Limitations of nanomaterials insights in green chemistry sustainable route: Review on novel applications

Abstract: “Nanotechnology” is an emerging as a significant development tool for the green synthesis of noble nanomaterial. Green synthesis is superior to conventional chemical methods as it is less expensive, reduced pollution, and enhances human health and the environment safety. Nanomaterial and their green synthesis from plants became an interesting aspect of nanotechnologies due to the many benefits they provide to living beings, as well as their low cost and minimal harm to humans and the environment. They also have a wide range of applications in biomedical research, diagnostics, and drug discovery and also in catalysis. The current review focuses on the synthesis of nanoparticle from plants using greener approach and their novel applications.

Keywords: green synthesis, nanomaterial, diagnostic, health, environment, plant extract

1 Introduction: global research background

Nanotechnology is a multidisciplinary field with diverse science and innovation applications that are rising rapidly [1–7]. The ever-increasing industrialization and population boom have a negative impact on the earth’s atmosphere, producing a massive amount of harmful and undesired elements. Green synthesis, which employs safe, cheap, non-toxic, and sustainable methods for synthesizing nanomaterial, is an emerging promise in nanotechnology to solve this issue [8].

In the literature, presently various chemical and physical ways for developing nanomaterials, with higher rates of production and well-controlled size and shape of nanomaterials, but the demerits of the methods are higher loss of energy and funds, use of toxic materials, and large amounts of waste production. These main issues have an economic and environmental impact on nanomaterials’ economic levels’ scale-up process. Compared to traditional methods, the greener approach to nanomaterial production provides cost-effective, eco-friendly, and benign ways [9]. In recent years, there has been a growth in the adoption of greener protocols for manufacturing nanomaterials. These methods offer significant advantages, such as having eco-friendly procedures, being less expensive, and producing small-sized nanomaterial [10]. Various natural resources, including microorganisms, plant leaves, and extracts, have previously been employed to produce nanoparticles [11,12]. This comprehensive review mainly exploring on recent advances in the green synthesis of nanomaterial from plant extracts and leaves.

2 Green chemistry approaches

The idea of “green chemistry” for “sustainable development” has been extensively researched during the last decade [13]. Sustainable development is defined as development that meets present demands while balancing future generations’ ability to meet their requirements [14]. Green chemistry is a developing field that promotes implementing principles aimed at reducing the use and production of toxic chemical chemicals [15]. As a consequence, greener techniques minimize the environmental impact of industrial work. Researchers have developed these methods to provide potential remedies to the
expensive processes and toxic materials found while employing traditional synthesis methods [16–19]. Green nanomaterial synthesis is the ideal method for reducing the adverse impacts of its manufacturing and utilization, reducing the risk level of nanotechnology [20]. While in the Figure 1 highlights the primary advantages of green chemistry approaches in simple and cost-effective routes.

“Green nanotechnology” enables us to avoid unfavorable outcomes. This technique has a commercial impact on nanomaterials or product development by eliminating or lowering contaminants, which implies it addresses present environmental issues [21], as seen in Figure 2.

“Green nanotechnology” provides tools for converting natural beings to environmentally friendly methods for synthesizing nanomaterials, offering a perfect way to lessen the negative effects of chemical and physical processes and use of nanomaterials to prevent any accompanying toxicity, thus reducing the riskiness of nanotechnology [22,23]. As shown in Figure 2, it deals with the 12 principles of green chemistry and engineering and how they can be applied to nanomaterials’ synthesis utilizing procedures that reduce waste, are eco-friendly, employ safe chemicals, use less energy, and minimize pollution. Again for the bioreduction of metal ions to their corresponding nanomaterials, the documented current green synthesis approaches involve plants or plant components in addition to microorganisms, including bacteria, algae, fungi, and yeast, among others [24].

There are a number of “greener” techniques to produce nanomaterials. It has been shown that using naturally occurring recyclable substances – such as vitamins, sugars, tea, or agricultural residues rich in polyphenols – as reducing and capping agents can help create less harmful nanomaterials [25]. At this early stage of the development of

Figure 1: The main advantages of green synthesis.

