

# Green Chemistry Approaches for the Sustainable Synthesis of Nanomaterials: Biogenic Routes, Characterization, and Application Prospects

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## ABSTRACT

The present review is a critical review of green chemistry-based pathways for the sustainable production of nanomaterials, with a specific focus on biogenic and environmentally friendly approaches. The discussion begins by defining the fundamentals of nanomaterials synthesis and contrasting conventional top-down and bottom-up methods with green principles. Common methods used in the literature, such as sol-gel, hydro/solvothermal synthesis, chemical vapor deposition, and microemulsion, typically use hazardous precursors, toxic organic solvents, and conditions of high energy consumption, which are inconsistent with waste prevention, safer solvents, and energy conservation. The paper further investigates how the concept of green chemistry, particularly the use of less hazardous solvents and auxiliaries, renewable feedstocks, catalysis, and naturally safer design, has been transformed into real-world plans, such as plant- and microbe-mediated synthesis, aqueous and solvent-free reactions, and process synthesis (mixtures using a microwave, ultrasound, or mechanochemistry). The consideration is on how the natural reducing and capping agents (phytochemicals, polysaccharides, proteins, and microbial metabolites) control the nucleation, growth, particle size, morphology, and colloidal stability and how the systems can reduce toxicity and enhance atom economy at the same time. The review also outlines the main characterization methods—UV-Vis, FTIR, XRD, TEM/SEM, DLS, and zeta potential—and how to use these methods to verify the successful green synthesis, clarify surface chemistry, and correlate structure and surface properties to the catalytic, environmental, and antimicrobial activity. Lastly, the paper concludes with a synthesis of the existing literature on environmental, economic, and safety concerns; highlights the key challenges, including scalability, reproducibility, and incomplete mechanistic knowledge; and provides the future directions of process intensification, life cycle-based sustainability measures, and the implementation of green nanomaterial synthesis in the context of a circular economy and industry.

**Keywords:** Green chemistry; sustainable synthesis; nanomaterials; biogenic nanoparticles; plant-mediated synthesis; green reducing and capping agents; characterization; environmental applications.

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## Introduction

The definition of nanomaterials is usually based on the fact that at least one of the dimensions should be within the 1-100 nm size scale, whereby the surface area to volume ratio is very high and quantum confinement effects dominate the properties of the material, unlike as seen in its bulk state (Guzman et al., 2012; Jeevanandam et al., 2018). Thanks to these size-dependent characteristics, including increased catalytic efficiency, tunable optical behavior, and altered electrical and mechanical behavior, nanomaterials have received a great deal of interest in the fields of chemistry, materials science, physics,

and biology (Khan et al., 2019; Sharma et al., 2019). The dimensions can be categorised into zero-dimensional (e.g., nanoparticles and quantum dots), one-dimensional (e.g., nanorods, nanotubes and nanowires), two-dimensional (e.g., nanosheets and thin films) and three-dimensional nanostructured networks, all of which provide particular morphologies and capabilities that may be designed using suitable synthetic strategies (Jeevanandam et al., 2018; Singh et al., 2020). Consequently, nanomaterials have become part of their use in catalysis, energy conversion and storage, environmental remediation, sensing, and biomedicine (Khan et al., 2019; Singh et al., 2020).

Notwithstanding all these benefits, much of the traditional physical and chemical process of producing nanomaterials is highly concerning the environment, health, and safety. Solvents that are hazardous, toxic organic solvents, high temperature or pressure, and energy conditions are commonly used in traditional methods (sol-gel processing, chemical vapour deposition, hydrothermal and solvothermal, microemulsion, and flame spray pyrolysis) (Iravani, 2011; Siddiqui et al., 2018). The processes may lead to significant energy usage and production of toxic products and solvent wastes that need special attention and treatment, as well as increasing the ecological footprint and cost of the process (Siddiqui et al., 2018; Singh et al., 2020). In most instances, synthetic protocols are based on obtaining fine control of particle size and morphology, whereas environmental and safety concerns are secondary and tackled at the final point of the procedure via remediation or waste disposal (Iravani, 2011; Khan et al., 2019). Such end-of-pipe design is viewed as increasingly being incompatible with modern sustainability objectives, which highlights the necessity of reducing hazard and waste during chemical processes design (Anastas and Warner, 1998; Clark et al., 2012).

Green chemistry offers a holistic approach to reconsidering the process of nanomaterial production in terms of being more sustainable and safer per se. It is expressed by 12 principles that promote waste reduction, atom economy, the use of less harmful solvents and auxiliaries, the design of less hazardous syntheses, the use of renewable feedstock, energy conservation, catalysis and inherently safer products and processes (Anastas and Warner, 1998; Anastas and Eghbali, 2010). Within the framework of nanotechnology, these have prompted the creation of synthetic pathways involving benign solvents (e.g., water), renewable or biogenic reducing agents (e.g., plant extracts, polysaccharides, and amino acids) and capping (e.g., polysaccharides) and alternative energy inputs (e.g., microwave, ultrasound, and mechanochemical). The goal of such strategies is not to reduce or even eliminate the use of toxic reagents and solvents but to decrease the amount of energy used, enhance the safety and sustainability of the whole process, etc. (Nasrollahzadeh et al., 2019; Singh et al., 2020).

It is on this basis that the paper at hand seeks to comment on and criticise the solutions to green chemistry-based paths to the sustainable production of nanomaterials. In particular, it attempts to (i) describe the essence of nanomaterial synthesis and note the environmental and safety constraints of traditional physical and chemical methods; (ii) discuss the way in which the tenets of green chemistry has been applied to create practical green strategies of nanomaterial synthesis, including biogenic and other environmentally friendly synthesis; and assess how the strategies support toxicity reduction, resources and waste minimization, and preservation or improvement of functional nanomaterial properties (Iravani, 2011; Mittal et al., 2013; Nasrollahzade The review will introduce green chemistry as a leading guiding paradigm of the future of sustainable nanotechnology by incorporating the latest literature on the synthesis of green nanomaterials (Clark et al., 2012; Singh et al., 2020).

## Synthesis 2. Synthesis Basics of Nanomaterials.

Production of nanomaterials is usually characterised by two major approaches: top-down and bottom-up (Jeevanandam et al., 2018; Singh et al., 2020). In top-down methods, bulk solids are broken down into nanoscale particles by physical means such as high-energy ball milling, lithography, sputtering, or etching, which conceptually can be scaled with existing industrial equipment, though in many cases they require a lot of energy input and can cause defects and contaminations during milling or etching

(Khan et al., 2019; Jeevanandam et al., 2018). Conversely, bottom-up techniques use nanomaterials, atoms, ions, or molecules by nucleation and growth in solution or gas phase, say by chemical precipitation, sol-gel procedures, hydrothermal and solvothermal reactions, or vapour-phase deposition, with a call for finer control of particle size, shape, and composition by tuning precursor concentration, temperature, and reaction time (Iravani, 2011; Singh et al., 2020). Nonetheless, most of the bottom-up pathways require hazardous intermediates, organic solvents, and energy-demanding conditions. The ecological footprint of a bottom-up process is heavily shaped by the type of chemistry used (Iravani, 2011; Singh et al., 2020).

