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"A Review of Plant-Based Green Nanoparticle Synthesis: Mechanisms, Metals, and Applications in Nanotechnology"

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Abstract:
The green synthesis of nanoparticles offer promising applications across environmental and biomedical fields by reducing reliance on toxic chemicals. This approach, particularly through the use of plant materials, presents a safer alternative for nanoparticle production. Plants possess inherent reducing and capping agents, which aid in the synthesis process. This paper reviews the principles of green chemistry and explores the recent advancements in plant-mediated nanoparticle synthesis, discussing the various metals involved, including gold, silver, zinc, titanium, and palladium. Traditional physical and chemical synthesis methods, while effective, are often costly and hazardous. In contrast, plant-based green synthesis is an eco-friendly alternative, involving mechanisms such as reduction, stabilization, nucleation, aggregation, and capping, followed by characterization. The rise of green nanotechnology highlights the potential for sustainable, safer, and less toxic solutions for diverse applications, ranging from biosensors and biomedicine to catalysis, electronics, and antibacterial technologies. This approach opens new avenues for the design of novel nanoparticles with desirable properties for various scientific and industrial uses.

Keywords: Green synthesis, Nanoparticles, Environmental and biomedical fields, Plant materials, Antibacterial technologies.

Introduction
Nanostructures and their associated science and technology have emerged as a significant area of research for achieving sustainable development in human society. This field is expanding rapidly, with advancements in technology having profound implications for future commercialization. The term "nanotechnology" was first introduced by Taniguchi in 1974, who defined it as a technology involving the processes of separation, consolidation, and deformation of materials at the level of individual atoms or molecules (Iqbal et al., 2012).
Nanotechnology involves applying science to manipulate and control matter at the molecular level. The remarkable growth in this field has unlocked new possibilities in materials science and engineering, spanning areas like nanobiotechnology, bio nanotechnology, quantum dots, surface-enhanced Raman scattering (SERS), and applied microbiology. Advances in organizing nanoscale structures into predefined superstructures ensure that nanotechnology will significantly influence many emerging technologies ***Fig. 1.***

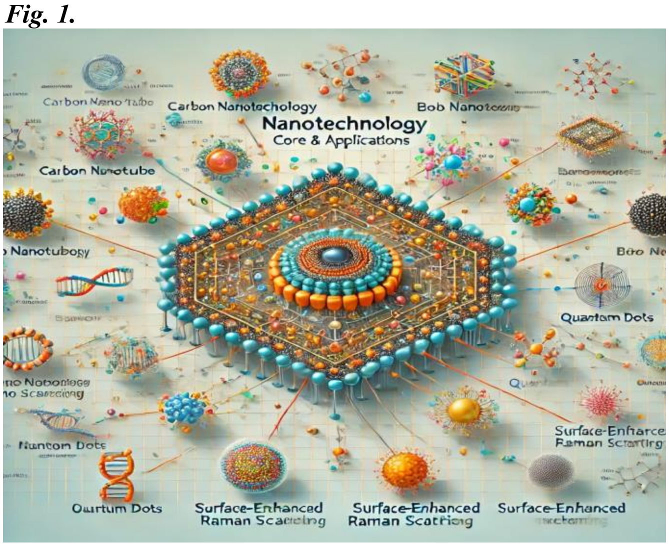

Fig. 1. Nanotechnology Core & Applications

This field is becoming increasingly important across diverse domains, including mechanics, optics, biomedical sciences, the chemical industry, electronics, space exploration, drug and gene delivery, energy science, catalysis, optoelectronic devices, photoelectrochemical applications, and nonlinear optical devices. For example, nano meter-scale germanium quantum dots (less than 10 nm) can be precisely formed for novel optoelectronic device applications, such as single-electron transistors (SETs) and light emitters. The ability to tune the optical absorption and emission properties of quantum dots by varying their size offers exciting prospects for band-gap engineering and the development of quantum dot lasers
.