Figure 2: Diagrammatic representation of green chemistry in the development of nanomaterials.
nanotechnology, using green chemistry 12 principles for developing new nanomaterials and applications is particularly important. It could result in new design guidelines that are eco-friendly and benign in the context of protecting the environment and human health [26].

3 Green synthesis and novel applications of nanomaterial

Green synthesis methods are more beneficial than traditional methods, although they are simpler and less expensive and do not contain toxic or environmentally unfriendly components; this technology has gained prominence in recent years as a result of the economic future for nanomaterial manufacturing [27]. A variety of microbes and plant and leaf extracts could be employed to produce nanomaterials effectively, and their applications are listed in Table 1.

Tewari and his coworker used a two-stage thermal procedure to develop an innovative top-down approach for the useful sequential production of 2D/3D graphene-based materials (GM) from the Drepanostachyum falcatum plant extracts and fiber. In the presence of ethanol (Figure 3), D. falcatum extract exhibited the formation of a luminous 2D framework of GM that is metal-doped graphene oxide (MDGO) at low temperatures (150°C). In the N₂ atmosphere, decomposition of the fiber component at 300°C revealed the formation of a 3D graphene nanoribbons. Many conjugated linkages with oxidative functional groups in 2D-MDGOs are required for their luminous blue behavior when exposed to UV light at 365 nm. However, 2D-MDGOs appear to have a lot of possibilities as bio-imaging probes for RWPE-1 prostate cancer

| Nanomaterials | Natural beings | Synthesized by | Size | Application | Reference |
|---------------|----------------|----------------|------|-------------|----------|
| ZnO | Bacteria | Aeromonas hydrophila | 57–72 nm | Antimicrobial properties against bacteria and fungi | [28] |
| TiO₂ | Bacillus mycoides | 40–60 nm | Synthesis of solar cell | [29] |
| TiO₂ | Bacillus subtilis | 10–30 nm | Photocatalyst | [30] |
| PbS | Bacteria strains, NS2 and NS6 (bacterium) | 40–70 nm | Bioremediation | [31] |
| AuNP | Fungi | Trichoderma harzianum | 32–44 nm | Antimicrobial agent and catalyst | [32] |
| ZnO | Aspergillus niger | 53–69 nm | Antimicrobial activity, dye degradation | [33] |
| AgNP | Fusarium oxysporum 405 | 10–50 nm | Colloidal stability | [34] |
| AgNP | Saccharomyces cerevisiae | 2–7 nm | — | [35] |
| AuNP | Saccharomyces cerevisiae | — | Enhancement of surface plasmon | [36] |
| ZnO | Pichia kudriavzevii | 10–61 nm | Antimicrobial and antioxidant activities | [37] |
| CdTe | Saccharomyces cerevisiae | — | Bio-imaging and biolabeling | [38] |
| Ag NP | Polysiphonia alga | 5–25 nm | Anticancer activity | [39] |
| AuNP | Marine algal extract | 8–20 nm | Green synthesis | [40] |
| PdNP | Chlorella vulgaris | 5–20 nm | — | [41] |
| CuO | Brown alga | 6–7.8 nm | Photocatalytic and antibacterial study | [42] |
| Au nanowires | Tobacco mosaic virus | 50 nm (diameter) 150–400 nm (length) | — | [43] |
| AuNP | Bacteriophage | 20–50 nm | Antibiofilm activity | [44] |
| TiO₂ | M13 virus | 20–40 nm | Semiconducting network | [45] |
| AgNP | Oryza sativa L. | 346.4 ± 36.8 nm | Inhibitor against pathogens | [46] |
| AgNP | Punica granatum (pomegranate) | 50 nm | Antimicrobial and antibiofilm activity | [47] |
| CuNP | Eclipta prostrata | 23–57 nm | Antioxidant and cytotoxic activity | [48] |
| AuNP | Punica granatum | 56–59 nm | — | [49] |
| AuNP | Justicia glauca | 32.5 ± 0.25 nm | Inhibitor against pathogens | [50] |
| AuNP | Alternanthera philoxeroides | 72.11 ± 2.87 nm | Antimicrobial activity | [51] |
cells (Figure 4). The hydrophobic characteristic of 3D-GNR resulted in improved adsorption to the organic dye methylene blue (MB). As a result, it is a viable contender for water purification [52].

