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Green synthesis of nanomaterials: An overview

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ABSTRACT

Nanotechnology has grabbed the attention of Chemists, Physicists, Biologists and Engineers by synthesizing nanoparticles with escalated properties than bulk materials. These nanoparticles find varied applications with certain modifications in their surface morphology. Physical and chemical route of synthesis of nanomaterials over a number of years in the recent past have authenticated harmful toxic effects on humans. This scenario powered the researchers to lean towards green synthesis of nanoparticles. This new method of synthesis shows decrease in toxic effects of nanoparticles over the environment and humans by integrating the available metabolites in biological extracts making them biocompatible. This review analyses the various methods of utilizing biological extracts for the synthesis nanoparticles and their advantages.

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1. Introduction

Nanotechnology has proved as the most potent field of science covering a diverse field and has emerged as a promising trend over the past decades. Nanoscience has inspired material science researchers for exploring innovative methods and develops new ways to engineer novel structures with significant properties and environmental impact [1]. The science of nanotechnology deals with manipulating materials at the level of atoms and molecules. Nano in general refers to size less than a billionth of a hair, corresponding to the size below 100 nm. Nanoparticles can be synthesized and are also available naturally such as living cells [2,3]. Nanoparticles find application in the field of physics, chemistry, medicine, healthcare, environmental science, space science, energy renewal, mechanics, electronics, civil, optics etc [Fig. 1] [4,5,94,95] . Nanoparticles have found an important place in the field of nanomedicine [6]. The size, shape and morphology of the nanoparticles show different properties and functions of the nanoparticles. Such properties can be controlled by the synthesis method [7]. Nanoscience deals with synthesis, characterization, exploration and exploitation of materials to the size of nm. Exploration of materials with nanosize has made a revolution in the field of material science. This has paved way for the altering of new materials with outstanding characteristics. The scaling of bulk material to nano alters the physical and chemical properties of the bulk material. The nanoparticles show significant properties that differ from the bulk material, due to the increase in surface to volume ratio. Nano sized materials find a number of applications in numerous fields [5,8,9,10]. One of the most promising applications of nanomaterials is in the field of medicine and biology. Some nanomaterials occur naturally and some are engineered [11]. (See Table 1.)

2. Synthesis of nanomaterials

Nanomaterials are generally synthesized by two methods, one is the top down approach and the other method is the bottom up approach [Fig. 2]. Top down approach is a method which involves the breaking of a superstructure to atomic or molecular level. This method is a subtractive method. This method involves the breaking of a bulk material and confining it to small structures by mechanical or chemical methods. Mechanical grinding, attrition, milling are some techniques that involve top down approach. The bottom up approach is an additive method where atoms or molecules are used as building units to build up a nanostructure. Some of the techniques that involve the bottom up approach are sol–gel technique, chemical vapour deposition, plasma spraying, microemulsion technique and laser ablation. Chemical method of synthesis involves the bottom up approach [12,13,14]. (See Fig. 3. Fig. 4.)

Nanomaterials are synthesized using physical, chemical and biological approaches. Physical method of synthesizing

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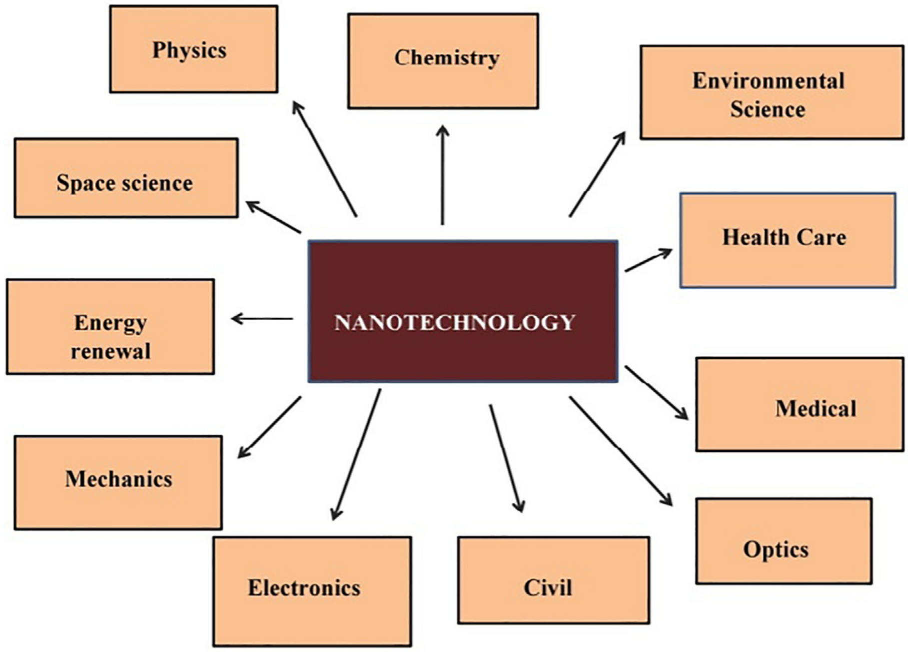