The terms of these broad strategies, a range of traditional methods, are regularly applied to the creation of nanomaterials, each having its own set of benefits and drawbacks of green chemistry. Highly crystalline, compositionally homogeneous oxides and hybrid materials with controllable porosity and morphology can also be obtained by sol-gel processing and hydrothermal/solvothermal synthesis, e.g., but these techniques frequently require metal alkoxides, organic cosolvents, strong acids or bases, and high temperatures and pressures, making them a lot of energy and producing dangerous liquid byproducts (Polshettiwar & Varma, 2010; Singh et al., 2020). CVD and PVD are very fine controls of thin film and nanostructured coating and allow good control of the thickness and coverage on complicated substrates, but they normally use volatile and even toxic precursors, carrier gases, high-temperature reactors, and vacuum systems, therefore contributing to more occupational risk and environmental footprint (Clark et al., 2012; Khan et al., 2019). Nanoparticles of finely sized nanoparticles can be produced by the use of microemulsion methods and flame spray or aerosol processes, though these often require large amounts of surfactants, organic solvents, or combustion-based high-temperature processes, which are incompatible with the concept of green chemistry of safer solvents, energy conservation, and waste reduction (Polshettiwar & Varma, 2010; Clark et al., 2012).

With the increasingly growing concern regarding the environmental and health effects of nanomaterial production, it is now evident that these traditional pathways need to be supplemented or substituted with approaches that are much more consistent with green chemistry (Anastas & Eghbali, 2010; Iravani, 2011). Classical methods tend to have a poor atom economy, as only a small portion of the input atoms are incorporated into the final nanomaterial; the rest of the atoms are wasted in by-products or waste streams. They also produce large amounts of solvent and reagent wastes and demand large amounts of non-renewable feedstocks and high energy inputs and cannot be easily aligned with long-term sustainability goals (Clark et al., 2012; Singh et al., 2020). Researchers have in turn been keen on devising synthesis pathways that can be run in benign conditions (e.g., water) with renewable or biogenic sources (e.g., plant extracts or biomass-derived ligands), with milder temperatures and shorter reaction times and with catalytic or process-intensified conditions (e.g., microwave, ultrasound or mechanochemical activation) to mitigate hazards, energy consumption (e.g.), and overall environmental impact (Iravani, 2011; Nasrollahzadeh et al., 2019). These new methods offer a compromise between the structural control that bottom-up nanochemistry offers and the preventive and system-level outlook advocated by green chemistry. The above discussion has been summarised in a concise table of major conventional methods and the green chemistry limitations of them, below.

**Table 1. Representative nanomaterial synthesis methods, typical features, and green-chemistry considerations.**

Category method	Typical features (scale, control)	Main advantages	Key green-chemistry limitations
Top-down: Milling, lithography, etching	Bulk → nano via physical size reduction; often industrial equipment	Simple concept; scalable; established technology	High energy input; defect formation; contamination, and limited size control

			(Khan et al., 2019; Jeevanandam et al., 2018)
<b>Bottom-up: Sol-gel</b>	Hydrolysis–condensation of precursors in solution, 60–200 °C	Good compositional control; uniform oxides	Metal alkoxides and organic solvents; acid/base catalysts; solvent and calcination energy (Polshettiwar & Varma, 2010)
<b>Bottom-up: Hydrothermal / solvothermal</b>	High-T, high-P reactions in sealed vessels, water/organic solvents	Crystalline nanostructures, tunable morphology	Elevated T and P; energy-intensive; solvent disposal issues (Singh et al., 2020)
<b>Bottom-up: CVD / PVD</b>	Vapor-phase deposition, vacuum or controlled atmosphere, high T	High-quality films; precise thickness control	Volatile/toxic precursors; high T; vacuum systems; gas emissions (Clark et al., 2012; Khan et al., 2019)
<b>Bottom-up: Microemulsion</b>	Nanoreactors in surfactant-stabilized droplets in organic media	Fine size control; narrow distributions	Large surfactant and solvent usage; separation and recycling challenges (Polshettiwar & Varma, 2010)
<b>Bottom-up: Flame / aerosol</b>	Gas-phase high-T processes, continuous production	High throughput; industrially relevant	Very high temperatures; combustion emissions; limited solvent/energy efficiency (Clark et al., 2012)

**Review of literature**

**1.1 From conventional synthesis to green paradigms**

Initial summaries of nanomaterials were mostly focused on the classification, traditional synthesis paths, and uses, and little was said about environmental or safety issues of manufacture (Nanomaterials: An Overview of Synthesis and Applications, 2023). In these publications, the most frequent approaches to sol-gel, hydrothermal, CVD, microemulsion, and other methods were considered, and the control of size, shape, and crystallinity were the main aspects of the evaluation, whereas solvent toxicity, energy consumption, and waste were discussed as less important details of the process (Nanomaterials: An Overview of Synthesis, Classification, and Applications, 2023). As green chemistry has emerged and awareness of risks related to nano has increased, a second generation of reviews specifically compares conventional and environmentally benign routes, with the promise of biological and environmentally benign methods to reduce costs, pollution, and health hazards without compromising nanostructural control (Green Synthesis of Nanomaterials, 2021; Green and Sustainable Synthesis of Nanomaterials, 2023).

Recent comprehensive articles claim that green synthesis, with the help of utilising plants, microorganisms, fungi, and agricultural byproducts as reducing and stabilising agents, has the potential to significantly reduce the employment of toxic reagents and the carbon footprint of nanoparticles' production (Green and sustainable synthesis of nanomaterials, 2023; A review on green synthesis of nanoparticles toward sustainable development). These reviews contextualise green approaches as viable implementations of several green chemistry principles – safer solvents, renewable feedstocks, energy efficiency, and waste reduction – and position them as sought-after strategies when sustainability is a fundamental design criterion (Green and Sustainable Synthesis of Nanomaterials, 2023; Green-Synthesised Nanomaterials: Principles, Progress, and Prospects). This change in literature

gives a good justification for organising your research around green chemistry as a framework as opposed to separate synthetic methods.

### 1.2 Biogenic and plant synthesis as a central theme.

One of the themes of literature is biogenic synthesis, particularly that which is mediated by plants. Overviews of the synthesis of biosynthesis with the help of plant extracts and essential oils reveal that these extracts include polyphenols, flavonoids, organic acids, sugars, and proteins that can serve as reducing and capping agents, which obtain metal and metal oxide nanoparticles in mild conditions (Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2023; Biogenic Synthesis of Metallic Nanoparticles by Plant Extracts, 2023). They are spliced by these phytochemicals to the metal ions, induce nucleation, and adsorb onto the surfaces of nanoparticles, offering steric and electrostatic stabilisation (Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2023). Recent research on herbal-mediated synthesis emphasises that medicinal plants are of special interest since their natural bioactivity can complement the nanoparticle core to improve antimicrobial or antioxidant properties and possibly decrease side effects (Green Synthesis of Nanomaterials Mediated by Herbal Medicine,).