Exploring Nanotechnology: Nanomaterials at the Nanoscale

Nanotechnology also focuses on the study of nanomaterials, which exhibit remarkable properties, functionalities, and phenomena due to their nanoscale dimensions (Khan et al., 2017). It involves understanding, fabricating, and manipulating materials at the nanoscale, typically in the range of 1–100 manometers (Roco, 2004). The word "nano" originates from the Greek word *nanos*, meaning small animals or plants, and one nanometre equals 10^{-9} meters.

At the nanoscale, materials display unique chemical, physical, and biological properties due to their high surface-to-volume ratio, where the surface area of nanoparticles increases as particle size decreases. This phenomenon arises from the increasing proportion of surface atoms relative to the total particle size (El Saliby et al., 2008). Consequently, nanoparticles exhibit distinctive optical, electrical, and magnetic properties compared to their bulk counterparts, primarily due to their exceptionally large surface area and high surface energy (Ichinose et al., 1992).

Furthermore, nanotechnology advancements are driving the creation of new magnetic resonance imaging (MRI) contrast-enhancing agents, such as small iron oxide particles, fullerenes encapsulating Gd^{3+} ions (Gado fullerenes), and single-walled carbon nanotube nano capsules containing Gd^{3+} ion clusters (Gado nano tubes). Nanoparticles are especially intriguing due to their extremely small size and high surface-to-volume ratio, which result in unique chemical and physical properties, such as enhanced mechanical strength, catalytic activity, thermal and electrical conductivity, and optical absorption, compared to their bulk counterparts ***Fig. 2.***

Fig. 2. Advancements in MRI Confast-Enhansing agents derived by nanotechnology

Nanoparticle Innovations: Applications in Medicine and Technology

By controlling the shape and size of materials at the nanoscale, scientists can design and produce materials with novel applications. The size- and shape-dependent properties of nanoparticles are valuable for a wide range of uses, including biosensing, catalysis, optics, antimicrobial applications, computer transistors, electrometers, chemical sensors, and wireless electronic logic and memory systems. Additionally, nanoparticles have diverse applications in medical imaging, nanocomposites, filtration systems, drug delivery, and tumor hyperthermia. Metal nanoparticles, in particular, play an essential role in medicine and pharmacy, offering innovative solutions to various challenges in these fields.

Nowadays, nanoparticles (NPs) are synthesized using various techniques, among which chemical methods, lithography, and laser ablation are expensive, time-consuming, and environmentally harmful. However, different plants exhibit the potential for agglutination of nanoparticles, encouraging scientists and technologists to utilize plants and their derivatives for nanoparticle synthesis. The presence of enzymes, phytochemicals, proteins, and other components in plants is commonly employed in the synthesis of silver nanoparticles using plant extracts (Kulkarni et al., 2011) ***Fig. 3.***