Fig. 1. Schematic diagram of various applications of Nanotechnology.

Table 1
Plant extract used in the synthesis of nanoparticles.

Metal	Plant Species and Part used	Size (nm)	Uses
Silver	*Salvia leriifolia*, Leaf	27	Antibacterial activity [28]
	Chrysanthemum indicum, Flower	25–59	Antilarval activity [29]
	Punica granatum L, Seed	–	Mechanical property and physical resistance [30]
Zinc	*Ailanthus altissimo*, Fruits	5–18	Antibacterial activity [31]
	Aloe vera, Leaf	25–40	Biomedical and cosmetic industrial applications [32]
	Petroselinum Crispum, *Allium cepa* and*Allium sativum*	40–60	Higher efficiency for the photo-degradation [33]
Iron oxide	*Camellia sinensis*	50	Catalyst for degradation of dyes [34]
	Punica granatum	26.52	Anticancer activity [96]
	Eucalyptus tereticornis, *Melaleuca nesophila* and *Rosemarinus officinalis*	50–80	Biological purpose [34]
	Passiflora tripartitavar	22	Pharmaceutical and biological purpose [34]
Gold	*Mimosa tenuiflora*	20–200	Drug nanocarrier and Fluorescent probe [35]
	Jasminum auriculatum, *leaf extraxt*	8–37	Antimicrobial and Antifungal [36]

nanomaterials involves cracking a superstructure and restricting their margin to nanosize. Some of the physical methods of synthesize includes mechanical grinding, milling, sonication and pulsed laser ablation. Chemical method of synthesizing nanomaterials involves chemical compounds to react in the presence of capping agents, reducing agents or stabilizers. Such reactions that are promoted in the presence of chemicals require less time for the process but however the chemicals used are toxic and are also non-eco-friendly. Some of the chemical methods of synthesize are condensation, sol–gel technique, chemical vapour deposition and other biochemical approaches [15].

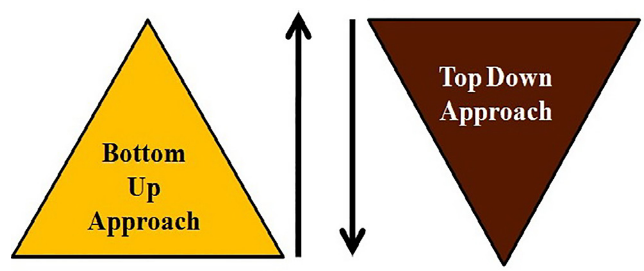

Fig. 2. Schematic representation of Top- down Approach and Bottom-Up Approach.

2.1. Green synthesis of nanomaterials

The environmental concern that has arisen recently has made the scientists to focus on avoiding harmful, non eco-friendly substance and move towards greener technologies. The awareness created for environmental issues over the recent years has forced researchers develop interest in biological approaches to synthesize nanoparticles free from toxic chemicals as a by-product [16]. Green synthesis of nanomaterials is a clean, economical, sustainable and environmentally friendly method. Some conventional methods of synthesis involve hazardous or toxic chemicals in the preparation process that may lead to the formation of lethal and toxic substances that may be harmful to human and surrounding [17,18]. Whereas green synthesis involves replacing hazardous chemical products and develops new process to reduce or even eliminate substances that are harmful to health and environment to produce eco friendly nanoparticles. The demand for green technology made nanoscience to explore the field of biology and provide a new platform for the synthesis of nanomaterials under an aseptic environment from plant extracts, bacteria, fungi. Green synthesis involves synthesis of nanomaterials from plant extracts, microorganism, fungi, proteins and biological molecules such as enzymes, sugar and also whole cells [19,20].