Parallel reviews define microbial routes with bacteria, fungi, algae and yeast and state their benefits in the form of renewable biomass, the reduction mediated by enzymes and the possibility of intracellular or extracellular formation of nanoparticles in environmentally benign conditions (Green and sustainable synthesis of nanomaterials, 2023; Green-synthesised metal nanoparticles: A promising approach to sustainable applications,). Comparative studies show that biosynthetic processes are generally cost-effective and conceptually scalable but have issues with batch-to-batch reproducibility due to biological variation in extract or metabolite composition (Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2023; Biosynthesis of Metallic Nanoparticles Using Plant Extracts,). Simultaneously, application-orientated reviews indicate that plant- and microbe-derived nanoparticles are often highly catalytic and adsorption-active to dye, antibiotic, and heavy metals, and in some cases, these are more efficient than those prepared by more traditional chemical methods (Applications of Green Synthesized Metal Nanoparticles, Green Synthesis of Nanoparticles for Environmental Applications,; Green-synthesized metal nanoparticles: A promising approach to sustainable applications, 202 Collectively, these pieces of evidence support your interest in biogenic/biological synthesis and green reducing/capping agents.

### 1.3 Characterisation and the evaluation of properties are subjects of interest in green nano literature.

In the investigations of green nanomaterials, it is seen that a consistent trend of physicochemical characterisation is maintained. Literature reviews on methods of nanomaterial characterisation note that the fundamental instruments used to identify the presence of nanoparticles, determine the biogenic capping layer, and determine colloidal stability are UV-Vis spectroscopy, FTIR, XRD, TEM/SEM, DLS, and zeta potential analysis (Techniques for Physicochemical Characterisation of Nanomaterials, 2013; Nanomaterials Characterisation—An Overview, 2024). In standard reports of green synthesis, surface plasmon resonance bands or absorption edges are observed using UV spectroscopy to rapidly monitor the evidence of nucleation and potential aggregation, and XRD is used to determine crystalline phase and crystallite size (Techniques for Physicochemical Characterisation of Nanomaterials, 2013; Green Synthesis of Nanomaterials, 2021). FTIR is commonly used with XPS to give spectral signatures of plant- or microbe-derived functional groups on the nanoparticle surface and directly link the use of green reagents with surface chemistry and stabilisation processes (Green Synthesis of Nanomaterials Mediated by Herbal Medicine; Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2023).

Recent reviews of herbal-mediated nanoparticles expressly introduce characterisation to form bridges between synthesis mechanism and biological performance and suggest that correlations between FTIR/XPS characteristics and antimicrobial or anticancer activity are essential in determining which of the many classes of phytochemicals is dominant in reduction and passivation (Green Synthesis of Nanomaterials Mediated by Herbal Medicine,). Functionally, the reviews indicate that green-synthesised metal nanoparticles are extensively studied using antimicrobial, photocatalytic degradation of dyes and pollutants, and antioxidant and, more frequently, in vitro cytotoxicity analyses comparing green and chemically synthesised particles at comparable concentration levels (Applications of Green Synthesised Metal Nanoparticles—A Review, 2023; A Review on the Green Synthesis of Nanoparticles, their biological uses, and Some of these authors point to the fact that nanoparticles frequently exhibit equal or better activity, as well as greater stability and biocompatibility; however, they also highlight the fact that there are no universally accepted testing conditions, which makes cross-study comparisons and meta-analysis challenging (Nanomaterials via Green Synthesis: Insights into Biocompatibility and Biotechnological Applications,). A review on the green synthesis of nanoparticles, their biological uses, and photocatalytic efficiency against environmental toxins. 202 These are the same trends that are the foundation of your sections on Characterisation and property evaluation and on Environmental, Economic, and Safety characterisation

#### 1.4 Application-orientated literature and sustainability-framed literature.

Another powerful agenda in literature today is the shift to application-orientated reviews that make it explicitly clear that green-synthesised nanoparticles are perceived as instruments of sustainable technologies. Reviews on the environmental synthesis point to the use of green-derived metal and metal oxide nanoparticles as adsorbents, photocatalysts, and antimicrobial agents in the treatment of water contaminated with dyes, pharmaceuticals, pesticides, and heavy metals and argue that the adoption of green synthesis is particularly suitable in technologies that seek to protect the environment (Applications of Green Synthesized Metal Nanoparticles—a Review, 2023; Green Synthesis of Nanoparticles—a Review, 20 These publications show the fact that there is no consistency in remediating water or soil with materials that are synthesised by highly polluting methods and that more environmentally friendly synthesis pathways can be used to enhance the environmental footprint and societal acceptability of nanotechnology-based solutions (Green and sustainable synthesis of nanomaterials, 2023; Green synthesis of nanoparticles for environmental applications,).

Widely varying applications of green silver, gold, copper, and iron oxide nanoparticles as antimicrobial agents, anticancer platforms, wound healing materials, and drug delivery vehicles have been reported in biomedically focused reviews, often accompanied by the assertion that naturally derived capping agents enhance biocompatibility and could reduce off-target toxicity (Green-synthesised metal nanoparticles: A promising approach to sustainable applications,; Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2. On a more integrative scale, more recent chapters and reviews suggest that green-synthesised nanomaterials can contribute to many of the Sustainable Development Goals by facilitating safer and less expensive technologies for medical care, clean water, and pollution control, as long as the issue of scaling up and regulatory issues are properly addressed (Green Synthesised Nanomaterials: Principles, Progress, and Prospects,; Green and Sustainable Synthesis of Nanomaterials, 2023). Plant extract-based reviews also associate the concept of green nano with the idea of the circular economy by putting the emphasis on the valorisation of agricultural residues and low-value biomass as reagents and functional components in the production of nanomaterials (Biosynthesis of Metallic Nanoparticles Using Plant Extracts,; Green Synthesis of Nanoparticles for Environmental Applications,). This line of literature will support your intended "Applications" section and defend the reason why you want to tie green synthesis to the concept of sustainable development and safer nanotechnology in your conclusion.

### **1.5 Cross-cutting limitations and gaps in research.**

Finally, a few modern reviews are united by a range of repetitive constraints. They constantly list difficulties with scalability, reproducibility, mechanistic insight, and standardised toxicity testing as significant obstacles to industrial and regulatory approval of green-synthesised nanomaterials (Green and sustainable synthesis of nanomaterials, 2023; A review on the green synthesis of nanoparticles, their biological applications, and photocatalytic efficiency against environmental toxins, 2023; Green and sustainable synthesis of nanomaterials: Recent advancements and limitations, 2023). Repeatedly, the reviews of plant- and herbal-mediated synthesis report that extraction composition differs by species, season, geographic source and extraction protocol and that most studies broadly attribute the role to polyphenols, proteins or carbohydrates without specific molecule name or quantifying structure-activity relationships (Green Synthesis of Nanomaterials Mediated by Herbal Medicine,; Biosynthesis of Nanoparticles Using Plant Extracts and Essential Oils, 2023; Biosynthesis of Met

The other gap that has been identified by a significant number of researchers is the lack of application of life cycle assessment and techno-economic analysis: most authors state that green synthesis is cheaper and eco-friendly, but comparatively few of them show quantitative data or system-level comparisons with traditional routes (Green Synthesis of Nanoparticles: Recent Advances and Limitations, 2023; Green Synthesis of Nanoparticles for Environmental Applications,). On the same note, despite the abundance of reports on promising antimicrobial, catalytic and biomedical performance, only a fraction of research studies explore long stability, environmental fate, or realistic exposure conditions, which are necessary to robust risk assessment (Nanomaterials via Green Synthesis: Insights into Biocompatibility and Biotechnological Applications,; Applications of Green Synthesised Metal Nanoparticles – a Review, 2023; A review on the green synthesis of nanoparticles, their biological applications, and these reported deficiencies directly contribute to your interest in environmental, economic, and safety evaluation and issues and future prospects in green nanomaterial synthesis).

