

An overview of the green road to the synthesis of nanoparticles

Abstract— Nanotechnology is progressing at a very fast pace and has an overwhelming number of applications in medicine, agriculture, cosmetics, etc. Daily more and more discoveries and innovative applications are being brought to light. This new and exciting technology involves materials and devices in nanometer dimensions. The synthesis/fabrication of these all important nanoparticles should be in a clean and safe manner with minimum risk to the environment. This article examines and reports the ways of synthesizing nanoparticles in a green way, with low carbon footprint and minimum health hazards.

Keywords: *nanoparticles, environmental safety, green synthesis, plants, microorganisms*

Introduction

All matter and life originates at the nanoscale with atoms and molecules and this provides us with a very useful set of tools and techniques called Nanotechnology, which includes nanoparticles (NP), nanofabrication, nano biotechnology and other cognitive sciences. The unifying force is the manipulation of nanoscale matter for the diverse applications that we see today. By definition nanomaterials have dimensions of 1-100 nm and the main appeal is their large surface to volume ratio which gives them unique and enhanced properties. The size, shape and type of the NPs greatly influence its properties and field of applications. Nanomaterials find applications in environment and toxic gas sensing [1-5], food and agriculture [6-8], drugs and medicine [9-12] and in energy [13-15]. While nanotechnology is making many things in life easier and providing a lot of benefits to society, the large scale production of nanomaterials and the use of self replicating nano-machinery can pose incalculable risks. It is important to understand the role of nanoparticles in the uptake of pollutants and nutrients and also the toxicity of nanoparticles in food and agriculture. Safer design and manufacturing practices have to be adopted to ensure minimum risk to environment and human health. The concerns of toxicity and energy efficiency have lead to substantial research on green and sustainable production of NPs. This overview is an attempt to highlight the different green routes that can be taken to produce NPs with the minimum of environmental contamination and added benefits of antibacterial and antimicrobial properties of green NPs. The review is organized under the sections: importance of green synthesis, methods of green synthesis, disease inhibition using green NPs and finally conclusions.

I. GREEN SYNTHESIS AND WHY IT IS IMPORTANT

A. *What is green synthesis?*

Green synthesis is the production of NPs using natural resources like plant extracts, microorganisms and energy saving methods in a sustainable, non-toxic and economical way. Extracts from different plants can be used to produce NPs with special characteristics and functionality to suit a specific application [10, 16-17]. The microorganisms can be bacteria, fungi, yeast etc and the choice will be based on the type, size and functionality that is desired of the NP [18-20].

B. Benefits of Green Synthesis

Why use green synthesis when convention methods of production exist? The answer lies in the numerous benefits that come with the use of a green route for NP synthesis. First of all, NPs produced in this manner are more stable and effective in comparison with those produced by physicochemical methods. Next, they are eco-friendly, sustainable, inexpensive and free of contaminants. Purity of NPs is a major consideration for biological and medical applications. In addition, they are energy efficient and do not need high pressure, temperature, special culture preparation/isolation techniques or toxic chemicals. Moreover, most NPs produced by the green method show excellent antifungal, antibacterial and anti-parasitic properties. Other advantages are the ease of large scale synthesis and disposal of the non-toxic waste products.

II. METHODS OF GREEN SYNTHESIS

The production of nanoparticles (NP) using natural substances is an important and emerging area in nanotechnology. The conventional methods of synthesis of NPs using chemicals as precursors or reducing agents have potential risks of toxicity and in general are not environmentally friendly or quick processes. To overcome these disadvantages the use of renewable resource natural biological systems to produce NPs is finding widespread acceptance. The different methods of green synthesis will be expanded based on the type of resource used and classified under: a) Use of micro-organisms b) Use of plant extracts and c) use of energy saving methods.

A. Use of plants and plant extracts

The Green synthesis using biological molecules from plant extracts is proving to be far superior to chemical means. The huge plant diversity provides a natural bank of resources that can be utilized to rapidly synthesize in a one step protocol different types of NPs having a range of antimicrobial activity and application. The use of plant extracts to produce NPs of high quality, specific morphology and function is wide spread due it the simple steps involved in nanoparticle recovery. Fig 1 shows a schematic diagram of the steps involved [21]. The steps involved are extraction of plant by hand grinding/blender, filtration of the extract, addition of metal NP salt, stirring the resultant solution and finally recovery of salt from precipitate.

