosyl flavones (vitexin, orientin), quercetin, caffeic acid. Peel: Pectin-rich (GalA-rich) and phenolics.	AgNO ₃ precursor, pH (~8–9), ~40–60 °C for 30–120 min.	10–50 nm (Leaf: 15–25 nm; Peel: 20–35 nm), spherical/quasi-spherical, stable negative Zeta potential (≤ −20 to −25 mV).	Anticancer against MCF-7 (IC ₅₀ : 25 µg/mL) and SW480 cells via ROS generation and mitochondrial apoptosis. Antibacterial against <i>E. coli</i> , <i>S. aureus</i> , and <i>B. subtilis</i> .	[25]
<i>Boerhavia diffusa</i> extract	Rich in alkaloids, flavonoids, phenols, punarnavine, and boeravinones. Flavonoids and polyphenols drive antioxidant/reduction pathways.	Aqueous extract mixed with 0.02 N AgNO ₃ at a standardized 2:8 (v/v) ratio; incubated at RT for 6 h.	30–40 nm (FESEM), crystallite size: 34 nm (XRD), face-centered cubic crystal structure, spherical.	Anticancer activity against cervical cancer cells (HeLa IC ₅₀ : 45.47 µg/mL) via apoptosis. Antioxidant activity (78.57% DPPH scavenging at 0.5 µg/mL).	[66]
Neem (<i>Azadirachta indica</i>) and turmeric (<i>Curcuma longa</i>) extracts	Combination of neem and turmeric bioactive components.	Extract (1:1 w/w ratio) mixed with AgNO ₃ solution (1:4 v/v), stirring at 700 rpm at RT for 24–48 h.	4 nm to 14.81 nm (XRD crystalline size), spherical, uniform morphology (SEM), 59.5% crystalline/40.5% amorphous.	Antimicrobial agent for oral healthcare. High efficacy against <i>S. aureus</i> , <i>Lactobacillus</i> spp., and <i>S. mutans</i> ; less effective against <i>C. albicans</i> .	[67]

Table 2. Cont.

Plant Extracts	Phytochemical Characterization	AgNP Synthesis Conditions	AgNP Size/Shape	Applications	Ref.
<i>Aloe vera</i> leaves, <i>Citrus limon</i> peels, <i>Capsicum annuum</i> fruit, <i>Crinum macowanii</i> bulbs, <i>Crinum asiaticum</i> leaves, and <i>Salix alba</i> bark.	Rich in alkaloids, amides, and UV-fluorescent flavonoids (rutin, tryptamine). Capping regulated by polyols and amides.	Extract mixed with AgNO ₃ (0.03 M for barks/bulbs; 0.6 M for peels/fruits) in water; boiled at 70 °C for 10–20 min.	13–35 nm (TEM range based on plant source), predominantly spherical, face-centered cubic crystalline structure.	Enhances luminol sensitivity, specificity, and chemiluminescence (>45 min signal). Detects blood on fabrics and hidden under 3 layers of paint. Extracts serve as UV-fluorescent substitutes (365/254 nm).	[57]
<i>Jatropha maheshwarii</i> leaf extract	Rich in phenolics, flavonoids, alkaloids, and terpenoids.	1 mM AgNO ₃ precursor mixed with aqueous extract (1:10 v/v) and heated at 60 °C for <12 h.	25.98 nm (XRD), topography range: 15–100 nm (AFM), spherical and flakes-shaped, polydisperse.	High antibacterial potency against <i>S. typhi</i> (ZOI: 19 mm at 100 µg/mL), <i>P. aeruginosa</i> , <i>S. aureus</i> , <i>B. thuringiensis</i> , and <i>E. coli</i> . Induces cytoplasmic leakage of proteins and reducing sugars.	[68]

* RT = room temperature.