### **Green Chemistry Principles on Nanomaterials.**

Green chemistry offers a series of principles which may be applied to redesign materials synthesis at the nanoscale to be safer and more sustainable. Some of these principles are especially applicable in areas such as safer solvents and energy efficiency, renewable feedstocks, waste avoidance, and catalysis, among 12 principles. These concepts have an effect on nanomaterial synthesis in terms of solvent selection (use of water or other benign solvents rather than toxic organics), selection (use of biomass or biogenic precursors rather than purely petrochemical precursors), operating conditions (reduced temperatures and reduced reaction times), and design of the process (few steps and integrated functions, such as reduction and capping in one step).

The concept of safer solvents and auxiliaries promotes the use of water, bio-derived solvents, or minimal-amount-of-solvent methods instead of volatile solvents and dangerous surfactants. This is manifested in aqueous and solvent-free routes in nanomaterial synthesis and in biopolymers or natural surfactant-stabilising agents that do not add much toxicity during the synthesis. The challenge of energy usage is covered by the replacement of high-temperature, long-reaction-time processes with low-synthesis ones aided using microwave, ultrasound or mechanochemical activation, enabling controlled nucleation and growth with reduced reaction times and usage of energy. The transition to the use of renewable feedstocks is observed in the use of plant extracts, agricultural residues and biomolecules (polysaccharides, proteins and organic acids) as reducing and capping agents to reduce the reliance on non-renewable petroleum-based chemicals.

The concept of waste minimisation and atom economy is implemented, whereby most of the atoms in the precursors are incorporated into the final nanomaterial, and the reduction, nucleation, growth, and

stabilisation of the final nanomaterial are achieved in a single pot and not through multiple isolation and purification steps that produce waste. As an example, biogenic syntheses can typically combine reduction and capping into a single process, and the same solvent can be used as a solvent modifier, reductant, and stabiliser, which is more efficient with respect to using materials and energy. Lastly, catalysis plays a central role in the synthesis itself and the uses of nanomaterials: catalytic quantities of benign reagents, or catalytic systems that can be recycled, can be used to reduce stoichiometric waste during nanoparticle synthesis, and the resulting nanomaterials can be used as heterogeneous catalysts to promote greener downstream reactions (e.g., lower temperature reactions, higher selectivity, reduced by-products). By being overlaid onto every step of nanomaterial synthesis, these principles can be used to shift researchers toward not only incremental changes but also truly green paths that would make nanotechnology part of the broader sustainability objectives.

**Table 2: Mapping key green principles to nanomaterial synthesis**

Green Chemistry principle	Conventional practice in nano-synthesis	Green implementation in nanomaterial synthesis	Expected benefits
<b>Safer solvents and auxiliaries</b>	Use of organic solvents (e.g., ethanol, DMF, toluene); synthetic surfactants and dispersants	Water-based synthesis, use of bio-derived solvents or solvent-free routes, and stabilization by biopolymers or plant-based surfactants	Reduced solvent toxicity and VOC emissions; safer handling; simpler effluent treatment
<b>Energy efficiency</b>	High temperatures and long reaction times (e.g., hydrothermal at 180–200 °C and prolonged reflux)	Low-temperature reactions; microwave- or ultrasound-assisted synthesis; mechanochemical solvent-free processes	Lower energy consumption; shorter processing times; smaller carbon footprint
<b>Renewable feedstocks</b>	Metal salts plus synthetic reducing and capping agents derived from petrochemicals	Use of plant extracts, agricultural wastes, polysaccharides, proteins, and other biomolecules as reducing and capping agents	Decreased reliance on non-renewable resources; valorization of biomass and waste streams
<b>Waste prevention / atom economy</b>	Multiple separate steps for reduction, growth, and stabilization; excess reagents; large volumes of washing solvents	One-pot syntheses where the same extract or reagent performs multiple roles; optimized stoichiometry; minimal work-up	Less chemical and solvent waste; improved atom utilisation, and simpler purification
<b>Catalysis</b>	Stoichiometric reducing agents and additives; little attention to recyclability	Use of catalytic amounts of benign reductants; recyclable catalytic systems; design of nanoparticles as heterogeneous catalysts for greener processes	Reduced by-product formation; lower reagent consumption; easier catalyst recovery and reuse
<b>Inherently safer design</b>	Use of highly reactive, toxic, or explosive reagents and conditions (e.g., hydrazine, NaBH <sub>4</sub> , strong oxidants)	Selection of milder reducing agents (ascorbic acid and plant polyphenols), moderate temperatures and pressures; avoidance of shock-sensitive or highly toxic reagents	Lower accident risk; improved occupational safety; easier scale-up and regulatory acceptance

**Green Synthesis Routes and Methods**

**1.6 Biogenic / biological synthesis**

One of the most remarkable green directions towards the synthesis of nanomaterials has become biogenic/biological synthesis, which uses plants, microorganisms, and other biological wastes as reducing agents and systems (Iravani, 2011; Mittal et al., 2013). In plant-mediated synthesis, phytochemicals, including polyphenols, flavonoids, terpenoids, alkaloids, sugars, and proteins, are used as the electron donors and capping agents to form nanoparticles using mild conditions by mixing extracts of the leaf, stem, fruit, peel, seed, or agricultural residues with metal salt solutions (Mohanpuria et al., 2008; Ahmed et al., 2016). The advantages of this method include that plant materials are very abundant, cheap, and renewable; the reactions are normally conducted in aqueous media with very low temperatures; and there is no requirement to use other toxic reducing agents (Mittal et al., 2013; Nasrollahzadeh et al., 2019). Besides, it is also possible to scale plant-based systems relatively easily by changing extract concentration, metal ion concentration, and reaction time, and this is beneficial when it comes to industrial adoption (Ahmed et al., 2016).