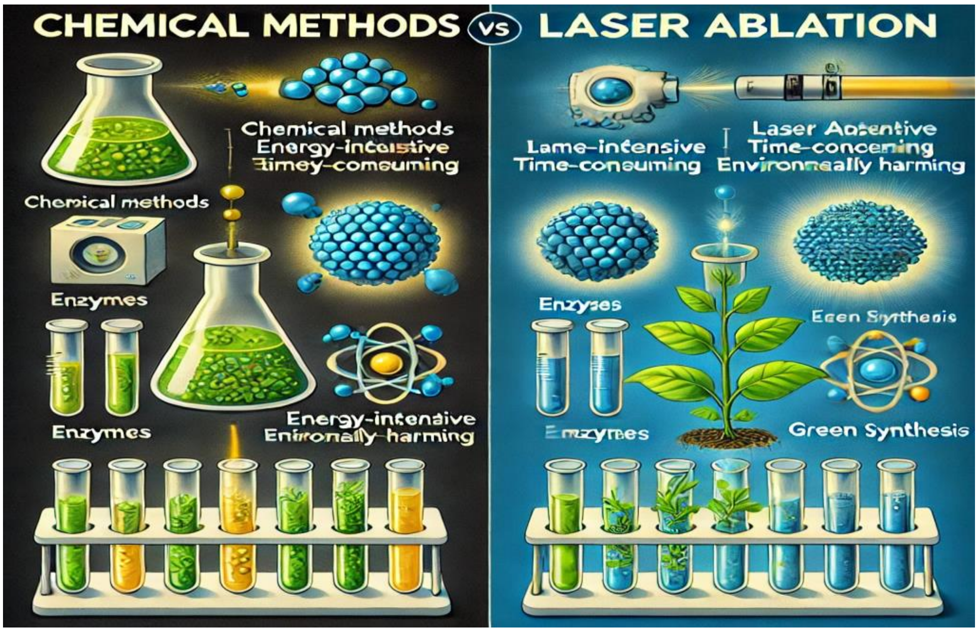

Fig. 3. Chemical vs Laser methods of Green synthesis of Nanoparticles

Applications of Gold and Silver Nanoparticles in Medicine

There are many important applications for metal nanoparticles in medicine and pharmacy. Gold and silver nanoparticles are the most common ones used for biomedical applications and in emerging interdisciplinary field of nanobiotechnology. For instance, oligonucleotidecapped gold nanoparticles have been used for polynucleotide or protein detection using various detection/characterization methods, including atomic force microscopy, gel electrophoresis, scanometric assay, surface plasmon resonance imaging, amplified voltammetric detection, chronocoulometry, and Raman spectroscopy. Furthermore, gold nanoparticles have been employed in immunoassay, protein assay, cancer nanotechnology (especially detection of cancer cells), and capillary electrophoresis. In the field of medicine, gold nanoparticles are used for different proposes. They can be used as markers for biological screening test. After cellular uptake, they can act as precise and powerful heaters (thermal scalpels) to kill cancer. Moreover, gold nanoparticles are capable of inducing apoptosis in B cell-chronic lymphocytic leukemia (chronic lymphoid leukemia).

Silver nanoparticles have drawn the attention of researchers because of their extensive applications in areas such as integrated circuits, sensors, biolabelling, filters, antimicrobial deodorant fibres, cell electrodes, and antimicrobials. Antimicrobial properties of silver nanoparticles caused the use of these nanometals in different fields of medicine, various industries, animal husbandry, packaging, accessories, cosmetics, health and military. Silver nanoparticles show potential antimicrobial effects against infectious organisms such as Escherichia coli, Bacillus subtilis, Vibria cholera, Pseudomonas aeruginosa, Syphillis typhus, and Staphylococcus aureus.

Biogenic Synthesis and Shape Control of Nanoparticles

In another study, $AuFe_3O_4$ composite nanoparticles were prepared with a combined chemical and biological reducing process (semi-biosynthesis method). Magnetic cores were primarily produced using a fabrication method consisting of coprecipitation of Fe^{2+} and Fe^{3+}. An ethanol extract of Eucalyptus camaldulensis was used for the reduction of Au+3 on the surface of the magnetite nanoparticles and for the functionalization of the $AuFe_3O_4$ nano-composite particles.

Armendariz et al. reported for the first time the formation of rod-shaped nanoparticles by biomaterials. They characterized the gold nanoparticles formed by wheat biomass exposed to a 0.3 mM potassium tetracholoaurate solution at pH values of 2–6 at room temperature. It was concluded that wheat biomass was able to reduce Au(III) to Au (0) forming fcc tetrahedral, hexagonal, decahedral, icosahedral multitwinned, irregular, and rod-shaped nanoparticles. In another study, pH dependent synthesis of rod-shaped Au nanoparticles using Avena sativa (oat) has shown that biomass might carry more positive functional groups such as positive amino groups, sulfhydryl groups and carboxylic groups which allowed the Au(III) ions to get more closure to binding sites and approved the reduction of Au(III) to Au(0). A 0.1 mM solution of Au(III) was reacted with powdered oat biomass at pH values of 2–6 for one hour. As in the case of wheat, oat biomass produced fcc tetrahedral, hexagonal, decahedral, icosahedral multitwinned, irregular, and rod-shaped nanoparticles.