3.3. Synergetic AgNP Synthesis in DES-Based Plant Extracts

The synergistic integration of Deep Eutectic Solvents (DESs) combined with biological plant extracts represents a strategic approach that maximizes the efficiency and sustainability of the green synthesis of silver nanoparticles (AgNPs). As demonstrated in Table 3, although the literature is recent and limited, the choice of DES composition does not function merely as a solvent, but rather as a eutectic system that enhances the recovery of bioactive compounds. These systems notably enhance the extraction of poorly water-soluble bioactive components like flavonoids and terpenes, which are frequently inaccessible through conventional aqueous processing [69]. The hydrogen-bonding framework of eutectic system effectively solubilizes these bioactive phytochemicals, where they can directly participate in nanoparticle nucleation and growth [15,70]. Consequently, DES-based plant extracts provide three main roles: acting simultaneously as the extraction solvent, the primary reducing agent for silver ions (Ag⁺), and the capping/stabilizing agent that dictates colloidal integrity. A systematic evaluation of the literature compiled in Table 3 reveals clear mechanistic correlations between the chemical architecture of the DES system, the biological origin of the extract, and the resulting physicochemical profiles of the synthesized AgNPs. The utilization of diverse plant-derived systems, such as *Camellia sinensis* (green tea) [71], and agro-industrial residues like peach pomace [70], and grape pomace [14], supplies a wide variety of secondary metabolites, including polyphenols, catechins, anthocyanins, and organic acids. Upon reaction, these bioactive compounds donate electrons to reduce Ag⁺ silver ions to Ag⁰ stable silver. Simultaneously, their functional moieties bind to the emerging metallic surfaces, establishing robust steric and electrostatic repulsion barriers that suppress uncontrolled crystal growth and secondary particle agglomeration [33].

This synergistic interaction between DES and biological reductants offers a significant advantage over conventional methods, enabling the production of highly stable and biocompatible silver nanoparticles [71]. The AgNP sizes observed ranged from 10–20 nm to maximum 53–161 nm in the betaine: glycerol (1:2) eutectic system, with predominantly spherical morphologies. Smaller nanoparticles (10–20 nm) are typically obtained using peach pomace [15] and grape pomace extracts [14] or DESs containing lactic acid, or lactic acid and glucose, whereas larger and more irregular nanoparticles (53–161 nm) are usually formed with green tea extracts in DESs based on betaine and glycerol or urea [48]. Analysis of the data indicates that DES-mediated biogenic AgNPs have multiple applications, including antimicrobial, catalytic, environmental remediation, and other functional uses.

This versatility underscores the potential for developing advanced materials for diverse sectors, from medicine to industrial catalysis [72].

Table 3. Selected examples of synergetic biogenic synthesis of silver nanoparticles using DES-based plant extracts.

DES Composition	Plant Source	Phytochemical Characterization	AgNP Synthesis/ Conditions	AgNP Size/Shape	Applications	Ref.
Betaine: Glycerol (1:2), Glycerol: Urea (1:1), Betaine: Urea (1:2), Glycerol: Urea (1:1)	Green tea (<i>Camellia sinensis</i>) leaves.	Highly enriched in catechins (EC, EGC, ECG, EGCG). DES extraction provides up to 235% higher catechin yields.	DES-based extract and 2 mM AgNO ₃ solution are mixed. Stirred in the dark at RT for 24 h.	43.11 ± 6.42 nm (Betaine:Urea), 39.12 ± 5.33 nm (Glycerol:Urea), 53–161 nm (Betaine: Glycerol) (DLS), spherical or nearly spherical. Stability: Stable for over 2 months at 4 °C.	In vitro anti-cancer activity (Dose-dependent cytotoxicity against human liver cancer cells (Hep G2)); at a dosage of 60 µg/mL, achieves an anti-proliferative apoptotic index fully comparable to doxorubicin standard drugs at 12.5 µg/mL.	[71]
Betaine: Lactic acid (2:1)	Grape Pomace (GPE).	Rich in hydroxycinnamic acids (~23%) and anthocyanins (~19%). Contains gallic acid (792.4 µg/g), (+)-catechin (511.3 µg/g), and caffeic acid (164.5 µg/g).	0.01 M AgNO ₃ mixed with GPE-DES extract (1:1 v/v). Heated in a water bath at 40 °C for 15 min.	10–20 nm (SEM)/15–20 nm (TEM), spherical (flattened spheroids), face-centered cubic crystalline structure (XRD). Stability: Colloidally stable for >1 month.	Antibacterial against <i>B. subtilis</i> (ZOI: 16 mm) and <i>E. coli</i> (ZOI: 9 mm).	[14]
Betaine: Lactic acid (1:2) Proline: Lactic acid (1:2)	Grape Pomace (GPE).	Hydroxycinnamic acids (~23%) and anthocyanins (~19%). Rich in gallic acid, (+)-catechin, and caffeic acid.	0.01 M AgNO ₃ mixed with GPE-DES extract (1:1 v/v). Heated at 40 °C for 15 min.	10–20 nm (SEM), spherical/round shape, wrapped. Stability: Colloidally stable for >1 month.	Antibacterial against <i>E. coli</i> and <i>B. subtilis</i> . Biocompatible nanotherapeutic raw material; safe for <i>Allium cepa</i> root models up to 10% dosage.	[15]
Lactic acid:glucose: water (5:1:3)	Peach Pomace (<i>Prunus persica</i> L. agrowaste).	Rich in chlorogenic acid (10.001 µg/g), gallic acid, ferulic acid, and quercetin-3-O-glucoside.	UAE extraction (27 kHz, 6 W/cm ² , 65 °C, 50 min) with hydromodule 1:20 to 1:45. Subsequently reduced with AgNO ₃ at 50 °C, diluted with 20% water.	10–20 nm (TEM/SEM), stable monodisperse spherical cores, face-centered cubic structure. Stability: N/A	Multifunctional green nano-catalyst and biocide. High catalytic efficiency for methylene blue degradation (completed in 11 min). Potent antimicrobial activity at low ranges (23–36 nM) against <i>E. coli</i> (ZOI: 11 mm), <i>S. aureus</i> (ZOI: 9 mm), and <i>C. albicans</i> .	[70]