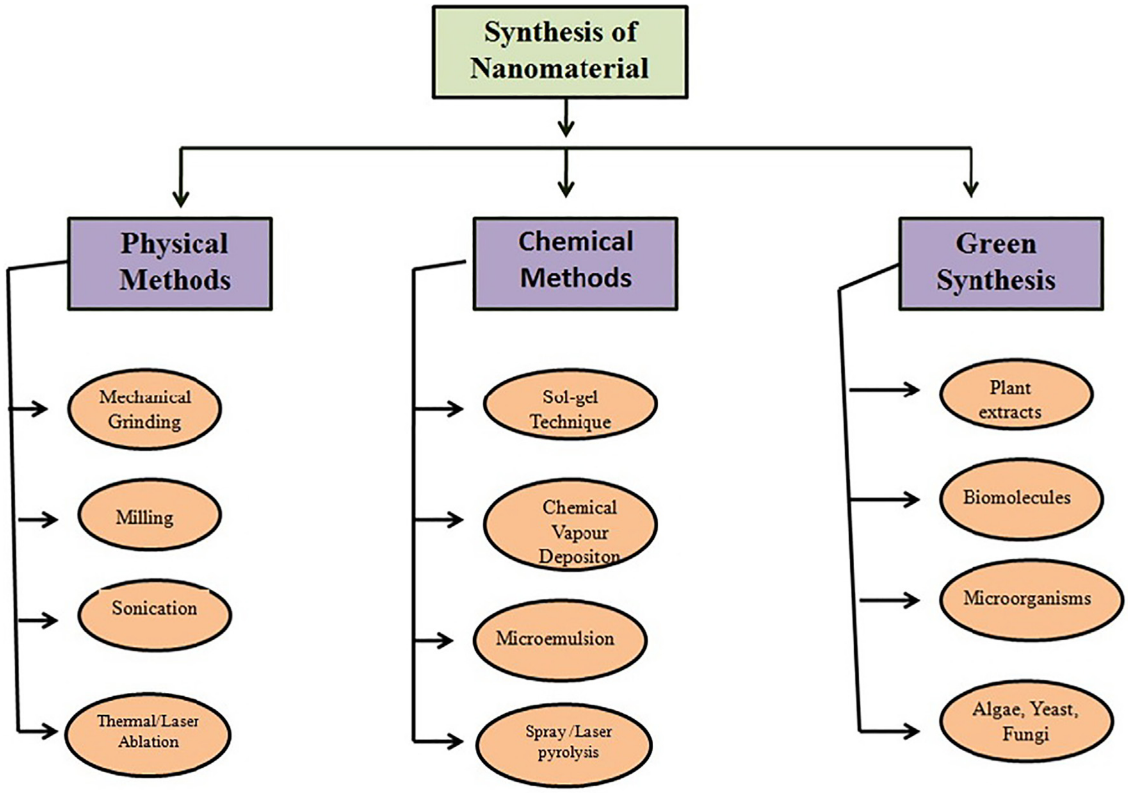

Fig. 3. Schematic diagram of approaches of Nanomaterial Synthesis.