Nasrollahzadeh et al. established a simple, low-cost, and environmentally friendly approach for producing silver nanoparticle-supported nano aluminum oxide (AgNPs-nano Al$_2$O$_3$) using leaf extracts from *Bryonia alba*. As a moderate, durable, nontoxic reducing and stabilizing agent, the plant extract is vital in anchoring Ag NPs on nano Al$_2$O$_3$. At room temperature, the resultant NPs act as an efficient catalyst for the reduction of 4-hydroxy nitrobenzene (4-HNB) (Figure 5) and 2,4-dinitrophenylhydrazine (2,4-DNPH) (Figure 6) and also for the degradation of dyes like congo red, methyl orange, MB, and rhodamine B. The catalyst can be recycled multiple times before losing its reactivity [53].

The Han research group created palladiumlentinan (Pd-LNT) NPs by using lentinan (LNT) as both a reducing and stabilizing agent. This process was straightforward, environmentally benign, and easily scaled up. Regarding catalytic efficiency for the hydrogenation of 4-nitrophenol, Pd-LNT NPs exceeded other catalysts [54]. The PdNPs were being prepared by Kadam and his worker using *Gymnema sylvestre* leaf extract and microwave method. The catalytic effectiveness of the NPs was investigated in the degradation of pollutant Cr$^{6+}$ to nontoxic Cr$^{3+}$ using a minimum amount of reducing agent. The probabilistic method for the reduction of PdNPs and the reduction of Cr$^{6+}$ to Cr$^{3+}$ is thoroughly explored in Figure 7 [55].

A novel, convenient green synthesis approach was applied under extreme basic conditions to synthesize CuO nanoparticles and CuO nanograins (CuONGs) utilizing CuCl$_2$·2H$_2$O as a copper salt precursor, curcumin as a conjugated agent with or without cetyltrimethylammonium bromide as a stabilizing agent. CuONGs were discovered to be suitable catalysts for the MB reduction,
with higher catalytic activity than spherical nanoparticles [56].

Barzinjy et al. used a green technique to manufacture Fe$_3$O$_4$ nanoparticles from Rhus coriaria extract. Biosynthesized magnetite nanoparticles are both inexpensive and recyclable. As a result, Fe$_3$O$_4$ nanoparticle catalyst can be used to synthesize several novel 2-naphthol bis-Betti bases via one-pot condensation of substituted aromatic aldehydes, 2-naphthol, and $p$-phenylenediamine (Figure 8). Betti bases are widely used in pharmaceutical and medicinal chemistry [57].

Bioaugmented zinc oxide nanoparticles (ZnO-NPs) were developed by the Faisal research group using aqueous fruit extracts of Myristica fragrans. ZnO-NPs also efficiently degraded MB dye as depicted in Figure 9 [58].

The Naranthatta research group presents surface-modified CdS generated by a straightforward and sustainable approach that employs several pharmacological leaf extracts for reaction mixture (Figure 10). A simple wet
A chemical approach successfully manufactured CdS nanoparticles via green synthesis. *Plectranthus amboinicus*, *Chromolaena odorata*, and *Ocimum tenuiflorum* leaf extracts were used to modify the properties of the CdS nanoparticle, which are available all year. Using the MTT assay, the cytotoxicity of the hybrid was assessed, and it was discovered that the CdSO *tenuiflorum* hybrid is less dangerous than unmodified CdS and other hybrid structures [59].

Chand et al. used a green tool to generate silver nanoparticles (AgNPs), which have a wide range of applications, including food preservation, cosmetic items, electronic parts, sensing material, cryogenics, dental materials, and drug delivery. In this study, a green synthesis technique was used to synthesize AgNPs utilizing neem extracts (NE) and a mixture of neem, onion, and tomato (NOT) plant extracts as a combined reducing and stabilizing agent at different pH levels. This is the first study to report on the green production and antibacterial activity of AgNPs utilizing extracts from various combinations at various pH values. The antibacterial activity of all produced AgNPs was tested by using the Kirby disk diffusion method in the growth of SA microorganisms, as shown in Figure 11 [60].