To provide comprehensive insight into the chemical and structural enhancements offered by this synergistic approach, the distinct nucleation and stabilization pathways of conventional plant extractions are directly contrasted against DES-mediated systems in Figure 5. While traditional aqueous extractions often struggle with limited stability and uncontrolled particle growth, the application of DES-based environments facilitates a more uniform reduction process, ultimately refining the physicochemical properties of the synthesized nanoparticles [73]. This strategic integration of green chemistry principles not only minimize harmful reagents to synthetic precursors but also promote scalable, reproducible synthesis protocols for advanced nanomaterial fabrication [74,75]. Furthermore, the precise modulation of synthesis parameters, such as precursor concentration and temperature, is key to establishing large-scale commercial production processes that maximize the conversion of these reagents into high-quality nanoproducts [76]. Ultimately, optimizing these factors remains a critical requirement for scaling production and ensuring the long-term chemical stability of nanoparticles intended for specialized clinical or industrial utility [77].

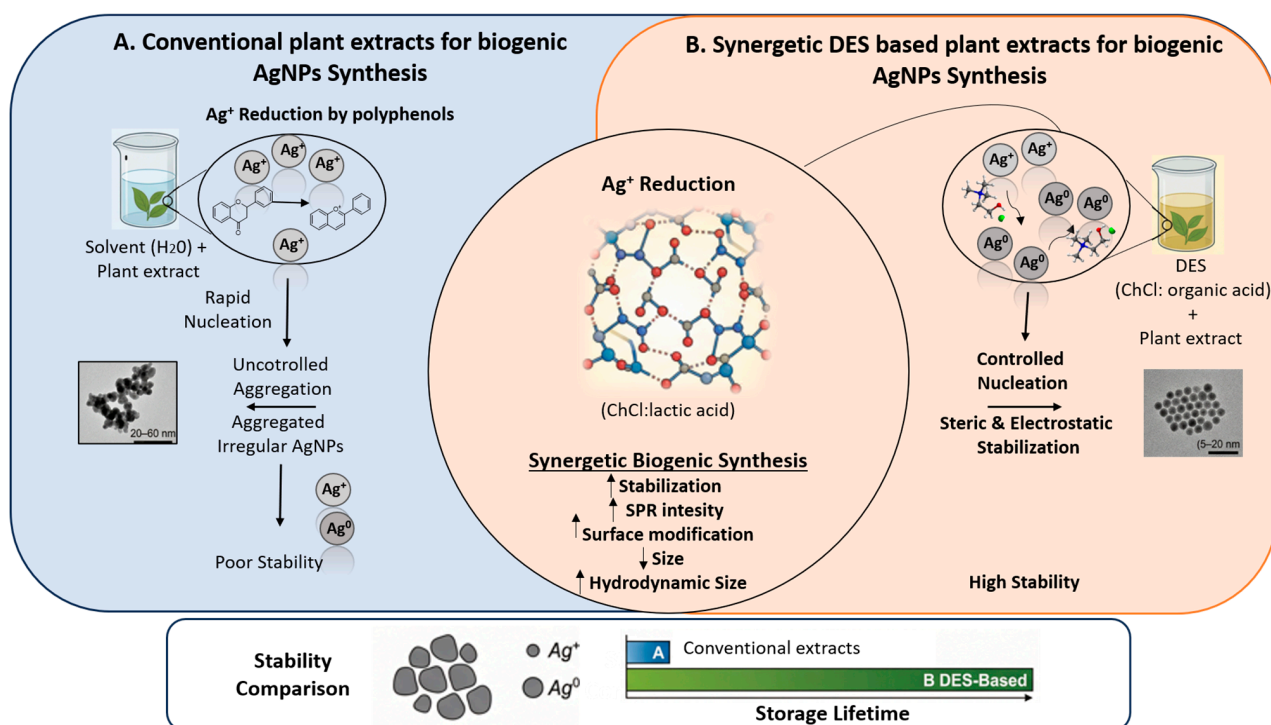


Figure 5. Comparative representation of the biogenic synthesis of silver nanoparticles (AgNPs): (A) Conventional method using plant extracts, which is characterized by rapid nucleation and uncontrolled aggregation. This process typically results in aggregated, irregular AgNPs with poor stability. (B) Synergistic approach using DES-based plant extracts, which achieves controlled nucleation and enhanced steric/electrostatic stabilization, where upward and downward arrows indicate an increase and decrease of the parameters, respectively.

As illustrated in Figure 5A, conventional biogenic synthesis utilizing complex aqueous plant extracts often suffers from rapid, unhindered nucleation pathways. In this approach, the high kinetic rate of silver reduction Ag^+ to Ag^0 is not sufficiently balanced by structural stabilization, leading to uncontrolled particle aggregation and the formation of irregular, polydisperse AgNP architectures characterized by poor long-term colloidal stability. Alternatively, the innovative DES-mediated approach (Figure 5B) exhibits a regulated, two-fold synergetic mechanism. Firstly, the extensive hydrogen-bonding network and high viscosity of the deep eutectic mixture impose strict mass transfer and diffusion limitations [21,22,39], effectively constraining the kinetics of crystal nucleation and preventing rapid growth. Secondly, the functional groups of the DES from secondary metabolites (such as sugars, organic acids) organize symmetrically around the newly formed silver cores. This architecture establishes powerful electrostatic and steric barriers, imparting superior colloidal stabilization and providing highly uniform, monodisperse spherical AgNPs with enhanced chemical stability [21,44,48]. Several environmental factors influence the yield, size, morphology, and stability of AgNPs during synthesis. Optimizing these factors is essential to achieving desired physicochemical properties. Variables such as concentration of the plant extract, temperature, pH, AgNO_3 concentration, and reaction time can greatly influence the physicochemical properties and activity of AgNPs [33,44,46]. Notably, the stability of AgNPs is highly affected by the pH and temperature, as their extreme levels negatively influence the nanoparticle formation and long-term storage time. For instance, while higher temperatures can accelerate the formation of AgNPs (with optimum levels typically around 40°C), lower temperatures can help maintain their long-term stability during storage. Similarly, pH is also a key point of synthesis of AgNPs: while mildly alkaline conditions ($\approx 8\text{--}10$) accelerate reduction to yield small, monodisperse quasi-spherical nanoparticles,