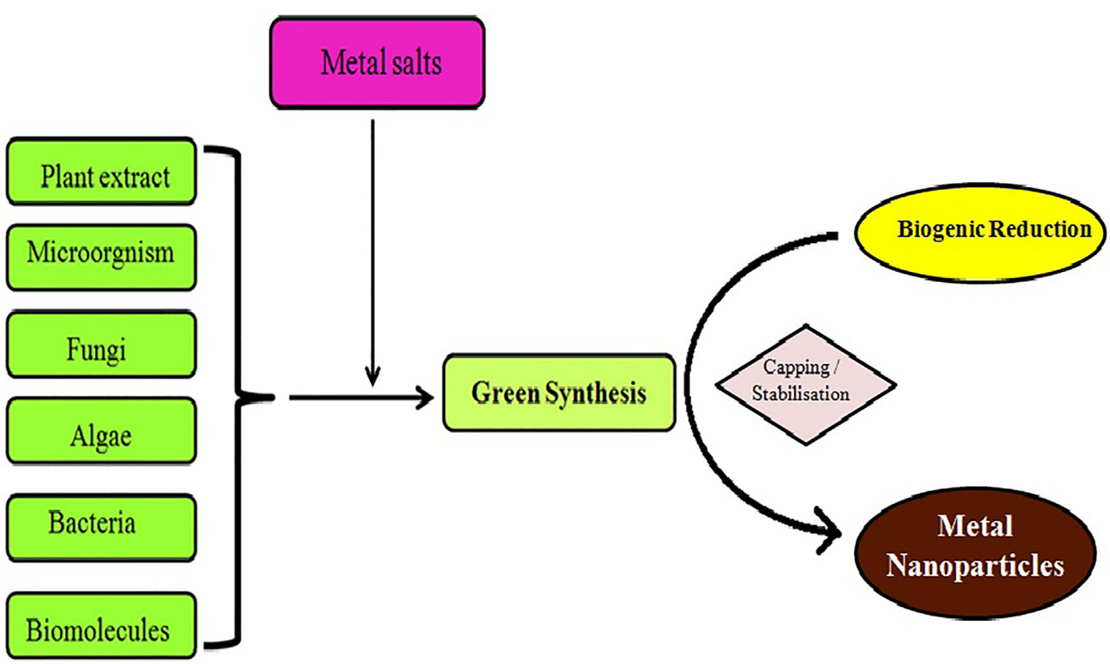

Fig. 4. Schematic diagram of synthesis of nanoparticles by Green Synthesis.

2.2. Plant extracts

Plant extracts serves as a better platform for the synthesis of nanoparticles as the plant extracts provide naturally available compounds that act as reducing, capping or stabilizing agent. This method is a single step process and it helps in reducing the cost of production [21]. Plant extracts are prepared from the various parts of a plant which includes leaves, stem, fleshy part of flower, bark

Table 2
Fungi used in the synthesis of nanoparticles.

Metal	Species	Size (nm)	Uses
Silver	*Tinospora cordifolia*	25–35	Cytocompatible and Hemocompatible [47]
	Penicillium oxalicum	60–80	Antibacterial and Antinflammation [48]
	Ganoderma lucidum	15–20	Anti fungaland Anti bacterial activity [49]
	Fusarium oxysporum	–	Anti bacterial [50]
	Aspergillus flavus	8–10	Antimicrobial activity [51]
Gold	*Fusarium solani*	40–45	Anti Cancer [52]
	Aspergillus niger	10–30	Anti larval [53]
	Aspergillus sydowii	8.7–15.6	- [54]
	Fusarium oxysporum	20–40	Non linear Optical Property [55]
Zinc	Periconium sp	16–78	Antimicrobial and Antioxidant [56]
	Aspergillus niger	76–183	Antilarval [57]
Copper	*Aspergillus niger*	500	Antidiabetic and Anti bacterial [58]
Iron	*Trichoderma asperellum*	25 ± 3.94	Crystalline [59]
	Phialemoniopsis ocularis	13.13 ± 4.32	Crystalline [59]
	Fusarium incarnatum	30.56 ± 8.68	Crystalline [59]

and fruits that are available naturally making the whole synthesis a cost effective method. It's also less time consuming than synthesizing nanoparticles using microorganisms [22,23]. Plant extracts contain phytomolecules like flavonoids, alkaloids and phenolic compounds. Such polyphenol based phytomolecules act as strong reducing agents and easily gets absorbed to the surface of nanoparticles. Such phenolic compounds present in the fleshy part of plants also posses antioxidant properties [24,25,26]. The reducing agent, capping agent, stabilizing and antioxidant properties present naturally in the plant extracts helps in reducing the metallic compounds to environmentally friendly nano metallic particles, hence avoiding toxic chemicals as reducing and capping agents [23,27]. Nanoparticles of metals such as silver, gold, copper, zinc, iron etc have been synthesized from plant extracts out of leaves, fruit, bark etc. Some nanoparticles synthesized from plant extracts are listed in the following table.

