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Review Article

Green Chemistry Based Benign Routes for Nanoparticle Synthesis

**Parth Malik,[1] Ravi Shankar,[1] Vibhuti Malik,[2]
Nitin Sharma,[3] and Tapan Kumar Mukherjee[4]**

[1] *Centre for Nano Sciences, Central University of Gujarat, Gandhinagar, India*
[2] *Department of Pharmaceutics, Hindu College of Pharmacy, Sonepat, Haryana, India*
[3] *School of Chemical Sciences, Central University of Gujarat, Gandhinagar, India*
[4] *Department of Biotechnology, Maharishi Markandeshwar University, Mullana, Ambala, Haryana, India*

Correspondence should be addressed to Tapan Kumar Mukherjee; tapan400@gmail.com

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Green chemistry has been an eye catching area of interest since the past few years. With the problem of energy crisis looming high and its constraint being particularly vulnerable on the developing economies, the need for giving alternative traditional chemistry a serious consideration as well as adequate room for development has received significant boost through the coveted efforts of multidisciplinary and interdisciplinary scientific fields. Nanoscience has been the right field in this dimension as it opens up the door to multiple opportunities through enabling a number of chemical, biochemical, and biophysical transformations in a significantly easier and reliable manner. The use of nanoparticles has made the fields of catalysis, synthesis, and enzyme immobilizations as well as molecular interactions a lot much easier, rapid and easily controllable. This review article sheds light on the popular alternative synthesis routes being employed for the synthesis of nanoparticles, the pivotal being from microbes, plants, and chemical routes via sonication, microwaving, and many others.

1. Introduction

Ever since the realization of unconventional properties of matter at nanoscale has assumed significant proportions, there have been numerous attempts to synthesize metallic and metal oxide based nanoparticles through several non-conventional routes. Nanotechnology has just occupied a very special place in the minds of researchers of chemical, biological, and physical backgrounds, which is especially interesting with the quantitative as well as qualitative outputs of nanoparticles. Though not all but silver, gold, zinc oxide, and platinum based nanoparticles have occupied the centre stage till now. The reason being obvious is that they are inert in themselves and can facilitate the surrounding chemical reactions increasingly well. Interestingly, the properties of nanoparticles synthesized using different routes have been found to be sufficiently different, which makes these routes even more powerful. Very easy and economical routes for their synthesis have been discovered. These do not require the technical expertise of well-equipped laboratory professionals. Moreover, these are relatively quicker in terms of output and can be carried out even at grass route levels, ranging from the vegetables we eat, plants we grow, and microbes we admire for their genetic diversities. The reason for the increasing interest in the synthesis of metal and metal oxide based nanoparticles through these routes lies behind their extraordinary abilities to function as catalysts and help in numerous processes of industrial, electronic, and physical applications. Their formational mechanisms using these routes are characterized by highly sensitive but equally specific oxidation-reduction reactions. We shall therefore first acquaint ourselves with the physicochemical impacts brought about by the variation in the oxidation states of metal based nanoparticles. The text ahead describes the synthesis of silver, gold, platinum, zinc oxide, and some other metallic nanoparticles through the simple biological, chemical, and physical methods that are

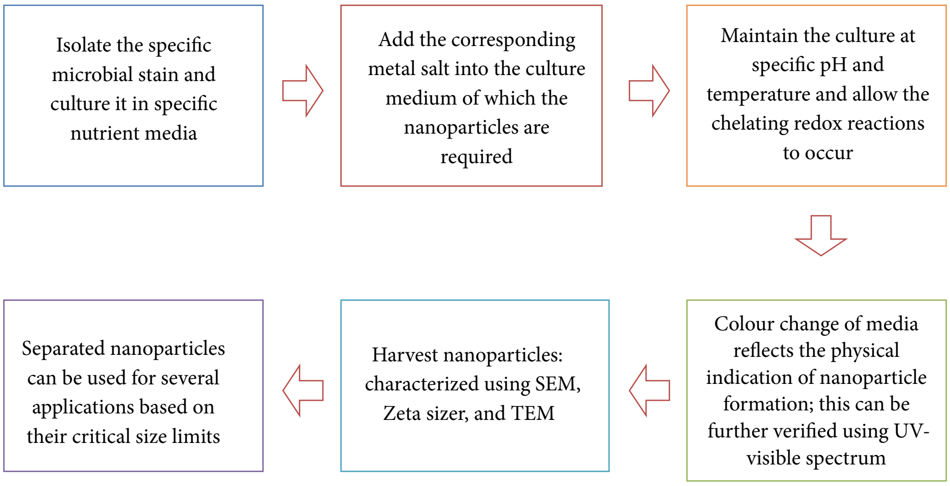


Figure 1: General mechanism of nanoparticle synthesis using microorganisms.

very traditional in terms of their experimental hierarchies. Although methods for the synthesis of nanoparticles fall into three broad categories, namely, physical, chemical, and biological, recent advances and interest coupled with accurate scientific perception in terms of accuracy and reliability of results in comparatively far reduced time have attracted several minds to go for better monitoring and optimization of biological methods for the synthesis of nanoparticles. Interestingly, biological route of nanoparticles synthesis also brings significant diversity with it, in the sense that nanoparticles can be synthesized using plants ranging from *Azadirachta indica* (neem) and *Ocimum tenuiflorum* (tulsi), vegetable extracts such as those of *Allium cepa* (onion), and microorganisms such as bacteria, fungi (mushroom extracts), algae, and perhaps even viruses. Besides this, a number of traditional physical methods purposely employed for grinding matter have been modified or retuned to operate at a higher scale so as to synthesize nanoparticles of different morphologies with fewer energy input, better specificity, and control. We will therefore discuss such green and alternate nonconventional routes for the synthesis of nanoparticles and the possible changing influences of their technical operations with respect to yield potential. A thorough knowledge and understanding of these methods is essential so as to understand the rationality of their incorporation in specific applications as per their yield potential.