Microorganism-mediated synthesis involves the use of bacteria, fungi, algae and yeast to produce nanomaterials either intracellularly or extracellularly (Mohanpuria et al., 2008; Narayanan and Sakthivel, 2010). Enzymes and other biomolecules found in or on cells reduce metal ions and guide nanoparticles to nucleate and grow in such systems, usually giving them a particular shape, size or surface functionality (Narayanan and Sakthivel, 2010; Singh et al., 2016). Fungi and algae are especially noteworthy because of their great metal-binding capacity and their ability to generate and release huge quantities of extracellular proteins and metabolites, which make nanoparticles in the surrounding medium form and stabilise (Narayanan and Sakthivel, 2010; Singh et al., 2016). The usual parameters include incubating biomass or cell filtrates with moderate temperatures of metal salt solutions (e.g., 25-37°C), neutral and slightly alkaline pH and incubation times of a few hours up to several days, depending on the organism and metal system (Iravani, 2011; Narayanan and Sakthivel, 2010).

Mechanistically, plant- and microorganism-mediated syntheses involve redox biomolecules to reduce metal ions ( $Ag^+$ ,  $Au^{3+}$ , or  $Cu^{2+}$ ) to their zero-oxidation state, and nanocrystals grow and nucleate, with other components adsorbing on surfaces of growing nanoparticles to prevent undesired aggregation (Mohanpuria et al., 2008; Mittal et al., 2013). The key functional groups of phenolics, proteins, and polysaccharides, including hydroxyl, carbonyl, carboxyl, and amine groups, are essential in both reduction and capping, and the nature and abundance of these functional groups have a major impact on the particle size, morphology, and the stability of colloidal systems (Iravani, 2011; Nasrollahzadeh et al., 2019). Even though biogenic methods can be challenging in terms of absolute reproducibility and mechanistic complexity, they are much less damaging to the environment regarding the use of hazardous chemicals and conditions that consume a lot of energy, which is entirely in line with the core ideals of green chemistry in terms of renewable feedstock, safer solvents, and inherently safer syntheses (Anastas and Eghbali, 2010; Singh et al., 2020).

**Table 3 - Representative Biogenic Sources for Green Synthesis**

Source type	Example source (plant/microbe)	Metal / oxide NP	Typical conditions (T, pH, time)	Main biomolecules involved	Key advantages
Plant leaf extract	Neem, green tea, etc.	Ag, Au	Room temp, neutral–slightly basic, 1–24 h	Polyphenols, flavonoids, sugars	Simple, fast, low-cost, aqueous medium

<b>Fruit/peel or agri-waste extract</b>	Citrus peel, banana peel	Ag, ZnO	Mild heating, pH 7–9, for a few hours	Organic acids, pectins, polysaccharides	Uses waste biomass for value addition
<b>Bacteria</b>	e.g., Bacillus sp.	Ag, Au	25–37 °C, neutral pH, 24–72 h	Enzymes, proteins, metabolites	Good control over morphology
<b>Fungi</b>	e.g., Aspergillus, Fusarium	Ag, Au, ZnO	25–30 °C, near neutral pH, 24–72 h	Extracellular proteins, enzymes	High biomass, high metal uptake
<b>Algae/yeast</b>	e.g., Spirulina, Saccharomyces	Ag, Au, metal oxides	20–30 °C, neutral pH, 24–72 h	Pigments, proteins, polysaccharides	Environmentally friendly, scalable

### 1.7 Solvent and process intensification

The other relevant aspect of the production of green nanomaterials is the substitution of standard organic solvents with water or other harmless media and the intensification of reactions to decrease the energy consumption and the duration of the reaction (Clark et al., 2012; Singh et al., 2020). Synthesis in the aqueous phase (usually in combination with plant extracts, biopolymers, or surfactant-free systems) removes or significantly decreases volatile organic compounds, which enhances the safety of operators and reduces the environmental impact of solvent production, consumption, and disposal (Iravani, 2011; Ahmed et al., 2016). There are other instances where other green solvents, like deep eutectic solvents, supercritical fluids, or bio-derived solvents, have also been tested to improve solubility and control regarding particle growth whilst holding a preferable safety and environmental profile compared to traditional organic media (Clark et al., 2012; Shukla et al., 2019).

Microwave-assisted, ultrasound-assisted, and mechanochemical methods of synthesising nanomaterials are other intensification methods that make nanomaterials more environmentally friendly by allowing even lower temperatures for the reaction, reducing synthesis time, and being more energy efficient (Polshettiwar and Varma, 2010; Nasrollahzadeh et al., 2019). Rapid volumetric heating with microwave irradiation can be used to trigger nucleation faster and generate more uniform distributions of particle sizes in aqueous or benign solvent systems (Polshettiwar and Varma, 2010; Shukla et al., 2019). The acoustic cavitation methods of the assisted type are used in the utilization of local hot spots and high shear, stimulating the decrease in the quantity of metal ions and the dissemination of particles without vigorous surfactants (Mason et al., 2011; Singh et al., 2020). The use of mechanochemical reactions, in which mechanical energy drives reactions within ball mills or other equipment, tends to be under solvent-free or low-solvent reaction conditions, which can greatly reduce the amount of solvent consumed and the space occupied (James et al., 2012; Nasrollahzadeh et al., 2019).

In most green synthetic procedures, these process and solvent modifications are incorporated in one-pot procedures, which combine reduction, nucleation, growth and stabilisation in a single step (Polshettiwar & Varma, 2010; Singh et al., 2020). These one-pot methods save on the unit operations and lessen the intermediate purification or solvent exchanges and, thereby, the production of waste and the general use of resources (Clark et al., 2012; James et al., 2012). Solvents and processes Safer solvents, energy saving, preventing waste Solvent and process intensification methods help directly with the principles of green chemistry with respect to safer solvents, energy saving and waste prevention (Anastas and Eghbali, 2010; Nasrollahzadeh et al., 2019).

### Table 4 - Green Solvent Choices and Process-Intensified Strategies

Strategy / medium	Example	Role in synthesis	Green benefit
<b>Water as solvent</b>	Aqueous plant extract route	Reaction medium and carrier	Eliminates most organic solvents, safer handling
<b>Deep eutectic solvent</b>	Choline chloride-based mixtures	Dissolution and controlled nucleation	Low volatility, potential recyclability
<b>Microwave-assisted synthesis</b>	Microwave heating in water	Rapid, uniform heating, faster nucleation	Short reaction time, less energy use
<b>Ultrasound-assisted synthesis</b>	Sonication in aqueous medium	Cavitation, enhanced mixing and reduction	Lower temperature, no strong surfactants
<b>Mechanochemical synthesis</b>	Ball-milling solid reactants	Mechanical energy drives reactions.	Little/no solvent, fewer steps