The Khan research group describes the green ZnONP generation using *C. equisetifolia* leaf extract and UV-A and UV-C irradiation. Antibacterial activity of green nanoparticles against *Bacillus subtilis*, *Pseudomonas fluorescens*, and *Pseudomonas aeruginosa* was tested by the Kirby disk diffusion method.
Pseudomonas aeruginosa strains was investigated. ZnONPs shows potent anticancer effects (Figure 12) and are biocompatible in nature [5].

The green approach was used by Shah et al. to synthesize silver AgNPs from seeds and wild Silybum plants. Highly crystalline and stable NPs with sizes ranging from 18.12 to 13.20 nm were prepared from wild plants (NP-1) and seeds (NP-3). The produced NPs and extracts demonstrated a wide range of biological activities, such as antimicrobial, antioxidant, anti-inflammatory, cytotoxicity, and antiaging properties [61]. The Srihasam research group use stevia extract as a reducing and capping agent for the synthesis of NiO-NPs. These NPs were much more potent against Gram-negative bacteria than Gram-positive bacteria. The antifungal activity of these NPs has been tested in the area of biopesticides as a replacement for ecologically destructive synthetic pesticides. NiO-NPs enter the microbial cell and enhance microbial suppression by having contact with electron transport, which damage the DNA by breaking the phosphate and hydrogen bond and denaturing the protein by modifying the 3D structure, damaging the mitochondria by oxidative ROS generated by metal and NiO-NP interactions, which eventually leads to cell death as explored in Figure 13 [62].

Anjum and his coworker reported the green synthesis of AgNPs, ZnONPs, and bimetallic Ag–ZnONPs from M. macroura leaf extract using UV-C irradiation. These nanoparticles have exceptional antiaging, anti-diabetic, and anticancer activities and are also biocompatible in nature [7]. AgNPs synthesized from onion peel is a by-product of onion processing reported by the Santhosh research group. In addition, the antibacterial properties of AgNPs were investigated against Staphylococcus aureus and Salmonella typhimurium. These NPs are also employed in constructing sensors for detecting dangerous metals like mercury [63].

The green approach created a new antibody-conjugated chitosan-gold nanoparticles (Ab-CS-AuNPs). This is employed by three kinds of optical biosensing systems (colorimetric, localized surface plasmon resonance, and paper-based dot-blot) to detect the target antigen (Ag) [64].

George et al. developed a green nanohybrid hydrogel-based composition for a photo-extracted quercetin (QE) medicine. Through crosslinking chitosan using dialdehyde cellulose, a bio-polysaccharide-based medication carrier was created and employed as a nontoxic alternative to the conventional chemicals. Green ZnO NPs were inserted into the hydrogel matrix, which was photo-synthesized utilizing musk melon seeds. Conventional QE and QE in onion peel drug (OPD)-loaded nanohybrid hydrogel’s inhibited bacterial growth. The QE/OPD-loaded nanohybrid hydrogels were compatible and showed anticancer properties.

**Figure 12:** ZnONPs have anticancer properties: (a) HepG2 cell survival measurement, (b) ROS/RNS production measurement, and (c) HepG2 mitochondrial membrane potential measurement in response to green-synthesized-ZnONP therapy [5]. Copyright © 2021; MDPI.

**Figure 13:** A possible antibacterial mechanism for NiO nanoparticles [62]. Copyright © 2020; MDPI.
properties was proved toward normal L929 mouse fibroblast cells and A431 human skin cancer cell lines [65]. The bioactive ZnO NPs were synthesized using Pandanus odorifer leaf extract MTT, and neutral red uptake assays were used to assess the anticancer activity of ZnO NPs in MCF-7, HepG2, and A-549 cells at various concentrations (1, 2, 5, 10, 25, 50, and 100 mg.mL\(^{-1}\)) [66].

Mehdizadeh et al. analyzed the influence of green-synthesized ZnONPs on the level of apoptotic cell death mostly in vitro (MCF7 and mouse mammary carcinoma [TUBO] cell lines) and in vivo (murine breast cancer model) investigations to determine whether ZnONPs can be employed as an anticancer agent as shown in Figure 14 [67].