2. Biological Synthesis Routes of Nanoparticles: A Glance at the Broadest Mechanism

The most versatile locations of the cellular structures of major biological entities are their cell membranes. This is because these are made up of lipids and membranes and are amphipathic in nature. These are the centres of most of the synthetic biochemical conversions following oxidation-reduction mechanisms. A vital characteristic of these membranous lipids is the fact that they are dynamic and flexible, meaning that their compositional influence is not always fixed. So, it enables a significant degree of diversity in their functioning which can drive redox reactions of biochemical concern with significant ease. As far as locational mechanisms are concerned, studies have revealed that both extracellular and intracellular driven synthesis of nanoparticles can be achieved using microorganisms by culturing them in specific environments which in turn makes them act as chelators to drive the coupled oxidation and reduction phenomenon. Another interesting observation stems from the fact that most of the extracellular synthesis of nanoparticles is based on electrostatic forces of attraction, which involve negatively charged phospholipids occupying the membranes of microorganisms and the positively charged metal ions that exist in the combined form in their corresponding salts [1]. These salts are deliberately added to the media in which the microorganisms are cultured. Figure 1 (ahead) gives us the idea for basic methodology or scheme of reaction mechanism involved in the biological preparation of nanoparticles. As depicted through this figure, we can vary the metal salts and specific culturing parameters to obtain nanoparticles of specific nature. In a way, we challenge the microbial species to grow in particular nutrient conditions. Metal ions from metal salts get detached and act in a positively charged state to combine with negatively charged membranous lipids. Thereafter, this leads to their reduction due to chelation brought about by extracellular membranous proteins of microorganisms. This results in the reduction of their oxidation states which in turn leads to the change in the physical appearance of colour of the culture media. This is the first indication of qualitative formation of the nanoparticles. We can incorporate the culture media with desired metal salts so as to prepare the desired metal based nanoparticles.

This choice of choosing the specific type culture media for a specific organism is critical because the interaction of the biological source, whether it is plant or microbial with the corresponding metal salt, forms the basis of nanoparticle formation and it may be possible that a particular combination of these two inputs may not provide the specific yield.

Table 1: Major bacterial species that are used for nanoparticle synthesis.

Bacterial strains exploited	Types of nanoparticle synthesized	Location of synthesized nanoparticles	Critical size range (in nm)	References
Pseudomonas stutzeri	Silver	Intracellular	200	[3]
Lactobacillus	Titanium dioxide	Intracellular	15–35	[4]
Acinetobacter spp.	Magnetite	Extracellular	10–40	[5]
Pseudomonas aeruginosa	Gold	Extracellular	15–30	[6]
Escherichia coli	Cadmium sulphide	Intracellular	2–5	[7]
Rhodopseudomonas capsulata	Gold	Extracellular, both at pH 4 and 7	(50–400) at pH 4 (10–20) at pH 7	[8]

3. Microbial Routes for Nanoparticle Synthesis

Microorganisms are by far the most diverse and significant living creatures across the world, largely because of their enriched genetic diversity. A number of bacterial, fungal, and algal species have been screened through numerous rigorous attempts for the synthesis of nanoparticles. These have been explored and are in most wide use for the synthesis of silver, gold, platinum, titanium dioxide, and zinc oxide nanoparticles. This route for nanoparticle synthesis is not only inexpensive but it is also less cumbersome, time consuming, complicated, and most importantly nontoxic. Moreover, with continuous interest and attempts, it has also been realized that some of the intended applications of nanoparticles are feasible only through their specific biological mode of synthesis. Another interesting aspect of microbiologically driven nanoparticle synthesis is the factor that it provides an excellent yield which is otherwise not achievable by the use of chemical and physical methods in a definite time span. An additional advantage of the synthesis of nanoparticles by biological route is the fact that this is a bottom-up approach and is very specific in nature. The significant edges that it incorporates in the nanoparticle synthesis include far less requirement of energy, less wastage of inputs, and more practical control of constituent ingredients. This is so as we have better control over the molecular units that will be forming the entire nanoparticle entities. The text ahead discusses the bacterial, fungal, and other microbial routes for nanoparticle synthesis in a step by step manner.

3.1. Bacterial Mediated Nanoparticle Synthesis. A number of methods exist for bacterial mediated synthesis of nanoparticles. The main bacterial species that have been used for this purpose are *Pseudomonas*, *Lactobacillus*, *E. coli, Actinobacter* spp., and *Klebsiella pneumoniae*. The location of synthesis has been evaluated to be both extracellular and intracellular. Interestingly, the particular kind of nanoparticle synthesis depends critically on the operational parameters such as those of pH and temperature. Variations in the physical conditions often lead to different size range of the synthesized particles. The size range of nanoparticles synthesized is a very vital parameter for their specific application because the novelty in terms of major physicochemical properties will be more pronounced at smaller sizes. So a multitude of factors need to be optimized for the specific synthesis of nanoparticles in a particular configuration. Interestingly, extracellular and intracellular synthesis of nanoparticles have been reported in some studies that has been chiefly due to specific alterations in the ionic atmosphere and temperature of reaction conditions.

Since bacteria possess a rich diversity of versatile biocatalysts, studies have reported the synthesis of silver nanoparticles from psychrophilic bacteria that live in highly low temperatures. In one such attempt, it has been comprehensively shown that it is due to intracellular bacterial proteins and the chelating activity of DNA subunits that nanoparticles are formed [38, 39]. This attempt has also shown excellent antibacterial activity of silver nanoparticles [40]. Moreover, studies have also shown that not always it takes same time for the formation of nanoparticles after the culture has been just ready. Some attempts have involved the incubation period of two hours while some have also taken twenty-four hours. Interestingly, these attempts present some cheerful results regarding the particle size which in turn form the basis of major applications of these entities [41–44].

Table 1 summarizes the different bacterial species that have been analyzed for the intracellular or extracellular synthesis of nanoparticles along with the specific size range reported and intended applications. A very interesting observation of this table is the synthesis of nanoparticles from *Rhodopseudomonas* species which synthesizes nanoparticles both at intracellular and extracellular locations but at different pH values.