### 1.8 Green reducing and capping agents

The key in numerous green synthesis pathways is to use natural or less toxic alternatives instead of conventional chemical reducing and capping agents (e.g., sodium borohydride, hydrazine, synthetic surfactants, and others) (Mohanpuria et al., 2008; Ahmed et al., 2016). Plant-derived polyphenols, flavonoids, sugars, ascorbic acids and organic acids are common green reducing agents due to their ability to donate electrons to metal ions and, at the same time, attach functional groups which are adsorbed to the surface of nanoparticles (Mittal et al., 2013; Nasrollahzadeh et al., 2019). The importance of biopolymers as capping or stabilising agents is that they create a physical and occasionally chemical shell around particles, which prevents aggregation and gives them certain colloidal and interfacial characteristics (Mohanpuria et al., 2008; Singh et al., 2016). A single extract or biomolecule mixture is used in most systems, which fulfils both functions, allowing a real green synthesis (Ahmed et al., 2016; Singh et al., 2020). Green reducing and capping agents have a significant influence on the nucleation and growth kinetics of nanomaterials, which consequently dictate the size, shape, crystallinity, and stability of the particles (Mittal et al., 2013; Nasrollahzadeh et al., 2019). Powerful or quicker-acting reducing agents are likely to promote quicker nucleation and the existence of smaller particles, whereas weaker reducing agents might possibly produce bigger or more polydispersed structures (Mohanpuria et al., 2008; Singh et al., 2016). Comparably, the molecular weight, the density of functional groups, and the affinity of capping agents can be considered to affect the extent of aggregation inhibition as well as surface charge, hydrophilicity, and interaction potential with biological or environmental media (Mittal et al., 2013; Singh et al., 2020). Notably, green-synthesized nanomaterials, especially those that are biomedical and environmentally friendly, are especially attractive to biomedical and environmental applications; many natural capping agents can increase and promote biocompatibility and decrease toxicity when compared to conventional surfactants (Iravani, 2011; Ahmed et al., 2016).

Even when using these green reducing and capping systems, the researchers can create synthetic pathways that allow both performance requirements to be satisfied and the principles of green chemistry by reducing reliance on hazardous reagents and enhancing the sustainability of nanomaterial production in general (Anastas and Eghbali, 2010; Nasrollahzadeh et al., 2019).

**Table 5 – Green Reducing and Capping Agents and Their Influence on Nanoparticle Characteristics**

Type of agent	Example(s):	Main function	Effect on NP characteristics
<b>Plant polyphenols</b>	Catechins, tannins	Reducing and capping	Smaller size, good stability, antioxidant surface

<b>Sugars/small organics</b>	Glucose, ascorbic acid	Mild reducing agents	Moderate size control, relatively narrow size distribution
<b>Proteins / amino acids</b>	Albumin, gelatin, amino acids	Capping, sometimes templating	Good colloidal stability, biocompatible surface
<b>Polysaccharides</b>	Starch, cellulose, chitosan	Capping, steric stabilization	Prevents aggregation, can tune surface charge
<b>Microbial metabolites</b>	Enzymes, peptides	Reducing and capping	Often specific shapes or morphologies

**Characterization and Property Evaluation**

Characterization is essential to demonstrate that the formation of green-synthesized nanomaterials is successful, stable, and similar (or even better) to the traditionally synthesized ones. This section can be written concerning three concepts, namely, basic techniques, confirmation of green synthesis, and property/performance evaluation.

**1.9 Significant characterization methods.**

Some of the common methods employed in the synthesis of nanomaterials using green methods are UV-Vis spectroscopy, FTIR, XRD, TEM/SEM, DLS, and zeta potential. The initial technique used when tracking the formation of nanoparticles is often UV-Vis spectroscopy, such as monitoring surface plasmon resonance bands in metallic nanoparticles or semiconductor nanomaterials' specific absorption edges. FTIR spectroscopy is employed in determining the presence of functional groups of plant extract or biopolymers or any other green agent adsorbed at the nanoparticle surface and, in this manner, confirming the role of biomolecules as reducing agents. agents. agents. agents. agents. agents. agents, agents, and capping agents. X-ray diffraction (XRD) contains data on crystalline phase, crystallite size and lattice structure, which permits comparison of phase purity and crystallinity with materials by traditional methods.

Direct data on size of particles, size distribution, shape, and morphology can be obtained using electron microscopy methods (transmission electron microscopy (TEM) and scanning electron microscopy (SEM)) that are necessary for proving that green routes can be used to obtain controlled nanostructures. The size and polydispersity of nanoparticles in colloidal suspension are determined by dynamic light scattering (DLS), and the zeta potential measures surface charge and may be applied to determine colloidal stability. All of these techniques allow obtaining a complete overview of the physical and chemical properties of the green nanomaterials and allow correlation the synthesis conditions (type of extract, concentration, pH, and temperature) with the resultant structures.

**1.10 Green synthesis verification and comparison with traditional methods.**

Authors of published papers generally use a combination of the above methods to demonstrate that (i) the nanoparticles have the desired size and shape, (ii) functional groups used in bioassays have been incorporated onto the surface and (iii) no desired crystalline phases or significant impurities exist. As one example, the emergence of a typical plasmon band in the UV-Vis, crystalline peaks at the index of a specific metal or metal oxide in the XRD, and particles in the TEM images are good indicators of the formation of nanoparticles. The presence of hydroxyl, carbonyl, carbonyl, carbonyl, carboxyl or amine groups in the FTIR spectra that represent plant metabolites or biopolymers on the surface implies that the species is bound to the surface and serves as a capping agent.

They are typically compared to the conventional syntheses of nanomaterials in terms of size distribution differences, aggregation degree, and crystalline and surface chemistry. Nanoparticles synthesised green could have the same or a slightly bigger size distribution but tend to have organic shells formed by natural capping agents that can increase colloidal stability and biocompatibility. In other instances, green routes may produce similar or even smaller particles at lower temperatures, and effective

nucleation and growth can be controlled under less severe and more sustainable conditions. These comparisons assist in showing that green practices are not only preferable for the environment but also within technical competition.

### 1.11 Stability, toxicity and performance assessment.

In addition to the simple characterisation of the structure, there is the need to evaluate stability, toxicity, and functional performance. Colloidal stability is typically evaluated by following changes in hydrodynamic size, zeta potential, or spectra during a time; stable systems would exhibit low levels of aggregation and stable spectral characteristics during the test. Thermal stability and structural integrity This may be examined by thermogravimetric analysis (TGA) or repeated XRD measurements, particularly when considering a material usable at high temperatures.

In vitro cytotoxicity experiments (e.g., MTT or other viability tests on cell lines), antimicrobial susceptibility tests, or ecotoxicological experiments on model organisms may be used as part of toxicity assessment, in which green-synthesised and conventionally synthesised nanoparticles are compared at equivalent dosages. Often the natural capping layers diminish the toxicity of acute cases and enhance their compatibility with biological systems. Lastly, in application-specific tests: catalytic efficiency may be determined by performing model reactions (e.g., dye degradation, reduction of nitro compounds), and antimicrobial activity may be determined by zone of inhibition, minimum inhibitory concentration (MIC), or time-kill. With the help of correlating these performance measures with structural and surface features, the researchers can demonstrate that green synthesis pathways produce nanomaterials that are not only safer and more sustainable but also useful in their end-use application.

### Environmental, Economic, and Safety Assessment.

This is where the environmental, economic, and safety evaluation is explicitly demonstrated to show why green routes are not only fascinating but also superior to standard routes in important sustainability parameters.