Cheng’s research group reported the synthesis of ZnONPs from Rehmanniae radix (RR) shows anticancer activities toward osteosarcoma cell line MG-63 must be examined to assess the chemotherapeutic, cytotoxic, and apoptotic efficiency of ZnONPs from RR against MG-63 cells. Taking everything into consideration, it appears that ZnONPs derived from RR can be used as a therapeutic regimen in chemotherapy [68].

*Ferula assa-foetida* used to green synthesize ZnONPs diagrammatically identified in Figure 15. These green-synthesized NPs had anticancer properties against human breast (MCF7 and MDA-MB231) and colon (HT-29) cancer cell lines [69].

At room temperature, ZnMn\(_2\)O\(_4\) nanoparticles were produced from corolla carpus epigeaus plant extract. The cyclic voltammetry investigations demonstrated the capacitor’s property and its increased charging and recharging capabilities. The electrochemical impedance investigation revealed that the produced nanoparticles have a high conductivity. These findings suggest that the preparation of ZnMn\(_2\)O\(_4\) nanomaterials was well suited for electrical and electronic applications, particularly energy storage systems [70].

Shaheen et al. performed the hydrothermal synthesis of spherical-shaped CoMoO\(_4\) electrode materials using

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**Figure 14:** Flow cytometry detection of the morphology and cell cycle status of treated cell lines. (a) MCF7 cell line morphology at various ZnONPs treatment doses compared to untreated control cells. At high concentrations, their morphology shows apoptotic death. (b) The morphology of the TUBO cell line after various doses of ZnONPs treatment in comparison to untreated control cells. At high ZnONPs concentrations, apoptotic death might also be observed in the MCF7 cell line [67]. Copyright © 2019; Wiley Online Library.

**Figure 15:** Green synthesis of ZnO NPs uses *Ferula Assa-foetida* [69]. Copyright © 2021; MDPI.
an inorganic–organic template. Organic substances have been extracted from *Euphorbia cognata* Boiss. Assisted by organic compounds, CoMoO$_4$ revealed the stability of octo-drine and cyclobutanol and supported the development of electrical sites for energy storage systems. To improve the electrochemical characteristics of CoMoO$_4$-fabricated electrodes for supercapacitor applications, *E. cognate* nanofeatures and organic compounds were identified [71].

MnO$_2$ nanoparticles were created using plant extracts and are being used as a catalyst for biofuel production. The plants chosen for this study were *Rosmarinus officinalis*, *Origanum vulgare*, and *Artemisia dracunculus*. These extracts reduce Mn$^{7+}$ from KMnO$_4$ to Mn$^{4+}$ in the final MnO$_2$ product as catalysts in the generation of biofuel from grape residue and seed oil investigated [72].

AgNPs were created by reducing silver nitrate (AgNO$_3$) with various leaf extracts. The Ag NPs have a spherical form and are very stable. The sensing properties of Ag NPs were tested using the agrofungicide mancozeb (MCZ). The surface plasmon resonance peak position showed a linear response with the concentration of MCZ. It is also used as a photocatalyst using a 0.5 mM MCZ solution under UV-visible irradiation. Surface plasmon-based biosensors were created using green-synthesized Ag NPs and MCZ as a paradigm [73]. To investigate the applicability of *Butea monosperma* seed extract for pressure sensors, a high yield of single-phase orthorhombic vanadium oxide (V$_2$O$_5$) nanoparticles is generated in very short succession at 500°C using a solution combustion approach [74].

Over the last decades, anthraquinone (AQ) process of manufacturing has dominated H$_2$O$_2$ production [75]. AQ is a waste- and energy-intensive oxidant that is effective, environment-friendly, adaptable, and green. Because it releases greenhouse gases and harmful organic waste and uses hydrogen as a feedstock, the AQ process is inextricably linked to low sustainability [76,77]. For direct, ambient, and efficient H$_2$O$_2$ synthesis in distributed electrolysis cells, electrochemical oxygen reduction following a two-electron (2e) pathway is a viable option that ideally only needs water, oxygen, and renewable electricity [78].