3.1.1. Extracellular and Intracellular Synthesis: Defining Aspects. The versatile aspect of biochemically exceptional microbial genomes is the fact that they enable intracellular as well as extracellular synthesis of different types of metallic nanoparticles. Some interesting studies recently have found that few microbial species exist and colonize within the industrial mines and deposit metal in the crude form inside their bodies with the help of their enzymes at the metallurgical sites. For instance, pedomicrum bacteria which reproduces via budding, has been found to intracellularly deposit iron, manganese oxide in the nanophase form, has just recently been found to deposit gold in the nanoscale form [45]. Similarly, *Bacillus subtilis* 168 have been found to be implicated in the aqueous reduction of gold from trivalent to zero-valent state and to deposit it intracellularly in the form

Table 2: Major fungal strains for nanoparticle synthesis at intracellular locations.

Fungal species	Type of nanoparticle	Location and morphology	Size limit (in nm)	References
Verticillium sp.	Au	Intracellular	(25–30)	[9]
Aspergillus flavus	Ag	Intracellular	(8–10)	[10]
Trichothecium sp.	Au	Intracellular	Not determined	[11]
Verticillium sp.	Ag	Intracellular	(25–35)	[12]

of nanoparticles with dimensions of 5–25 nm and an octahedral morphology of shapes. These nanoparticles have been found to prevail inside the bacterial cell walls [46]. Several other microbial species have been explored that mediate the intracellular synthesis of metallic nanoparticles of different types. One of these is sulphate reducing bacteria which, when enriched with gold salts in the gold mines, can produce gold from gold-thiosulfate complex in the metallic form of 10 nm size, releasing hydrogen sulphide (H_2S) as the end product of its metabolism. Similarly, quite recently, *Escherichia coli* DH5α has been just observed to accomplish the biochemical reduction of gold from aurochloric acid to gold nanoparticles. The nanoparticles get adhered onto the surface and are mostly spherical in shape with some percentage of triangular and hexagonal morphologies also. Since these nanoparticles are bound to the cell surface, they have been richly exploited for promising applications considering their similarity of origin with iron complexed haemoglobin and other *in vivo* proteins [47]. There are some *in vivo* factors also which decide whether the microbial synthesis of nanoparticles will be extracellular or intracellular. Curiously enough, this depends on the particular locations of the bioreducing enzymes present in the microbes. However, there have been certain complications in retrieving the intracellularly synthesized nanoparticles which range from additional reduction and isolation steps that together make the downstream processing of the overall process expensive and time consuming. These require the high energy treatments through ultrasound and treatment with chelators in the form of detergents. An immense benefit of extracellular synthesized nanoparticles is the fact that they are native after getting formed and can be immediately tapped for several applications such as those of optoelectronics, bioimaging, electronics, and sensor integration. Another sensitive aspect of synthesized nanoparticles is their particular shape which favours them for particular applications. This is because applications from different fields require different functions to be performed and that is why the shapes of nanoparticles have decisive roles as they dictate their particular functionalities.

3.2. Fugal Mediated Nanoparticle Synthesis.

Even though fungal culture is risk prone, studies have shown the synthesis of a range of nanoparticles, both at extracellular as well as intracellular locations. Fugal strains such as *Fusarium*, *Penicillium,* and *Aspergillus* species have been reported multiple times for the synthesis of several different kinds of nanoparticles. Fungal cultures possess some additional attributes with respect to their bacterial counterparts. For instance, the optimization for scale-up of fungal cultures has revealed that fungal mycelia can withstand the culturing fluctuations of the scale-up treatment in the bioreactor which perhaps plant and bacterial based extracts cannot. Moreover, fungal species also possess a fastidious nature of growth and this is a very vital aspect in the nanoparticle formation through the use of fungal species. This is so because this enables the release of very vital enzymes and proteins in sufficient concentrations that in turn enables easier bioreduction of corresponding metal salts to form the biochemically reduced metallic ions as zero-valent nanoparticles. Their fast growth and prompt participation in the overall nanoparticle synthesis also eliminate the technical hurdles of the downstream processing involved. Fungal species, till date, have been explored for both extracellular and intracellular synthesis of nanoparticles. Just as in case of bacterial mediated nanoparticle synthesis, there are some highly localized aspects which are concerned with specified extracellular or intracellular synthesis of nanoparticles.

In general, nanoparticles synthesized at intracellular locations are smaller in size and thus are more specific as far as their application requirements are concerned. However, in their case, the downstream processing approaches are very typical and the extraction procedures are tough. This makes them suffer from disadvantage of low yields. In case of extracellular nanoparticles, we can readily isolate them, comparatively with a lot more ease, and the downstream processing is also very simplified in nature. In addition, since these are synthesized outside the cells at cell surface or at the periphery, they are easy to be tapped for several applications and can readily be made use of without the involvement of individual different extractive methodologies. In one of the earliest attempts to synthesize nanoparticles at the intracellular locations within the fungal genomes, Mukherjee and coworkers who reported the synthesis of gold nanoparticles using *Verticillium* species. In their study, the contributors got the nanoparticles synthesized on the surface as well as on the cytoplasmic membranes of the fungal mycelia, which were found to be approximately of 20 nanometers in size by TEM analysis. Table 2 highlights the major fungal species that have been cultured with respect to their ability to synthesize nanoparticles as intracellular metabolites. A very notable aspect with respect to the utility of synthesized nanoparticles that critically affects their application potential is the morphology in which these are synthesized (Figure 5). Studies have shown a very close relationship between the critical shapes and functional potential of the nanoparticles. Most of the material science applications have favoured their use if they are spherical in their shapes. In addition, there are some other sectors which employ them such as those of cosmetics and antiseptics, which necessitate that

Table 3: Extracellular synthesis of nanoparticles from fungal species.