It was reported that most of the nanoparticles synthesized by using alfalfa, wheat, and oat at pH 2 had an irregular shape. However, it seems that pH has a major impact on the size of the produced nanoparticles rather than on the shape of them. Sterilized geranium leaves (P. graveolens) when exposed to chloroaurate ions separately resulted in rapid reduction of the metal ions and formation of stable gold nanoparticles of variable size. ***Fig. 4.***

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Fig. 4. Biomaterial-mediated Synthesis and Shape Control of Nanoparticles

Biosynthesis of Silver and Gold Nanoparticles via Biomass

The reduction of the $AuCl^{-}_{4}$ ions was nearly complete after 60 min of reaction and the particles (20–40 nm) were predominantly decahedral and icosahedral in shape. Not only silver nanoparticles (55 to 80 nm) could be produced, but also triangular or spherical gold nanoparticles could be easily formed by reaction of the novel sundried biomass of Cinnamomum camphora leaf with aqueous silver or gold precursors at ambient temperature. Size dispersity of quasispherical silver nanoparticles as well as triangular or spherical shapes of gold nanoparticles could be facilely controlled by simple variation of the amount of biomass reacting with aqueous solution of $AgNO_3$ or $HAuCl_4$.

Eco-Friendly Plant-Based Synthesis of Nanoparticles for Diverse Applications

Nanoparticles possess a high surface-area-to-volume ratio and include materials such as cadmium sulfide, zinc sulfide, gold, zinc oxide, and silver, which play vital roles in various fields (Malarkodi et al., 2014). The plant-based biological synthesis of nanoparticles is gaining importance due to its eco-friendly nature. The biosynthesis of gold nanoparticles using plants such as *Tamarindus indica* (Kantak and Gogate, 1992), *Cinnamomum camphora* (Singh et al., 1996), lemongrass (*Sharma et al.*, 2003), alfalfa (*Shetty et al.*, 2006), *Emblica officinalis* (Sood et al., 2006), *Aloe vera* (Gupta et al., 2006), and *Azadirachta indica* (Samjon et al., 2007) has been well-documented.

Plant-based drugs are also used in the treatment of various conditions, including Parkinson’s disease, cardiovascular diseases, pulmonary diseases, Alzheimer’s disease, cancer therapy, diabetes, and osteoporosis. The development and design of plant-derived herbal nanoparticles are emerging as significant areas of research in nano formulation. Currently, nanoparticles are being widely developed to enhance bioavailability and treat cancers, such as lung, breast, and pancreatic cancers. Common nano formulated herbal drugs are derived from *Curcuma longa*, *Panax ginseng*, *Withania somnifera*, *Silybum marianum*, *Salvia miltiorrhiza*, and *Gymnema sylvestre* (Jadhav et al., 2014) ***Fig. 5.***