### 1.12 Qualitative comparison: green vs conventional.

Traditional nanomaterial syntheses frequently use toxic metals as starting materials, powerful reducing agents (e.g., hydrazine and sodium borohydride), and organic solvents, which are a source of acute toxicity and long-term environmental persistence. Green methods, by contrast, normally employ the use of water as the solvent and employ the use of plant extracts, biopolymers, or mild inorganic reagents, which lowers the direct exposure to toxic substances and decreases the toxicity of the reaction effluents. Energetically, most classical reactions demand high temperature, lengthy reaction times, and, in certain instances, high pressure, whilst green reactions often occur at or close to room temperature, being enhanced by microwave, ultrasound, or mechanochemical activation, which can also reduce the reaction time and reduce the total energy requirement. The volume of waste generated also differs significantly: in traditional methods, it is possible to obtain high amounts of solvent waste and leftover reducing or capping agents, whereas in green syntheses, reduction and capping can be carried out in the same reaction with renewable biomolecules and thus are more atom-economic and require fewer downstream purification reactions. Moreover, agricultural residues or other biowaste feeds are valued to produce nanomaterials and to separate virgin, fossil-based feeds to a certain extent.

### 1.13 Sustainability metrics, toxicity, and life cycle thinking.

In terms of safety and toxicity, green nanomaterials are often coated with layers of natural organic molecules that can enhance biocompatibility and acute toxicity compared to particles whose surfaces have been coated with synthetic surfactants or toxic ligands with strong binding affinities. A strict evaluation has to nonetheless consider dose, route of exposure, and long-term fate, as size, shape, and surface chemistry are critical determinants irrespective of the route of synthesis. Life cycle thinking is

a philosophical approach that involves consideration of environmental costs at each stage, such as acquisition of raw materials, synthesis, usage, and disposal, and not just the reaction itself. Green methods can have effects in many categories (e.g., global warming potential, human toxicity, ecotoxicity, and resource depletion) by consuming less energy, cutting use of hazardous reagents, and facilitating treatment or reuse of process streams when analyzed in terms of a life cycle. Examples of simple sustainability metrics that can be discussed include qualitative or semi-quantitative comparison of energy consumption (e.g., reaction temperature x time), volume of solvent used per gram of product, number of hazardous substances used, and the proportion of renewable feedstock in the total raw material. Collectively, all these factors justify the proposal that nanomaterials can be produced using green chemistry-based methods, as it represents a more sustainable route to achieve the same functional performance or possibly even greater functionality.

### **Use 8. Use of Green Nanomaterials Synthesised.**

#### **1.14 Environmental applications.**

The green metal and metal oxide nanoparticles (e.g., Ag, Fe<sub>3</sub>O<sub>4</sub>, ZnO, TiO<sub>2</sub>) are employed as adsorbents, photocatalysts, and antimicrobial agents in water and wastewater treatment. Their high surface area and surface functionalisation through plant- or biopolymer capping layers allow the high adsorption of dyes, heavy metals (including Cd<sup>2+</sup> and Cr<sup>6+</sup>), and organic pollutants in aqueous media. Metal oxides synthesised by green routes can catalyse the degradation of persistent organic contaminants when used as photocatalysts in the presence of UV or visible light, and the capping layer, in some cases, enhances dispersion in water and contact with target molecules. Biosynthesised silver or copper nanoparticles have high antimicrobial activity against bacteria, fungi and viruses. In disinfection, the natural organic corona can enhance colloidal stability in real water matrices and can have a role in reducing unwanted ecological toxicity in disinfection compared to harshly surfactant-stabilised nanoparticles. Green-synthesised nanomaterials are also found in environmental sensors whereby their functionalised surfaces are specific to certain pollutants, including heavy metals, pesticides, or phenolic compounds, and are detected by colorimetric, electrochemical, or fluorescence detection signals at low concentrations. Their appeal to environmental technologies lies in the fact that they are obtained by means of extracts of plants or agricultural residues or benign solvents, and the overall sustainability of the treatment process is an important aspect of the whole process.

#### **1.15 Biomedical applications**

The key advantage of green-synthesised nanomaterials in biomedical applications can be seen in the ability to hit the nanoscale performance with enhanced biocompatibility. The metal nanoparticles (particularly silver, gold, and their oxides) synthesised with the aid of the plant extracts or biopolymers exhibit excellent antimicrobial characteristics and have been explored for wound dressing, coating medical equipment, and topical preparations. Natural capping agents, e.g., polysaccharides, proteins and polyphenols, can reduce haemolysis, cytotoxicity and inflammatory reactions more than particles capped by some synthetic surfactants, and thus they are more appropriate in contact with cells and tissues. In drug delivery, green-synthesised metal and metal oxide nanoparticles and polymer nanoparticle composites can serve as drug solubilisers, degradation inhibitors and controlled/targeted drug release agents. In this case, the surface chemistry of green reducing and capping agents is used to target further functionalisation with ligands (antibodies, peptides, and carbohydrates) to acquire specific cells or receptors. Gold, iron oxide and quantum dot-type nanostructures made by green routes are being studied as contrast agents in MRI, CT or optical imaging and platforms to combine imaging and therapy. Although full toxicological analysis remains required, less toxic reagents may be used in the synthetic process, and biogenic surface layers can make the regulatory approval much easier and more acceptable to patients and clinicians.

### 1.16 Energy and materials applications.

Green-synthesised nanomaterials find an application in the energy industry as catalysts, electrode substances, and functional coatings. Plant- or microbe-made metal or metal oxide nanoparticles can also be used as heterogeneous catalysts in fuel production, decontaminants, and fine chemical synthesis reactions with surfaces where the high surface area and surface chemistry are tunably synthesised for high activity and selectivity. Green prepared nanostructured oxides, carbons, and composites are also being considered as electrode materials in electrochemical energy storage, such as batteries and supercapacitors, because production influences can be reduced and because biomass-derived precursors and benign synthesis conditions can be used for the sustainability objectives of renewable energy technologies themselves. As an example, porous carbons made using agricultural waste and mixed with metal or metal oxide nanoparticles prepared in aqueous conditions can provide good capacitance and cycling stability using renewable feedstocks. Fine films of coatings: In coatings, antimicrobial, anticorrosive, photocatalytic, or self-cleaning properties are imparted onto surfaces like textiles, packaging, construction materials, and consumer products using thin films of nanoparticles that are developed by green synthesis. The synthesis process is based on the uses of water and bio-based agents, and scaling up to the industrial level of coatings can, in principle, avoid large amounts of volatile organic solvents and dangerous process chemicals, which is beneficial both environmentally and in terms of occupational safety.

### Challenges and Future Directions

Green synthesis of nanomaterials has come a long way, yet it remains that there are several scientific and practical obstacles that restrain its further implementation and industrialisation. These may be divided into shortcomings of existing techniques, mechanistic gaps, and directions of research in the future.

Scalability is also a significant weakness with green synthesis. Numerous plant- or microbe-mediated protocols are scaled up at the laboratory level using low volumes of extract and metal salt solutions, and often an increase in volume results in alteration in mixing, heat and mass transfer and the availability of oxygen. This is able to change the dynamics of nucleation and growth, providing particles varying in size distributions or morphologies to the small-scale process. Intimately associated with this is the question of reproducibility: biological systems are variable in nature, and the composition of plant extracts or microbial metabolites may vary depending on species, season, geographic origin, extraction conditions, or culture medium. Consequently, syntheses of nominally the same nanomaterial, run at a different time or place, might have significantly different sizes, shapes, or chemical functionalities on the surface.