Fungal strain	Type of nanoparticle	Morphology and size	References
Fusarium oxysporum	Au	Spherical and triangular, 20–40 nm	[13]
Colletotrichum sp.	Au	Spherical, 20–40 nm	[14]
Aspergillus niger	Ag	Spherical, 20 nm	[15]
Volvariella volvacea	Ag and Au	Spherical and hexagonal, 20–150 nm	[16]
Penicillium fellutanum	Ag	Spherical, 5–25 nm	[17]
Fusarium oxysporum	CdSe	Spherical, 9–15 nm	[18, 19]
Fusarium oxysporum	Magnetite	Quasi-spherical, 20–50 nm	[20]
Fusarium oxysporum	Si, Ti, and Zr	Spherical, 5–15 nm	[21, 22]

Table 4: Major viral species for nanoparticle synthesis.

Microorganism	Nanoparticle	Location/morphology	References
Tobacco mosaic virus (TMV)	SiO_2, CdS, PbS, and Fe_2O_3	Nanotubes on surface	[23]
M13 bacteriophage	ZnS and CdS	Quantum dots, nanowires	[24, 25]

they should be very good supportive mixers and facilitate excellent adsorption. In such cases, the intact morphology of synthesized nanoparticles need not always be spherical. Moreover, there are some applications which involve the incorporation of nanoparticles in the form of nanocoatings and anticorrosive applications. All these are significantly wayward applications chiefly characterized by the shapes of nanoparticles.

This is so because, other than size, the shape of nanoparticles is a very dominating aspect for their physicochemical behaviours and this also affects the basic chemical aspects in terms of the arrangements of atoms at such minute dimensionalities.

Table 3 (ahead) represents the major fungal species that have been exploited for extracellular synthesis of metal based nanoparticles. It is clearly visible from this that *Fusarium oxysporum* remains the most favoured species for nanoparticle extraction. Another observation is the fact that the resultant nanoparticles from each species are of different size limits and shapes which are the deciding features of their applications. Extracellular synthesis of nanoparticles remains a favourable route for far less complication involved in recovery of the metabolites.

3.3. Viral and Yeast Mediated Nanoparticle Synthesis. The studies with bacteria and fungi have yielded the synthesis of nanoparticles that are mostly metal based or in some very specialized conditions, the metal oxide nanoparticles (Table 4). However, fungus may lead to heterogeneous nanoparticle synthesis but such studies with bacteria are far less in number (Table 5). When we talk about the application of nanoparticles, a significant focus is seen to be highlighted over the electronic aspects, the way they improve semiconducting applications. The mechanisms by which they lead to phenomena such as those of cathodoluminescence and surface plasmon resonance really present some intriguing aspects. Such applications require the synthesis of the nanoparticles that are made up of inorganic materials such as those of cadmium selenide, cadmium sulphide, iron oxide, and lead sulphide. Viruses, though almost impossible to culture *in vivo*, can be unique assets.

4. Synthesis of Nanoparticle from Plants

The most interesting biochemical and yield specific source for synthesis of nanoparticles is the plant biodiversity. Plants with highly rich genetic variability possess a number of interesting biomolecules in the form of coenzyme, vitamin based intermediates, and so many others which can reduce metal ions to nanoparticles in a single step. Moreover, these methods can be easily conducted at room temperature and pressure, without any hard and fast technical requirements. Furthermore, plant based nanoparticle synthesis approaches are easy to scale up and are traditionally also favoured because of their environment friendliness. Plant metabolite materials serve as excellent reducing agents, which include phenolic compounds, alkaloids, and sterols. Additional advantage is that it is a green synthesis method and, along with the use of plant extracts, live plants can also be used for nanoparticle synthesis. Till date, most of the studies have focused on the use of plant material for silver and gold nanoparticles. The thrust behind plant mediated nanoparticle synthesis attracting significant boost is due to the fact that this route of nanoparticle synthesis enables the products which can be exploited for multiple applications such as those of nanomedicine based innovations. One significant advantage of plant mediated nanoparticle synthesis getting more favorability and reliable application potentials has been the fact that plant modified materials are easy and inexpensive to be cultured as compared to those of microorganisms. Another significant factor is the ease of procedural and result based advantages coupled with relatively quicker applicational administrations which make plants better and more favoured destinations. Studies have been reported in the literature which has involved the use of whole plant based material as extracts for the synthesis of nanoparticles [48, 49]. In comparison to using whole plant tissue as extracts, studies with plant extract materials as inputs for making

Table 5: Major yeast strains involved in nanoparticle synthesis.

Microorganism	Nanoparticle	Size, shape	Location	References
S. cerevisiae	Sb_2O_3	3–10 nm, spherical	Intracellular	[4]
C. glabrata	CdS	20 A, spherical	Intracellular	[26]
S. pombe	CdS	1–1.5 nm, hexagonal	Intracellular	[27]
Torulopsis sp.	PbS	2–5 nm, spherical	Intracellular	[28]
Yeast strain MKY3	Ag	2–5 nm, hexagonal	Extracellular	[29]

Aloe vera *Ocimum tenuiflorum* (tulsi) *Azadirachta indica* (neem)

Geranium species *Camellia sinensis* (tea) *Datura metel*

Figure 2: Some plant species used to make nanoparticles.

nanoparticles have reported much better control and also significantly better results. With advancements and increasing requirements of nanoparticles, the plant extract based nanoparticle synthesis has received much needed boost in the recent years [31, 34, 50–64]. Plant extracts are believed to act as reducing agents and stabilizing agents in the nanoparticle synthesis. The nature of plant extract affects the kind of nanoparticles synthesized in a highly critical manner with the source of plant extract being the most vital factor affecting the morphology of synthesized nanoparticles [65]. Interestingly, this is so because different plant extracts contain different concentrations of biochemical reducing agents [66].

In the production of nanoparticles from the plant extracts, the plant extract is simply mixed with a solution of metal salt at room temperatures. The reaction is completed within few minutes and, as a result of biochemical reduction, the metals are converted from their mono or divalent oxidation states to zero-valent states. This marks the formation of nanoparticles, which is physically indicated through the colour change observed in the culture medium vessel. Synthesis of gold, silver, and a number of other metal based nanoparticles have been reported in this manner [67]. These plant based biochemical reductions are so versatile in nature that silver nanoparticles have been produced from extremely common plants such as those of *Azadirachta indica* (neem) and *Ocimum tenuiflorum* (tulsi), which are familiar in almost every household. Figure 2 highlights some of the most frequently employed plant varieties for nanoparticle synthesis. Every new plant species has some excellent biomolecule in its genome through which it brings about the biochemical reduction. For instance, during the synthesis of silver nanoparticles from geranium leaf extract, the synthesized particles formed quite rapidly and a size limit of 16–40 nanometers was obtained [14]. In another

Table 6: Major plant species employed for nanoparticle synthesis.