2.3. Microorganisms

Microorganisms are a collective group of bacteria, fungi, yeast and algae. Such microorganisms naturally have enzymes or biomolecules that help in reducing metal ions to metallic nanoparticles. The synthesis of metallic nanoparticles from microorganisms is inexpensive, undemanding, less time consuming and biocompatible which has created the necessity to search for microorganisms that synthesize metal nanoparticles [39]. Nanoparticles are synthesized intracellular or extracellular from microorganisms. The size and structure of the nanocrystals depends on the culture conditions such as temperature, pH and pressure [40].

2.4. Fungi

Fungi a class of eukaryotes are decomposers that are available naturally in the environment. Fungi naturally have the potential of bioreduction and bioaccumulation which has made fungi prove a better source for producing nanoparticles. Fungi are available in the nature in enormous quantity helps in easy broth preparation and large quantity making the method cost effective. The enzymes and proteins present in fungi act as reducing agents that helps in hydrolyzing the metals easily. Some of the enzymes available in fungi that mediate the bioreduction process are hydrogenase, nitrate dependent reductase etc. the factors that influence the size and shape of the nanocrystals are the proteins, enzymes, organic acids and polysaccharides that are secreted by the fungi [41,42,43]. A few fungi that mediated the bioreduction process to produce nanoparticles such as gold and silver are *Aspergillus niger, Fusarium solani, Coriolus vesicolous* and *Aspergillus fumigates.* The high wall binding capacity and intracellular uptake of metal, allows the fungi to internally absorb the metals. This causes the fungi to digest the extracellular materials and secrete enzymes that help in hydrolyzing the bulk composition to nanostructures. The purification process of the synthesized nanoparticles is easier as they are synthesized extracellularly. The fungi mediated nanoparticles synthesis has proved as a better method as it is cost effective, easy to maintain, easy downstream process, toxic free, and easy biomass handling. Factors that influence the characteristics of nanoparticles are metal concentration, pH and response time [44,45,46]. Table 2 shows some of the nanoparticles synthesised from fungal species.

2.5. Bacteria

Bacteria mediated synthesis of nanoparticles is an enzymatic process that produced nanocrystals of high antioxidant, antiproliferative, anticancer nature. The synthesis process is invitro. Bacteria posses a network of nanocellulose of nanofibrils that form nanocrystal structures of good crystalline structure with excellent purity and mechanical stability [60]. The nanocellulose structure helps in the biosynthetic process by producing reactive oxygen species extracellularly. Bacteria also possess a remarkable reducing property in synthesizing nanostructures intra and extracellularly [61,62]. Bacteria are capable of extirpating the heavy toxic metals. This reaction method is easy as the scaling up of bacterial culture is easy and cost effective as it is freely available in nature. But in case of some species it is time consuming. The stability of nanoparticles depends on pH, temperature and the bacterial strain [63] . Some of the nanoparticles synthesised from bacteria are listed in Table 3. (See Table 4.Table 5.)

2.6. Biomolecules

The idea behind the method involving biomolecules for the synthesis process is the interfacial activity between the metal and the

Table 3
Bacteria used in the synthesis of nanoparticles.

Metal	Species	Size (nm)	Uses
Gold	*Bacillus subtilis*	5–10	Anti bacterial and anti fungal [64,65]
	Bacillus licheniformis	20–75	Anti microbial [66]
	Bacillus niabensis	10–20	Anti microbial [67]
	Lactobacillus kimchicus	5–30	Diagnosis of cancer, drug delivery systems, photothermal therapy, biosensing, and medical imaging [68]
Silver	*Bacillus subtilis*	4–8	Antibacterial, Anti fung [64]
	Bacillus brevis	41–68	Antimicrobial [69]
	Pseudomonas sp.	10–40	Antimicrobial [70]
	Escherichia coli	5–50	Antimicrobial [71]
	Streptomyces sp.	11–21	Anti microbial activity [72]
	Spirulina platensis	74	Anti bacterial [73]
Magnetite	Thermoanaerobacter sp	25–50	Antimicrobial [74]

Table 4
Biomlecules used in the synthesis of nanoparticles.