The energy-intensive AQ process, which is now the industry standard, might be replaced by the electroreduction of O$_2$ into H$_2$O$_2$, but this still needs materials with high catalytic efficiencies [79]. Dong and his coworker have demonstrated that a co-tetra-methoxyphenyl porphyrin-carbon nanotube (CoTMPP/CNT) nanohybrid functions as a high-performance catalyst with quick electron delivery to active sites toward electrochemically producing H$_2$O$_2$ under acidic aqueous conditions, attaining an H$_2$O$_2$ selectivity from over 95% and achieving strong stability [80].

### 4 Limitation of nanomaterial

Green synthesis of nanomaterial has tremendous opportunities; however, it faces challenges in selecting raw materials, reaction conditions, control of product quality, and applicability. These factors provide obstacles to the development of green nanomaterial for its manufacturing and large-scale use. These shortcomings are discussed in greater detail indicated in Figure 16 [81].

![Figure 16: The problems and limitations of green synthesis technology that must be considered in future research](https://example.com/figure16.png)

*Figure 16: The problems and limitations of green synthesis technology that must be considered in future research [81]. Copyright © 2022; Elsevier.*
Researchers investigated various locally accessible plants and discovered they are viable materials for producing green NPs. These investigations suggest that it is possible to utilize native plants completely, but substantial worldwide nanomaterial synthesis is difficult [82]. Time restrictions may make using raw ingredients in real production challenging. The cotton leaf should be used to obtain the materials needed to prepare Ag NPs throughout the flowering period [83].

Coffee arabica is also utilized; however, arabica trees take roughly 7 years to completely grow and are often planted at an altitude of 1,500 m [84]. So that the limitation period for getting leaves has been extended. Moreover, a few raw materials are supplementary products that require additional processing, increasing the technique’s complexity and cost until they can be used in the green synthesis of nanomaterials. As a result, the usefulness, economic viability, and cost of these substances must be shown.

The optimum temperature for several greener synthetic methods is quite high, and the synthesizing period is protracted, necessitating enormous energy consumption that may harm the environment. Despite using environmentally acceptable starting ingredients, the process does not always adhere to the principles of sustainable synthesis [85]. Another significant barrier to green synthesis is a lack of understanding of the synthesis pathway, which makes obtaining actual chemical reactions to illustrate the synthesis process difficult [86]. The shape and size of nanoparticles produced by different extracts vary widely, and the quality assessed is insufficient. According to current sources, particle diameter varies greatly, making green technology unsuitable for large-scale manufacturing and particle size management a significant challenge throughout the manufacturing process [87]. The impact of plant extracts on synthesis could only be demonstrated in a recent investigation, but the specific chemical pathways involved are still unable to explain. The shape and size of nanoparticles synthesized by various extracts vary greatly, and the qualities determined are inadequate. According to current sources, there are large variances in particle size, making green technology unsuitable for large-scale manufacturing and regulating particle size during manufacturing great trouble [88].

5 Conclusions, outlook, and future prospective

This review summarizes the current progress in green nanomaterial production and their potential uses. Green nanotechnology has emerged as a key technique for synthesizing nanomaterials in past years. Compared to other conventional methods, green synthesis methods give a safe, nontoxic, and environmentally friendly approach to nanomaterial synthesis. Furthermore, low yield, irregular particle size, complicated separation processes, periodical, local raw material accessibility, and many other obstacles must be solved before the sustainable synthesis of nanomaterial and its applications can be realized. There is already a diverse range of green nanomaterial synthesis methods and procedures available, with more on the way in the future. In today’s culture, advanced approaches to the issue, which involve automotive and stationary systems, are becoming more essential. As a result, the first component of green nanotechnology is to use more environmentally friendly or energy-efficient manufacturing procedures. The second stage entails creating ecologically friendly things. Indeed, environmental pollution and diseases like the COVID-19 pandemic are currently big problems in every country and can be partially resolved through nanotechnology. Due to its affordability and ecofriendliness, green nanomaterial production has enormous significance. This opens the door for numerous uses of nanomaterials inside the disciplines of environmental cleanup, medicinal applications, sensing technology, energy storage, and catalysis. Future researchers have been given some guidance through talks of knowledge gaps and potential applications of green nanomaterial. Green is likely to produce a lot of positive outcomes in a variety of applications.

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