Plant involved	Type of nanoparticle	Morphology and size	References
Acalypha indica	Ag	20–30 nm, spherical	[30]
Aloe vera	Au and Ag	50–350 nm, spherical, triangular	[31]
Azadirachta indica (neem)	Ag/Au bimetallic	50–100 nm	[32]
Cinnamomum camphora	Au and Pd	3.2–20 nm, cubic hexagonal crystalline	[33]
Datura metel	Ag	16–40 nm, quasilinear superstructures	[34]
Geranium leaf	Au	16–40 nm	[14]
Jatropha curcas L. latex	Pb	10–12.5 nm	[35]
Nelumbo nucifera (lotus)	Ag	25–80 nm, spherical and triangular	[36]
Rhododedendron dauricam	Ag	25–40 nm, spherical	[37]

nice modification, a study reported the synthesis of silver nanoparticles from geraniol, a natural alcoholic substance found in some plants. This compound reduced silver ions from its monovalent state from the silver nitrate salt to its zero-valent state, which was gathered together with a size range of 1–10 nm [68].

Subsequent studies with these synthesized nanoparticles revealed their anticancer potentials when they were used at a concentration of 5 micrograms per mL with a potency of almost 60% [68, 69]. Similarly, synthesis of silver nanoparticles was reported using the extract of plant *Desmodium* triflorum. These were attributed to the bioreducing abilities of hydroxyl ions, NAD+, and ascorbic acid in the extract [70]. Similarly, excellent nanoparticles, in terms of size and morphology, were obtained from the leaf extract of *Datura metel* by Kesharwani and coworkers. The product in this study had excellent stability and size limit was also highly appropriate within the range of 16–40 nanometers. The most interesting aspect revealed in this study was the presence of several bioactive compounds in the concerned leaf extracts, ranging from alkaloids, amino acids, alcoholic compounds, and several other chelating proteins, which were collectively considered responsible for the reduction of silver ions in the nanoparticle form. Further analysis found that alcoholic intermediates such as those of quinol and chlorophyll pigments were responsible for reduction of silver ions to the zero-valent forms and their excellent stabilization as product formation [34]. Table 6 provides us a detailed picture regarding the major plant species used for nanoparticle synthesis. An interesting aspect of plant mediated nanoparticle synthesis is the fact that the bioconversions are under much better control as compared to other biological methods employed for nanoparticle synthesis.

Many useful plant species such as those of *Jatropha*, *Geranium*, and common lotus plant (listed in Table 6), have been viciously used for nanoparticle synthesis. A significant observation drawn out from Table 6 clearly shows that most of the plants have been used for the synthesis of gold and silver nanoparticles. Another interesting aspect of concern is the fact that these plants give these products only when specifically cultured under a particular set of variable conditions that include temperature, pH, and characteristic salt concentrations administered. The only thing that makes the plant derived nanoparticle synthesis route, less popular, is the fact that plant cell culture is relatively difficult when compared to microbial cultures. Moreover, in some cases, the callus development is essential which imparts more complicacy to the process.

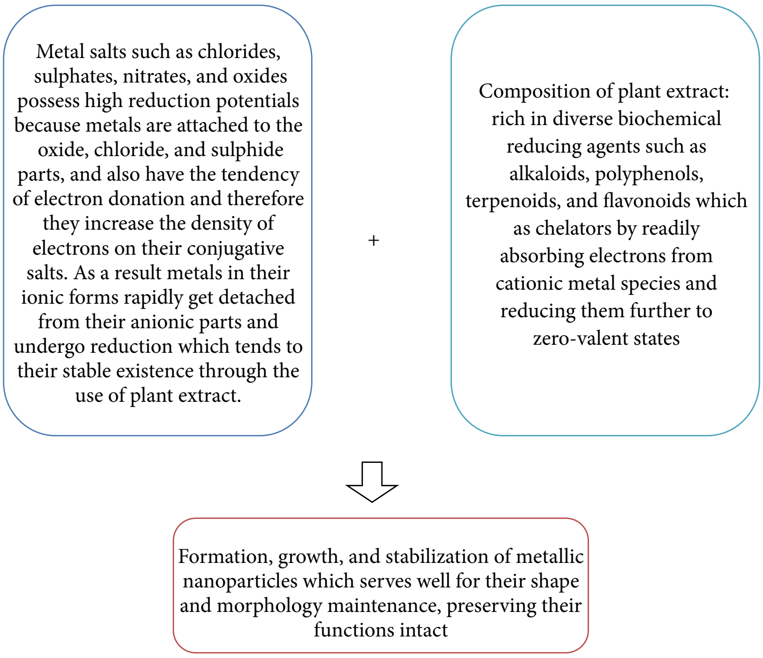
Figure 3 presents the summary of plant mediated nanoparticle synthesis which tells us what the possible configurations for nanoparticle synthesis through the biochemically rich plant species can be. This figure is just an analogue of Figure 1 but it only specifically tells us about plant mediated nanoparticle synthesis. Plant extract material is rich in compounds of different nature such as those of flavonoids, terpenoids, and many other phenolic intermediates which brings about the bioreduction of metal salt solutions administered during the culture. Figure 4 further explains how plant driven nanoparticle synthesis can be directed towards highly selective and specific nanoparticle formation which can be either in the form of dictated aggregation mediated through self-assembly or the nanoparticle stabilization by their synthesis within controlled structures that can hold them without altering their stabilities. This particular ability can be very useful for applications of integrated nanostructure assembly.