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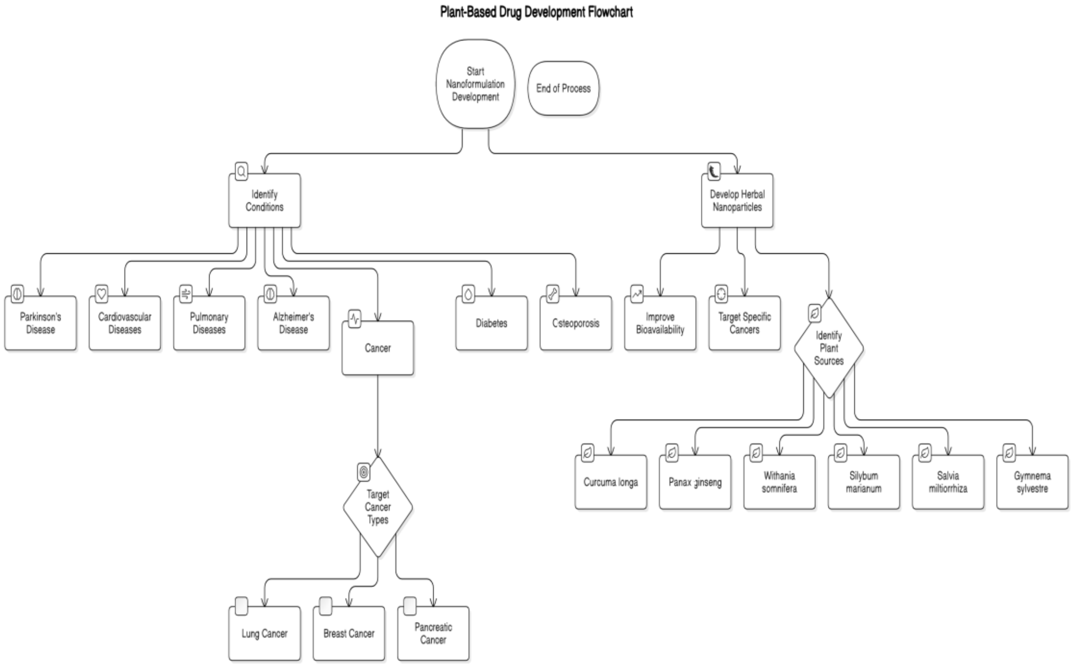

Fig. 5. Plant-Based Drugs and Herbal Nanoparticles in Treating Various Diseases

Exploring Herbal Nanoparticles for Combating Microbial Resistance in Healthcare

The rise of microbial resistance to antibiotics and traditional treatments poses a significant challenge in healthcare. Scientists are exploring the development of cost-effective and efficient antimicrobial drugs. Herb-based nanoparticle medicines have shown potential to counter microbial resistance more effectively than antibiotics (Nagarajan and Rajagopalan, 2008). Herbal nanoparticles have demonstrated antibacterial efficacy and cytotoxicity toward human cells, providing promising therapeutic options (Bhattacharya and Rajinder, 2005).

Green chemistry integrates nanotechnology and biotechnology for the biological synthesis of nanoparticles. The biosynthesis of nanoparticles such as silver, gold, gold-silver alloys, tellurium, selenium, platinum, silica, palladium, titania, zirconia, quantum dots, magnetite, and uraninite using phototrophic eukaryotes, including plants and their products, has been reported (Gardea et al., 1999). While biologically synthesized nanoparticles are non-monodispersed and slower to produce, their stability and eco-friendliness make them valuable alternatives.
Phytochemicals present in plants and their parts play significant roles in nanoparticle synthesis. Specific compounds used include oxidoreductive labile metabolites like ascorbates, catechol, and polyhydroxy components (e.g., alkaloids, flavonoids, polysaccharides), as well as proteins, enzymes, and secondary metabolites such as terpenoids, quercetin, and phenolic compounds (Shankar et al., 2003; Jha et al., 2009; Lin et al., 2010). These phytochemicals facilitate the green synthesis of nanoparticles, making the process both efficient and sustainable.
The biological synthesis of nanoparticles using enzymes, fungi, plants, or plant extracts is a promising eco-friendly alternative to traditional physical and chemical methods. Utilizing plants or their parts in nanoparticle synthesis eliminates the need for maintaining complex microbial cultures, making it a simpler and more sustainable approach (Klaus et al., 1999).