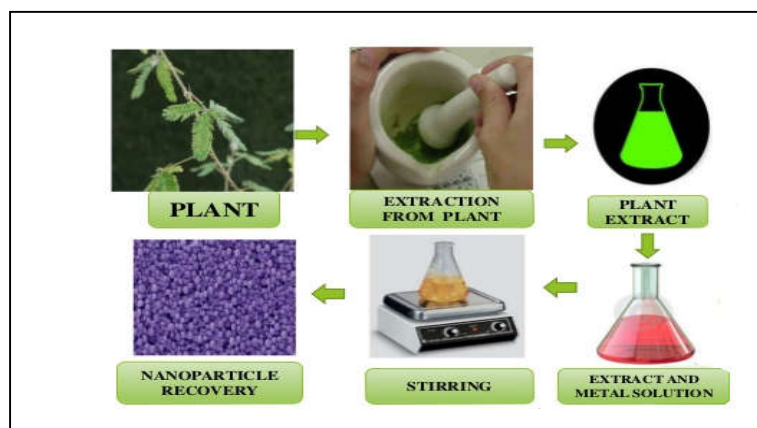


Fig. 1 The various steps involved in the extraction of nanoparticles using plants [21]

Different parts of the plant like stem, fruit, fruit peels, bark, root, leaves etc can be used to produce the NPs. Taking Silver (Ag) NPs as an example the specific parts of the various plants used for synthesis is presented in Table 1 adapted from Ahmed et al [10].

TABLE I. SYNTHESIS OF SILVER NANOPARTICLES USING EXTRACTS FROM DIFFERENT PARTS OF VARIOUS PLANTS

Plants	Size (nm)	Plant's part	Shape	References
Alternanthera dentate	50–100	Leaves	Spherical	[22]
Acorus calamus	31.83	Rhizome	Spherical	[23]
Boerhaavia diffusa	25	whole plant	Spherical	[24]
Tea extract	20-90	Leaves	Spherical	[25]
Tribulus terrestris	16-28	Fruit	Spherical	[26]
Abutilon indicum	7-17	Leaves	Spherical	[27]
Ziziphora tenuior	8–40	Leaves	Spherical	[28]
Cocous nucifera	22	Inflorescence	Spherical	[29]
Pistacia atlantica	10–50	Seeds	Spherical	[30]

The advantage of using plant and plant extracts over other biological methods is that there is no need for elaborate culturing and cell maintenance. Also, it is an easily scalable process. The success of producing NPs by this method has been reported in several research articles and reports [10, 16, 17, 21-30].

B. Use of micro-organisms

Many microorganisms can be considered as nano factories that produce metal nanoparticles with different efficiency, size and shape. The use of physical and chemical means for NP synthesis may result in contamination due to toxic solvents, precursors and generate harmful byproducts with generally low yields. In contrast the use of micro-organisms like fungus, yeast etc for NPs synthesis is nontoxic, safe, reliable, clean and environmentally friendly with high yields. Fungi act as reducing agents of metal salts through secretion of enzymes and proteins. The mechanism may be extracellular that is outside the cell or between group of cells or intracellular meaning inside the cell or cytoplasm. This form of biosynthesis has great potential as large scale production of NPs from various strains of fungi is possible and they can even be grown in vitro. Table 2 lists some of the NPs obtained from diverse fungi and yeast species.

The extracellular biosynthesis of Ag NPs using filamentous fungi like 'Aspergillus fumigatus' has been reported by Kuber et al [18]. These fungi are excellent candidates for extracellular process applications, since, they secrete a variety of enzymes and are easy to grow and handle. Well dispersed Ag NPs of 5-25 nm were formed within minutes of silver ion coming in contact with the cell filtrate showing that the extracellular reduction process is a very fast and feasible biosynthesis method for Ag NPs.