Figure 4 explains that nanoparticles are not only synthesized by plants but they can also be formed if the surrounding environment presents with stabilizing environment to mediate the redox status required for their critical formation. This is further helpful for the optimization of these nanoparticles with respect to their properties.

First step explains the formation of zero-valent nanoparticles which lead to the growth of these particles upon their aggregations mediated via noncovalent interactions. The second step shows the matrix stabilization of a particular type of nanoparticles which can be in a resin matrix or in some other hybrid form. The formation of phenolic resins composed of nanoparticles of a particular kind is one such application of this kind. Plants can therefore serve as readily available and faster biochemically rich sources for nanoparticle synthesis.

5. Nonbiological Green Approaches for Nanoparticle Synthesis

Owing to the extraordinary ability of the nanoparticles to work as efficient catalysts and enable faster reaction mechanisms to mature and exceptional ability to develop into



Metal salts such as chlorides, sulphates, nitrates, and oxides possess high reduction potentials because metals are attached to the oxide, chloride, and sulphide parts, and also have the tendency of electron donation and therefore they increase the density of electrons on their conjugative salts. As a result metals in their ionic forms rapidly get detached from their anionic parts and undergo reduction which tends to their stable existence through the use of plant extract.

Composition of plant extract: rich in diverse biochemical reducing agents such as alkaloids, polyphenols, terpenoids, and flavonoids which as chelators by readily absorbing electrons from cationic metal species and reducing them further to zero-valent states

Formation, growth, and stabilization of metallic nanoparticles which serves well for their shape and morphology maintenance, preserving their functions intact

Figure 3: The mechanism of plant mediated nanoparticle synthesis.

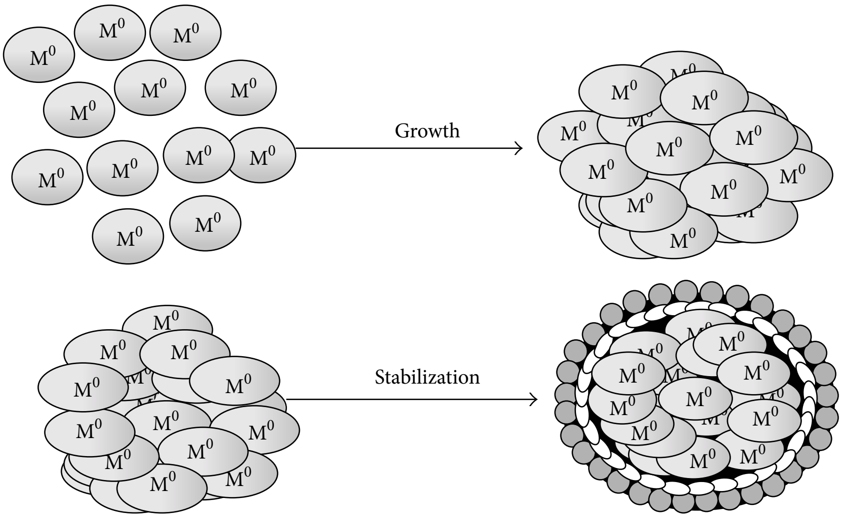


Figure 4: Formation, growth, and stabilization of nanoparticles mediated via plant cultures [2].

integrated complexes and networks, a number of interesting chemical approaches have been developed for the synthesis of nanoparticles. The most significant and challenging parts concerned with the green method selection are the optimization of energy needs of the synthesis method and the corresponding energy constraints of the process. A number of traditional physical methods with reasonable modification in their methodology have been mastered for controlled synthesis of nanoparticles. The distinguishing benefits of these methods range from their energy requirements, far less degree of hazard generation ease of applicability and feasibility, and higher yield potential. Major inroads have been made by methods like microwave treatment, ultrasonication, flocculation with surfactants, and many others. In this reference, sonication presents a very reliable option and controllable measure to synthesize nanoparticles as it involves the energy generated via production of sound waves. This is not only a clean route for nanoparticle synthesis but it is also far less technical, sophisticated, and time consuming. Ultrasounds with frequencies as high as 20,000 Hz are very effective energy carriers and ensure a very easy breakdown of bulk precursors to yield nanoparticles with specific applications and morphology. Sonochemistry has thus been very reliably employed for the synthesis of nanoparticles. Studies

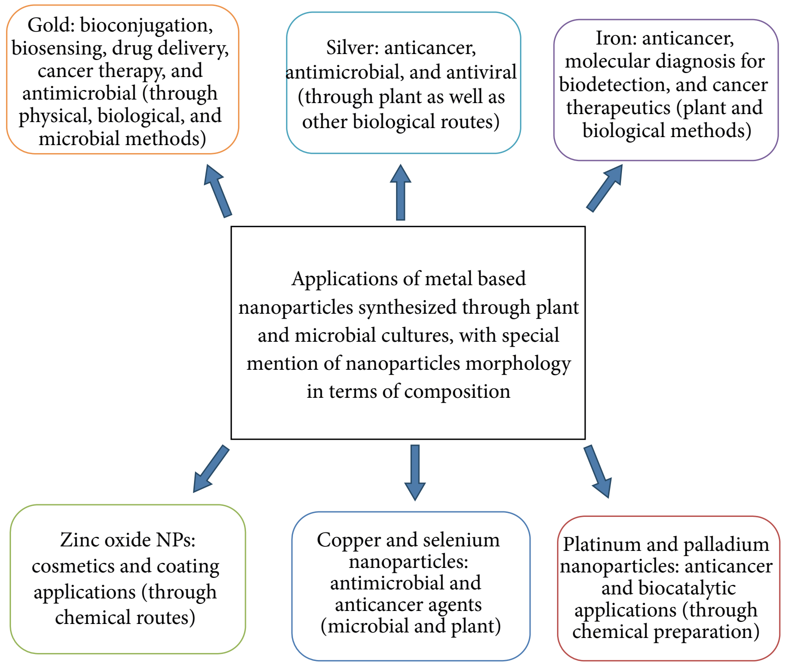


Figure 5: Applications of different kinds of nanoparticles with specification of methods employed.

and investigations in the different parts of the world report that the mechanism through which ultrasound forms or aids in the nanoparticle synthesis is via acoustic cavitation, which is best described by the formation, growth, and violent collapse of bubbles in a liquid. Subsequently, the extreme conditions generated during the bubble collapse result in the formation of nanoparticles [71]. The development of other nonconventional routes such as those of microwave-enabled synthesis and room temperature coprecipitation with the aid of emulsification is also very promising approach being developed and considered alongside sonication as green methods for nanoparticle synthesis. Although these methods have been understood since long, some recent and very extraordinary research attempts have established the usability and specificity of these methods beyond any doubtful element and argument.