Principles of Sustainable and Green Chemistry
The concept of **Green Chemistry** for **Sustainable Development** has been universally studied for less than 15 years (Clark and MacQuarrie, 2008). Sustainable development can be defined as the process that meets the needs of the present while ensuring future generations can meet their own needs (Robert et al., 2005). This concept holds particular significance for chemistry-based industries due to its focus on pollution reduction and the sustainable use of natural resources (Omer, 2008).
Chemistry has long been perceived as a hazardous science, with the term "chemical" often associated with danger and toxicity (Wilson and Schwarzman, 2009). While protective gear is commonly used to mitigate risks, failure of safety precautions can lead to increased exposure and hazards. In high-risk situations, such failures can result in disastrous consequences, including severe injury or loss of life (Crowl and Louvar, 2001; Anastas and Eghbali, 2010). Therefore, designing safe, sustainable chemicals and processes requires minimizing inherent hazards and reducing the risk of accidents and damage (Centi and Perathoner, 2009; Al Ansari, 2012).

Green Synthesis of Nanoparticles
The green synthesis of nanoparticles involves three primary conditions:
1. Selection of environmentally friendly solvents.
2. Use of effective reducing agents.
3. Application of safe stabilizing materials.

Various synthetic routes are employed for nanoparticle production, with physical, chemical, and biosynthetic methods being the most common. However, chemical methods are often costly and involve hazardous chemicals that pose significant environmental risks (Nath and Banerjee, 2013). In contrast, the biosynthetic route provides a safe, biocompatible, and eco-friendly alternative, utilizing plants and microorganisms for biomedical applications (Razavi et al., 2015).

Plant-Based Nanoparticle Synthesis
Plant-based synthesis is an eco-friendly and sustainable approach that utilizes the natural phytochemicals found in various plant parts, such as leaves, fruits, roots, stems, and seeds, to facilitate the reduction and stabilization of nanoparticles. This method capitalizes on the inherent properties of these phytochemicals, which act as both reducing agents and stabilizers during the synthesis process. For example, Narayanan and Sakthivel (2011) demonstrated that certain plant extracts, rich in phenolic compounds and flavonoids, could efficiently reduce metal salts to their respective metal nanoparticles while simultaneously stabilizing the resulting nanoparticles to prevent aggregation.
The application of plant-based synthesis offers a significant advantage over traditional chemical methods, which often involve toxic chemicals and energy-intensive processes. By using natural substances from plants, this approach is more environmentally friendly, reducing harmful byproducts and promoting green chemistry principles. Moreover, the use of plant-derived reducing agents eliminates the need for additional chemical reagents, further contributing to the sustainability of the process. Narayanan and Sakthivel (2011) emphasized how various plant species, including medicinal plants, could be utilized to achieve the desired reduction of metal ions, ultimately producing nanoparticles with unique properties.
For instance, plant-based synthesis has been employed to create silver nanoparticles, which have found applications in areas such as antimicrobial coatings and drug delivery systems. The leaves of plants like *Azadirachta indica* (neem) and *Cinnamomum verum* (cinnamon) have been identified as excellent sources of phytochemicals capable of reducing silver ions to silver nanoparticles. These nanoparticles, stabilized by the plant extracts, exhibit enhanced antimicrobial activity, demonstrating the potential of plant-based synthesis in producing materials with practical uses in healthcare and other industries.
Furthermore, plant-based synthesis is not limited to metallic nanoparticles. It has also been successfully applied to the synthesis of semiconductor and alloy nanoparticles, offering a versatile and efficient alternative to conventional methods. The ability to tailor the properties of the nanoparticles by selecting specific plant extracts adds to the flexibility of this green approach. Studies by Narayanan and Sakthivel (2011) illustrated how varying the plant source and the extraction method could influence the size, shape, and stability of the synthesized nanoparticles, allowing for the design of materials with specific functionalities for diverse applications.
In conclusion, plant-based synthesis presents a promising and sustainable alternative to traditional nanoparticle synthesis methods. The ability to harness the natural reducing and stabilizing agents present in plant materials not only minimizes the environmental impact but also provides a cost-effective and scalable process for producing nanoparticles with unique properties. As demonstrated by Narayanan and Sakthivel (2011), this approach has a broad range of applications, from environmental remediation to the development of advanced materials, making it a significant area of research and innovation in nanotechnology. Nanoparticle synthesis methods can be categorized into two approaches:

Plant-Based Synthesis: Bottom-Up and Top-Down Approaches
Nanotechnology has gained immense popularity in recent years due to its potential applications in medicine, environmental science, and material engineering. One of the most eco-friendly and sustainable methods for nanoparticle synthesis is plant-based synthesis, where plant extracts are used as reducing and stabilizing agents. The two main approaches for nanoparticle synthesis are the Bottom-Up approach and the Top-Down approach. Each method has its advantages and is used in different contexts depending on the desired properties of the nanoparticles.

Bottom-Up Approach in Plant-Based Synthesis
The Bottom-Up approach involves the assembly of nanoparticles from atomic or molecular precursors. This method mimics biological processes where molecules self-assemble to form larger structures. In plant-based synthesis, this approach is widely used as plant extracts contain various biomolecules, such as flavonoids, phenols, and alkaloids, which facilitate the reduction of metal ions and control the shape and size of nanoparticles. For example, gold nanoparticles (AuNPs) can be synthesized using green tea extract. The polyphenols present in green tea act as reducing agents, converting gold ions (Au^{3+}) into gold nanoparticles. Similarly, silver nanoparticles (AgNPs) have been synthesized using neem (Azadirachta indica) leaf extract, where the biomolecules present in the extract reduce silver ions (Ag^{+}) to form

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stable silver nanoparticles. These plant-based nanoparticles exhibit excellent antimicrobial, antioxidant, and catalytic properties, making them suitable for medical and industrial applications.

The Bottom-Up approach is advantageous as it allows precise control over the size and shape of nanoparticles and requires lower energy input. Additionally, it is more environmentally friendly than conventional chemical and physical methods. However, the main limitation is the difficulty in scaling up the synthesis process while maintaining uniformity in particle size.

Top-Down Approach in Plant-Based Synthesis

The Top-Down approach involves breaking down bulk materials into nanoscale structures using mechanical, chemical, or biological methods. This method is generally used when a larger material needs to be converted into nanoparticles with specific characteristics. A good example of the Top-Down approach in plant-based synthesis is the mechanical grinding of plant-derived carbon materials to produce carbon-based nanoparticles. For instance, carbon dots (C-dots) can be synthesized by pyrolyzing coconut shell or banana peel and then grinding the resulting carbonaceous material into nanoparticles. These carbon-based nanoparticles have excellent fluorescence properties and are widely used in bioimaging and drug delivery applications. Another example is the biosynthesis of cellulose nanofibers (CNFs) from plant fibers such as cotton or bamboo. In this case, the plant fibers are first mechanically processed into smaller structures and then subjected to enzymatic or acid hydrolysis to obtain nanocellulose. These cellulose nanofibers have high strength, low toxicity, and excellent biodegradability, making them ideal for packaging, biomedical applications, and composite materials. The Top-Down approach provides better scalability and allows for the production of a large quantity of nanoparticles. However, it often requires high energy input, specialized equipment, and additional purification steps to obtain uniform particle sizes.

Both the Bottom-Up and Top-Down approaches have their own advantages and limitations in plant-based nanoparticle synthesis. The Bottom-Up approach is ideal for precise and eco-friendly synthesis using plant extracts, whereas the Top-Down approach is beneficial for large-scale production from bulk plant materials. By integrating these methods, researchers can develop sustainable and cost-effective nanomaterials for various industrial and biomedical applications. **Fig. 5.**