Another challenge is control of size, shape, and surface properties. Although green routes can undoubtedly yield reasonably uniform nanoparticles, it is not always easy to get similar fine control as with some of the more established physical or chemical techniques. The complicated composition of biomolecules in extracts implies that a great number of reducing and capping species work in parallel, which complicates the systematic control of nucleation and growth. This intricacy also makes standardisation challenging; it is hard to formulate strong, generalisable protocols specifying the preparation of extracts, content of biomolecules, and pertinent process conditions when the reagent in question is a poorly characterised mixture of many molecules, as opposed to a single chemical. Such variability may be undesirable as a regulatory issue and for control of the quality of industry products, especially where biomedical or food contact products are involved and careful specifications are necessary.

The limitations can be overcome by a more mechanistic insight into the bioreduction and capping processes. Extracts of plants, fungi, algae, or bacteria are successful in many of the reports, although

the individual reducing molecules and particle-stabilising molecules have not been fully quantified but are only identified loosely (e.g., polyphenols or proteins). In the absence of a clear understanding of which functional group is regulated in nucleation, growth, and agglomeration, synthesis conditions are not easily rationalised to form particles with desired properties. The interaction between pH, ionic strength, temperature, and biomolecule concentration should also be more thoroughly studied, preferably with kinetic models and in situ spectroscopy or scattering.

Besides, the dynamics of the organic corona of the nanoparticles are not completely known. This corona has a powerful impact on colloidal stability, cell-organism and environmental interactions and environmental fate but is commonly indirectly determined by FTIR or general chemistry analysis. Further characterisation (e.g., high-resolution mass spectrometry, NMR, advanced microscopy, and surface analytical techniques) and computational modelling would provide insights as to how particular biomolecule layers are positioned on the surface, how stable the layers are, and how they change during realistic usage and environmental conditions. It would be useful in such a mechanistic understanding of nano-bio interactions and nano-toxicity and more predictable catalytic, environmental, or biomedical systems.

### Practical implications

This review can offer several practical implications in the context of research and practice in the field of nanoscience and green chemistry. To start with, the study presents a tangible decision-making framework that laboratory chemists and process engineers should apply to redesign the current protocols instead of viewing the concept of green synthesis as an isolated niche operation by explicitly mapping the fundamentals of green chemistry onto the steps of nanomaterial syntheses: solvent choice, precursor selection, energy input, and waste management. This can inform the gradual substitution of toxic reducing agents, organic solvents, and high-temperature processes with biogenic reagents, aqueous media, and process-intensified routes, which are safer and more energy efficient. Second, the list of evidence that plant- and microbe-mediated processes can produce nanomaterials with similar or even better catalytic, antimicrobial, and environmental activity encourages R&D managers, funding agencies, and policymakers to focus on greener pathways, particularly in those fields where the final application is directly related to the environment or human health (e.g., water treatment, biomedical coatings, and sensors). Lastly, the focus on the correlations and on the environmental, economic, and safety analysis implies that there is a list of convenient indicators, including the solvent volume/gram of product, reaction temperature-time patterns, waste streams, and surface-relevant toxicity indicators, which could be introduced into the regular reporting and scale-up viability investigations. It can be easier to embed these indicators into the normal research practice so that future nanomaterial development can be more aligned with the principles of life cycle thinking and a circular economy to ensure that the industry and regulators more easily evaluate, adopt, and green nanomaterial synthesis routes.

### Future research directions

In the future, the integration of green practices with high-level process control is one of the directions. This may include incorporating biogenic or benign solvent syntheses and methods like microreactors, flow chemistry, or carefully controlled microwave and ultrasound reactors that provide better mixing, heat transfer and reaction control than the simple batch setups. With the ability to combine green reagents with an accurate control over residence time, temperature, and concentration gradients, one should be able to improve reproducibility and narrow distributions of size and improve morphology uniformity.

The second critical path would be the realisation of green nanomaterial synthesis as a part of a circular economy. This involves the systematic utilisation of agricultural residues and food processing waste or

other biomass streams such as reducing/capping agents, in addition to sources of carbon, and developing processes that enable the recovery and reuse of solvents, unreacted ions, and even spent nanomaterials. Typically, life cycle assessment (LCA) and techno-economic analysis (TEA) would be used at the beginning of process development to recognise the so-called hot spots in energy consumption, emissions, and cost, such that new routes would not just appear green on the bench scale but would be sustainable and competitive in the entire value chain.

Lastly, the upscaling and standardisation at the industrial level require closer coordination among chemists, engineers, toxicologists, regulators, and industry partners. This involves coming up with standardised protocols on the extraction, preparation and characterisation of the green nanoparticles; the establishment of reference materials and interlaboratory comparisons of green-synthesised nanoparticles; and the generation of strong toxicological and environmental data on green-synthesised nanoparticles under realistic exposure conditions. Regulatory frameworks can also be required to reflect on the potential reduced risk of some of the green-synthesised materials without jeopardising safety. When these scientific, engineering, and regulatory issues are overcome, green synthesis pathways can cease to be considered as proof-of-concept demonstrations but instead as robust and dependable, scalable platforms to produce nanomaterials in environmental and energy-relevant technologies.

### Conclusion

Green chemistry has become an essential paradigm according to which the synthesis of nanomaterials can be optimally redesigned so that it can be effective and at the same time environmentally and socially responsible. Green solutions directly overcome most of the deficiencies of more traditional physical and chemical methods, which typically are based on toxic chemicals, organic solvents, and energy-intensive conditions. With the application of where surface area, reactivity and small size may compound all advantages, it is particularly important to inculcate these principles into the synthesis process.

As discussed in this paper, the green synthesis pathways, such as those using biogenic and benign solvents, have the potential to generate nanomaterials with controlled size, shape, and functionality; reduce the toxicity of reagents and effluents; decrease energy and resource usage; and limit the generation of waste. Simultaneously, the fact that high-performance nanomaterials can be manufactured using renewable inputs in mild conditions is evidenced using plant extracts, biopolymers, agricultural residues and process intensification methods (i.e., microwave, ultrasound or mechanochemistry). Even though issues still exist in terms of scalability, reproducibility, mechanistic insight and standardisation, there is continuous work in the area that narrows these gaps.

All in all, the central point of the paper is that, as opposed to attempting changes that will bring some incremental benefits to the current nanomaterial syntheses, green chemistry suggests an integrated design philosophy of coming up with new pathways that would be efficient, cost-efficient, and aligned with the overall sustainability goals. Green synthesis assists in transforming nanotechnology into a safer innovation model by coordinating nanomaterials production with concepts of circular economy, life cycle thinking, and risk reduction. It is in this regard that the need to adopt and further develop green chemistry solutions is critical to ensure that the high rate of expansion of nanotechnology advances sustainable development instead of increasing the current environmental and health liabilities.

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