In a comprehensive compilation put forward by National Institute of Standards and Technology, USA, the importance of sonication and the physical basis of genesis of the sonication in liquid media has been discussed well in detail. Two specific outcomes which concretely enrich the knowledge about the method of sonication being a potent tool to synthesize nanoparticles emerge out of this contribution. Firstly, there has been a detailed description of direct and indirect sonication in the liquid media, whereby direct sonication has been referred to as the method in which there is active generation of ultrasound waves *via* immersion of an ultrasound probe and the indirect sonication has been referred to as the immersion of a container further in an enclosure in which the fluid can be sonicated via the sonication of the liquid already in the enclosure. Both modes have their own specific constraints to optimize their usage for nanoparticle synthesis. Secondly, the compilers of this contribution have put forward the fact that these methods are employed for the core synthesis of engineered nanomaterials (ENMs). Further, the fact which is most essential as well as informative is that the sonication results in prevention of agglomeration by manifestation of energy of sound waves of high frequency, so a lot depends on the optimization of physical factors affecting the rate of sonication, even though it is a green process [72].

Literature is further enriched with studies reporting the synthesis of nanoparticles via sonication and ultrasonication approach, but some recent reports are very encouraging with the specific aspects of reliability and energy considerations of the process. In a study reported in 2003, Pang et al. have synthesized lanthanum and strontium conjugated manganese dioxide nanoparticles using the sonication mediated coprecipitation. The optimization of their reported synthesis method has yielded nanoparticles as low as 24 nanometers in size after the thermal processing of the synthesized nanoparticles. The scientists associated with this study have also investigated the magnetic behaviour of the synthesized nanoparticles and also found that the magnetic nature of the particles is very sharp, with transition from paramagnetic to ferromagnetic behaviour being smoothly observed for all the properly processed samples at 366 K [73]. In another fabulous attempt, Zhongli et al. have reported the synthesis of silver nanoparticles via sonication method. In their attempt, the authors observed that the synthesis of nanoparticles is achieved through efficient coupling of precursors' silver nitrate and the polymer polyethyleneimine which is accomplished via micellation to enable the viable diffusion of these which further enables the synthesis of nanoparticles in requisite morphology. The investigators engaged in this study also characterized the synthesized nanoparticles via X-ray diffraction, UV-spectrophotometry, and transmission electron microscopy to qualitatively assure the synthesis of silver nanoparticles. The critical role of sonication in this study is to facilitate the synthesis of colloidal silver nanoparticles in required specific shape which resembles that of the cherry as the shape specificity is a very important factor to decide the critical performance features of nanoparticles in specific applications [74]. In yet another very interesting attempt by AL-Kaysi et al., the sonication method has been employed for the conversion of amorphous phase zwitterionic organic nanoparticles into the crystalline ones in the solution phase. This proved to be a boon as previously the same investigators reported the synthesis of nanoparticles in water through reprecipitation procedure but the synthesized particles very soon segregated themselves into different entities. However, with the use of nanoparticles, very fine and stable nanoparticles were formed, which possessed disk shaped morphology and diameter of 140 nanometers, which not only were crystalline but also remained stable over the course of weeks. The authors have thus postulated that the sonication is a very excellent approach to enhance the colloidal stability of the particles as well as their shape and structural optimization [75].

Within the nanoscale limit, graphene functionalization has attracted significant interest as graphene is a very versatile material in perspective of its structure as it possesses room for significant surface engineering and can act as scaffold like cushion for constructing well-controlled nanotechnological assemblies and platforms. A number of studies in this reference have reported the absorption of silver nanoparticle, which are already very well known for their numerous applications, into the graphene sheets following the modification of graphite structure, through the use of microwave based radiation incidence and ultrasonication mediated energetic absorption. In one of these very significant attempts, Shanmugharaj and Ryu have used microwave assisted spark derived energetic influence to incorporate the absorption of silver nanoparticles into the graphene structure. Not only this, the authors of this extraordinary literature source have also verified the electrochemical performance of silver immobilized graphene sheet and found the performance to be significantly higher than those of graphite structures alone. This significant breakthrough attempt with revealing energy output proves the worth of microwave assisted sparking as a green approach which can be efficiently as well as effectively implemented to improve the potential of confronting energy deficiency problems via efficient development of alternative energy routes, that too without much expense and technology [76]. Almost a similar attempt by Hui et al. also attempts to embed the silver nanoparticles into the graphene oxide modified from graphene through ultrasonication and control the dimensionality of the assembly by having a control over the size of the silver nanoparticles incorporated in the entire assembly. This is again an evidence of green technology manifestation towards the improvement of energy potential of existing sources. The most significant aspect of this study is the fact that it has used biocompatible vitamin C as a reducing agent, in the form of a bioreducer of the precursors so as to enable the nanosize to be reached and enable the compatible fusion of the two materials. The authors of this study have rigorously characterized the synthesized assembly through X-ray diffraction, energy dispersive spectroscopy, and transmission electron microscopy. The overall structure has been reported to be developed from the precursors of silver and graphene oxide and it was found that the size of the silver nanoparticles being embedded is sharply influenced by the amount of silver nitrate and the extent of sonication accomplished [77]. Another very recently reported study by Fernandez-Marino et al. also highlights the synthesis of graphene and graphene-metal nanoparticle hybrids through sonication and biochemical reduction achieved through the action of environmentally friendly and biocompatible natural antioxidants as catalysts. The recent origin of all these studies clearly figures out the increasing thrust the energy crisis is facing all over the world. These innovatory and traditional mechanisms are just a boon to the alternative science and technology development and shift the domain of conventional science advancement towards the traditional techniques and are also evident proof of faster emergence of green chemistry and technology as an emerging field of science. There are a number of such similar cutting edge studies which demonstrate and exemplify the importance and usefulness of sonication like green chemistry approaches in the preparation and surface engineering of nanoparticles to make them capable of fitting in the domain of complex interdisciplinary fields of sciences. Amongst these, one excellent investigation reports the lanthanum and strontium conjugated manganese oxide nanoparticles and their engineering via mineralization to make them capable catalysts [78]. Similarly, another very recent study has reported the synthesis of polyvinyl alcohol capped silver nanoparticles through ultrasonication and investigated the antifilarial potency of these. Here, the investigators have revealed that, by the use of ultrasonication, time consumption is less, product yield is better, and the shape of synthesized silver nanoparticles is better controlled and built [79]. The charm of these ever reliable, simple, and adorable nonconventional routes of nanoparticle synthesis routes is ever increasing as highlighted by some related studies, of similar background [80–82]. This mounting development of alternative synthesis routes for nanoparticle synthesis clearly exemplifies that better control is achieved through these methods and energy requirements as well as technical sophistication is far less.