acidic conditions retard reduction kinetics and broaden particle size distributions. Consequently, the synergy between polyphenolic electron release and eutectic-controlled mass transfer establishes the fundamental basis for structural homogeneity and long-term colloidal stability. Additionally, the chemical interaction between phenolic aromatic rings and metal ions facilitates an effective complexation process that controls the ultimate core size [78]. Coordinating functional groups, including -OH and -NH₂ groups, bind directly to the nanoparticle surface [79], modulating interfacial electron density and inhibiting the tendency of newly formed particles to grow into larger, less stable nanoparticles [58,80]. The wide variety of functional groups provided by plant extracts thus enables a synergistic stabilization system, where both electrostatic repulsion and steric hindrance act synergistically with the eutectic solvent to maintain a highly uniform particle size distribution [18]. The synergistic mechanism operating in DES–plant extract systems is driven by a clear division of roles between the plant extract and the eutectic mixture. The plant extract acts as the primary electron donor, where phenolic hydroxyl groups donate electrons to reduce Ag⁺ to Ag⁰ [58,81]. At the same time, the DES acts as a reaction template that regulates diffusion. The high dynamic viscosity of deep eutectic solvents imposes severe diffusion limitations on dissolved silver cations. It is observed that the diffusion coefficient of silver ions is reduced by one to two orders of magnitude in eutectic media compared to aqueous solutions [21,82]. This suppressed mass transfer slows the crystal growth rate relative to the nucleation rate, effectively decoupling nucleation from subsequent particle growth [18,21]. Consequently, the system favors the rapid formation of numerous small nuclei while preventing uncontrolled secondary growth, resulting in monodisperse, spherical nanoparticles (10–20 nm) with enhanced colloidal stability [15,71]. A critical synthesis of the physicochemical characterization data summarized in Table 3 highlights the direct structure–property relationships governed by the eutectic mixture. Morphologically, the synergistic interaction between DES components and plant secondary metabolites yields mainly spherical and near-spherical nanoparticles, with particularly narrow core diameters typically falling within the 10–20 nm range for agro-waste extracts (like grape and peach pomace), in contrast to the broader polydisperse structures often obtained via conventional aqueous routes [14,70]. Finally, the evaluation of colloidal stability demonstrates the superior shelf life of AgNPs prepared with DES, which maintain stable surface plasmon resonance (SPR) profiles and resist aggregation or sedimentation for extended periods (>1 to 2 months). This durability is due to the strong electrosteric stabilization, which is caused by high negative surface charges (zeta potentials often exceeding –25 to –32 mV) and the physical capping barrier exerted by the surrounding supramolecular DES system [15,71].