TABLE II. NANOPARTICLES OF VARYING SIZE AND SHAPE FABRICATED FROM FUNGAL AND YEAST SPECIES

Fungi and Yeast	NPs	Size (nm)	Shapes	Location	Ref
<i>Alternaria alternata</i>	Au	12 ± 5	Spherical triangular hexagonal	Extracellular	[31]
<i>Aspergillus clavatus</i>	Au	24.4 ± 1 1	Triangular spherical hexagonal	Extracellular	[32]
<i>A. fumigatus</i>	ZnO	1.2–6.8	Spherical hexagonal	Extracellular	[33]
<i>A. oryzae</i> TFR9	FeCl ₃	10–24.6	Spherical	–	[34]
<i>A. sydowii</i>	Au	8.7– 15.6	Spherical	Extracellular	[35]
<i>A. terreus</i>	Ag	1–20	Spherical	Extracellular	[36]
<i>A. tubingensis</i>	Ca ₃ P ₂ O ₈	28.2	Spherical	Extracellular	[37]
<i>Aureobasidium pullulans</i>	Au	29 ± 6	Spherical	Intracellular	[38]
<i>Candida albicans</i>	Au	5	Mono dispersed spherical	Cell-free extract	[39]
<i>C. glabrata</i>	CdS	–	–	Intracellular	[40]
<i>Coriolus versicolor</i>	Au	20–100, 100– 300	Spherical ellipsoidal	Intra- and extracellular	[41]
<i>Cylindrocladium floridanum</i>	Au	19.05	Spherical	Extracellular	[42]
<i>Fusarium oxysporum</i>	Pt	70–180	Rectangular triangular spherical aggregates	–	[43]

Another typical example is the size controlled synthesis of silver NPs using ‘Fusarium oxysporum’ to obtain well-dispersed nanoparticles with size between 5 and 13 nm by Husseiny et al [9]. The NP size is controlled by the environmental and nutritional parameters viz substrate concentration, temperature, pH, weight of biomass etc. The biosynthesized NPs showed antibacterial and antitumor activities which will be discussed in more detail in section IV.

C. Use of energy saving methods

The synthesis of molybdenum disulfide nanostructures (MSNs) for host of applications by the ‘green’ microwave-assisted (MW) solvothermal synthesis method [44] is a clear example of energy saving techniques for green NP synthesis. In this process, Ammonium Molybdate and elemental Sulphur are mixed in 1:1 molar ratio in 10 ml of hydrazine monohydrate and 30 ml deionized water under magnetic stirring for 5 minutes. The resultant solvent mixture is transferred to a Teflon vessel and subjected to microwave radiation of 270 Watt in a microwave oven for 10 minutes, and is allowed to cool down naturally to room temperature. Black precipitate settled at the bottom of the solution is filtered, washed with distilled water, diluted hydrochloric acid and ethanol successively and centrifuged to remove any un reacted precursors. The final product is dried in vacuum oven at 50 degrees Celsius for 4 hours to obtain MoS₂ nanostructures. This technique qualifies for the energy efficient ‘greener’ approach by drastically reducing the reaction time (~300 times faster than the

conventional method). Microwave radiation penetrates through Teflon vessel and interacts with the solvents directly causing localized heating and thus generates supercritical conditions favorable for nucleation and growth of nanoparticles. The Schematic of the strategy for MW green synthesis of MSNs via generation of supercritical conditions is shown in Fig. 2 taken from the work of Qureshi et al [45].

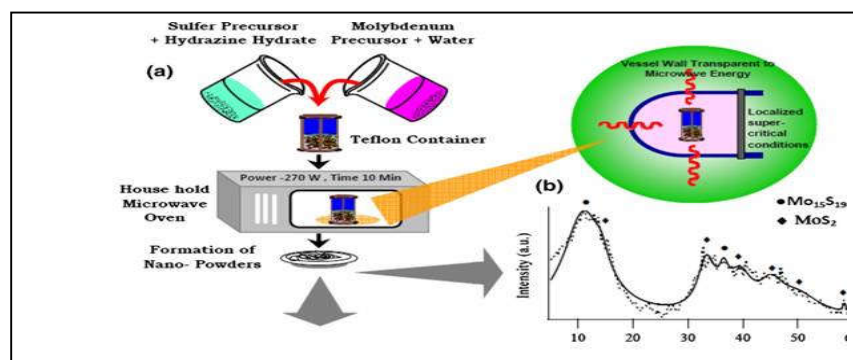


Fig. 2. The Schematics for microwave assisted green synthesis of Molybdenum disulphide nanoparticles [45]

In their work they demonstrated interestingly, biofilm inhibition and antimicrobial behavior of MSNs produced using this method. This is a significant discovery since the biofilm protects pathogenic organisms from drugs and immune system by resisting entry and recognition, respectively. They also showed the MSNs to be non-cytotoxic which gives them biocompatibility and increases their antimicrobial potential.