6. Conclusion

In all, we can say that green chemistry routes characterized by bioreduction are very vital alternate or nonconventional solutions to their energetic counterparts. The main focus of this article was to put forward a comprehensive picture or idea of the biochemical diversities of plants and microbes. These have not been still fully explored and researches across the world are increasingly poised to increase the yield of nanoparticles, either in native or in combined or in still novel formulations with numerous applications of multiple importance. Another interesting aspect has been the applications of nanoparticles synthesized through green routes. A question of significant interest, crawling in the minds of scientific community, the world over is the fact whether nanoparticles synthesized through plant and microbial culture methods can achieve that level of applicational competency in comparison to their chemically or physically synthesized nanoparticles. One particular and critical observation that is rightly justified is that these non-conventional methods are inexpensive as well as far less complicated. What more friendliness a researcher can ask for, after knowing that silver nanoparticles can be synthesized from onion leaves abstract in just two hours' time.

This makes another observation of note which says that these methods are much less technical and sophisticated. However, an unanimously agreed observation in this discussion has been the fact that applications which chemically and physically synthesized nanoparticles can accomplish are widely different from the plant and microbial culture mediated nanoparticles. A brief account of applications of the plant culture and microbial culture nanoparticles is mentioned in Figure 3. Indeed these applications are far reaching and spanning multiple technologies; these are highly specific with respect to the type of method employed for synthesis. Moreover, nanoparticles synthesized in these green routes can also serve as excellent catalytic materials if there is some reaction going on with the same material which is involved alongside their preparatory extractable material. In such cases, excellent alteration for the reaction rates has been achieved and has also provided some wonderful results not readily possible through conventional approaches.

To conclude, we can say that the use of word green is justified for the discussed methods of nanoparticle synthesis for the fact that these do not pose any environmental hazard and also require far lesser energy in the form of input stimulus to proceed with the reaction.

There are many other such green chemistry based approaches for the synthesis of vital compounds of routine use. These methods have received very auspicious responses from the different corners of the world and current researches as well as funding are increasingly supplementing their faith in their better control, development, and wider usabilities. The nanoparticle synthesis through green routes now forms an integral part of inorganic chemistry and applied chemistry as well as biochemistry disciplines. For the involvement of experts from multidisciplinary fields, this augurs very well for the development of nanotechnology.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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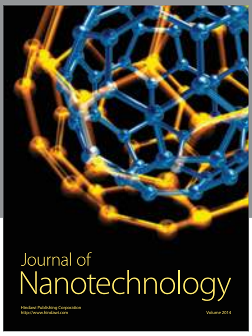
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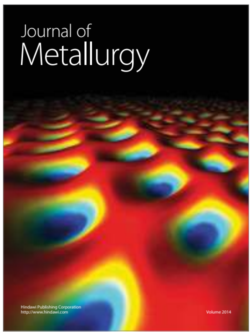
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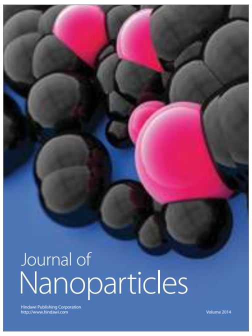
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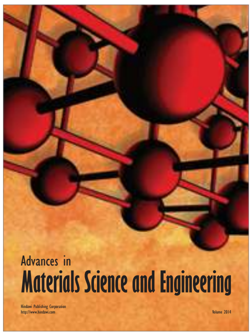
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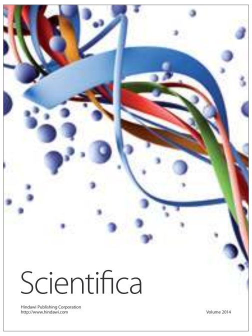
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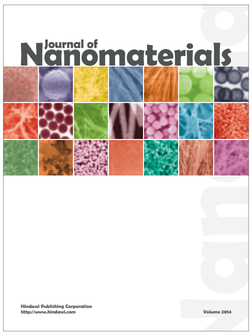
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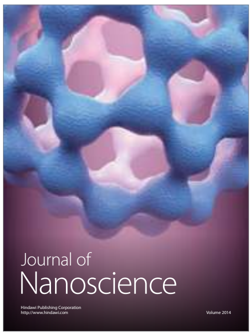
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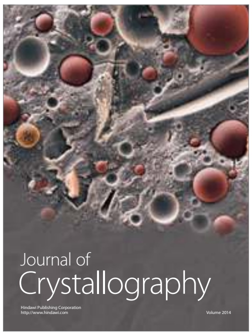
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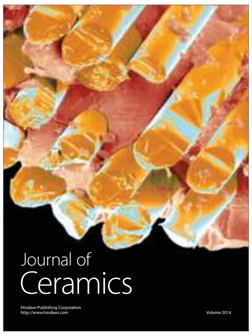
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