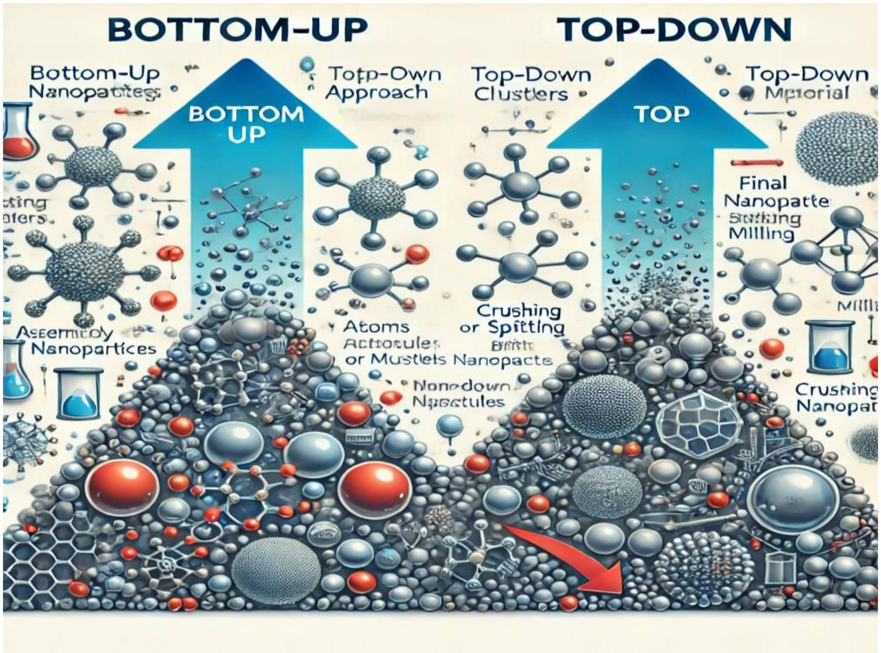

Fig. 5. Plant-Based Nanoparticle Synthesis: Bottom-Up vs. Top-Down Approaches Overview

Both top-down and bottom-up approaches for nanoparticle preparation involve chemical and physical methods, which can be expensive and environmentally hazardous due to the use of toxic chemicals that pose biological risks. In contrast, plant-mediated nanoparticle synthesis does not rely on these physical or chemical methods. It is an environmentally friendly, biocompatible, and highly stable method, making it increasingly popular among researchers worldwide.

The stability, shape, and size of nanoparticles can be precisely controlled by adjusting variables such as temperature, pH, concentration of plant extract, metal salt solution, and incubation time. Siddiqi and Husen (2016) reviewed the synthesis of palladium and platinum nanoparticles, providing a comprehensive overview of synthesis techniques and their potential applications in diagnostics, biosensors, medicine, catalysis, and pharmaceuticals.

Conclusion

In recent decades, the growing demand for green chemistry and nanotechnology has led to the adoption of sustainable synthetic methods for producing nanomaterials using plants, microorganisms, and other natural sources. Green synthesis of nanoparticles has become a key area of research, with a focus on eco-friendly approaches. Much of the research has centered around plant extract-mediated nanoparticle synthesis, exploring their potential applications across various fields due to their cost-effectiveness, non-toxic nature, easy availability, and environmental friendliness.

Traditional methods of nanoparticle synthesis are often expensive and generate toxic byproducts, necessitating efforts to minimize the risk of contamination from chemicals used in chemical and physical processes. As a result, the use of plant extracts in nanoparticle generation, known as green synthesis, has emerged as a vital aspect of nanotechnology. Plant extracts are readily accessible, making them an ideal resource for developing efficient, sustainable routes for scaling up and industrializing the production of well-dispersed metallic nanoparticles.

This review highlights recent advancements in the plant-assisted synthesis of metal nanoparticles and critically examines the various mechanisms proposed to explain these processes. The plant-assisted synthesis offers several advantages, including eco-friendliness, biocompatibility, and cost-effectiveness. Researchers have focused on understanding the biochemical pathways and enzymatic reactions involved in nanomaterial biosynthesis, as well as identifying and characterizing the biomolecules responsible for nanoparticle formation. Ongoing research continues to make significant contributions from diverse fields, providing innovative solutions to address key challenges in the field.

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