4. Applications, Challenges, and Scalability

AgNPs synthesized via synergistic DES - extract synthesis demonstrate potent broad-spectrum antibacterial efficacy against both Gram-negative (*E. coli*, *P. aeruginosa*) and Gram-positive (*S. aureus*, *B. subtilis*) strains, often exhibiting improved biocidal performance at nanomolar concentrations compared to conventional aqueous analogs [14,15]. In biomedical therapeutics, DES-stabilized AgNPs have demonstrated selective, dose-dependent cytotoxicity against human cancer cell lines (such as HepG2 and HeLa) through the production of intracellular reactive oxygen species (ROS) and apoptotic induction [3,71]. Furthermore, in environmental remediation and sensing, these nanostructures provide high catalytic degradation rates for persistent organic pollutants and serve as sensitive SERS/electrochemical sensor platforms for the detection of trace pharmaceutical and antibiotics [6,33]. Despite these advantages, transferring DES-assisted nanosynthesis to an industrial scale requires overcoming key mechanical barriers [44]. The high viscosity of

eutectic solvents can hinder mass transfer on a large scale, requiring elevated operating temperatures or controlled dilution with benign antisolvents (like water, ethanol) to optimize mixing in continuous-flow reactors [42,43]. Downstream purification and solvent recovery remain critical for the overall economics of the process. Methods such as ultra-filtration, centrifugation, and antisolvent-induced precipitation have shown promising results for the isolation of AgNPs, while allowing the recycling of DES in multiple operational cycles [42,44]. From a life cycle assessment (LCA) perspective, eutectic synthesis significantly reduces environmental E-factors by replacing hazardous reducing agents (NaBH_4 , hydrazine) and volatile organic solvents with biodegradable, non-volatile components, supporting the completion of the circular economy through the valorization of agro-industrial by-products [16,44].

5. Conclusions

The integration of Deep Eutectic Solvents (DESs) and Natural Deep Eutectic Solvents (NaDESs) with biogenic plant extracts represents an eco-friendly and alternative green synthesis of silver nanoparticles. This review highlights that DES systems do not act merely as sustainable extraction solvents, but function as active, tailored reaction media that enhance the extraction of bioactive phytochemicals and cooperatively direct nanoparticle nucleation, morphology, and long-term colloidal stability. Furthermore, by successfully utilizing agro-industrial by-products, such as grape pomace and peach pomace, this synergistic technology aligns perfectly with the principles of the circular economy, effectively upcycling organic waste into high-added-value nanomaterials. Future research must systematically investigate the engineering aspects of scaling up these processes, addressing the high intrinsic viscosity of certain DES systems, optimizing mass transfer limitations in large-scale reactors, and developing cost-effective solvent recovery and recycling approaches to ensure long-term economic viability. Additionally, further comprehensive investigations into the specific molecular mechanisms driving the interactions between constituent DES components and phytochemicals during nucleation are highly necessary to refine current synthetic methodologies and customize AgNP properties for targeted applications. These significant breakthroughs are particularly crucial given the rapidly growing demand for biocompatible silver nanoparticles in advanced biomedical applications, including advanced antifungal, antiviral, and antibacterial agents, where parameters like surface morphology, core diameter, and surface charge determine clinical efficacy and toxicological safety.

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