Metal	Biomolecule moiety	Size (nm)	Uses
Palladium	RNA	–	Showed hexagonal morphology [81]
Cadmium	tRNA	7–11.5	Non folded mutant[81]
Lead	RNA	600	Photostability[81]
Gold	Tryptophan	20	Highly fluorescent [82]
Silver	Tryptophan	2	Highly fluorescent [82]

Table 5
Algae used in the synthesis of nanoparticles.

Metal	Species	Size (nm)	Uses
Gold	Spirulina platensis	5	Anti bacterial [86]
	Sargassum cymosum	7–20 nm	Commercial application [87]
	Tetraselmis kochinensis	5–35 nm	Drug Delivery, biomedical applications, catalysis [88]
Silver	*Sargassum myriocystum*	18–22 nm	Anticancer,Anti bacterial [89]
	Padina sp	25–60 nm	Anti bacterial [90]
	Caulerpa racemosa	5–25 nm	Anti bacterial [91]
Zinc	*Sargassum muticum*	30–57 nm	Biomedical application [92]
Copper	*Sargassum polycystum*	–	Antibacterial and Anticancer [93]

biomolecules surface. The molecular structure is altered and packed by interaction of the molecule onto the surface of the metal and to the interface producing nanoparticles with higher surface area. The interface between biomolecules and nanostructure is optimized for developing nanoparticles. Some of the biomolecules that mediate the biosynthetic process are DNA, RNA, peptides, and proteins and aminoacids such as aspartate, sugar, lipids. DNA, a class of biomolecules, acts as building blocks and assembles to fabricate a nanostructure. Such nanostructures are engineered by enzymes such as DNA polymerase, restriction endonuclease and kinase. DNA is an efficient genetic substance that also finds application in the field of medicine [80].The green synthesis method that involves amino acids use amiable conditions that controls the characteristics of the nanoparticles. Amino acids are also natural reducing agent that doesn't need any additional reducing agent or capping agent or surfactants to synthesize nanoparticles. Sugar, another class of biomolecules that includes glucose, chitosan and mannose are also good source of raw material to synthesize nanoparticles [75,76,77,78]. Lipids another group of biomolecules, that consist of bilayer structure help in the preparation of nanoparticles that are biocompatible and water soluble. As the lipid layer covered nanoparticles find a huge application in the field of biomedicine such as drug delivery and gene transfection [79].

2.7. Algae

Algae, the largest photoautotrophic group of microorganisms are a source of metabolites, pigments and proteins. Algae are capable of absorbing metals in high concentration, hence making the raw material cost low. Though the method is cost effective, the synthetic process is very slow which stands a major drawback [83]. The biomolecules available in cell wall of algae plays the role of surfactants and stabilizers and catalyses the reduction of metal ions leading to the nucleation of nanoparticles. The biomolecules and their biochemical activity control the nucleation of nanoparticles other than the factors such as pH and temperature that controls the size and morphology of nanoparticles. The colloidal stability of nanoparticles synthesized is low leading to the agglomeration of nanoparticles [84,85].

3. Conclusion

The conventional methods of synthesizing nanoparticles are not only expensive but also produce some harmful products that play havoc with the environment and human systems. This has called for the need for synthesis of nanoparticles that have very less toxic effects over the surroundings. Green synthesis of nanoparticles has been identified as a fallback method as the synthesis process is modest, cost effective, less time consuming, eco-friendly and easy to scale up. This review has discussed about the green synthesis of nanoparticles using plant extracts, microorganisms, fungi, algae and biomolecules. Nanoparticles synthesized from biological extracts are more biocompatible, less toxic and eco-friendly; hence they find applications in the field of biomedicine, and pharmaceuticals.

CRediT authorship contribution statement

P. Aarthye: Conceptualization, Writing - original draft, Writing - review & editing. **M. Sureshkumar:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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