The green synthesis of Ag NPs with demonstrated antibacterial activity by Fatimah [16] using MW is another example of energy efficient green process for NP synthesis. The use of MW shows the rapid formation of Ag NPs with similar properties to those obtained through the time consuming aging method. In addition, the use of microwave irradiation yielded larger particles.

III. DISEASE INHIBITION USING GREEN NPS

The excellent antibacterial and anti-parasitic properties of green NPs allows them to play significant roles in medicines, clinical applications and in vitro diagnostic applications and also in agriculture, water treatment, food packaging and textiles.

Antibiotic resistance poses a major problem in healthcare due to the inherent tendency of microbial cells to alter their genes. In this context, the exploitation of inorganic nanoparticles to develop antiseptics that are deadly to microbes and demonstrate wide-ranging activity with lower prospects of microbial resistance is the most needed solution.

Especially, the use of Ag NPs in the biomedical sector has seen increasing number of applications with large number products such as ointments, dressing materials, body hygiene etc already in the market. Ag NPs have been reported to possess antimicrobial property against myriad array of pathogenic microorganisms. An excellent example is the work of Hussein et al [9] who showed the inhibitory capabilities of green Ag NPs towards bacteria and tumor. The NPs biosynthesized from 'Fusarium oxysporum' showed excellent antibacterial activities when studied using agar well diffusion and zone of inhibition method against pathogenic strains of *E. coli* and *S. aureus*. Also, their work reveals promising antitumor capability against human breast carcinoma cell line (MCF-7). Fig. 3 shows the antibacterial and antitumor activities taken from their work.

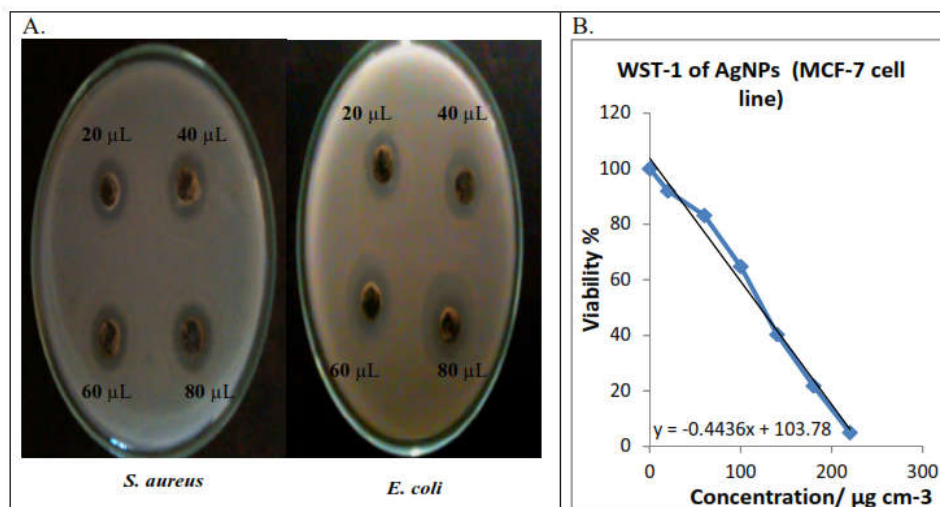


Fig. 3. The Antibacterial activity of different concentrations of biosynthesized AgNPs (A) against *E. coli* and *S. aureus* strains (B) viability chart of biosynthesized AgNPs against MCF-7 cell line. [9].

A serious concern is bacterial resistance to conventional antibiotics based on organic molecules. The prevalence of multidrug-resistant bacteria requires an effective solution and green NPs are coming to the rescue. An example is the interesting microbial resistance mechanism using non-cytotoxic MSNs by reactive oxygen species via disruption of cellular functions demonstrated in the work of Qureshi et al [45]. Fig. 4 taken from their work compares and illustrates the effectiveness of MSNs with other inorganic NPs against various forms of bacteria.

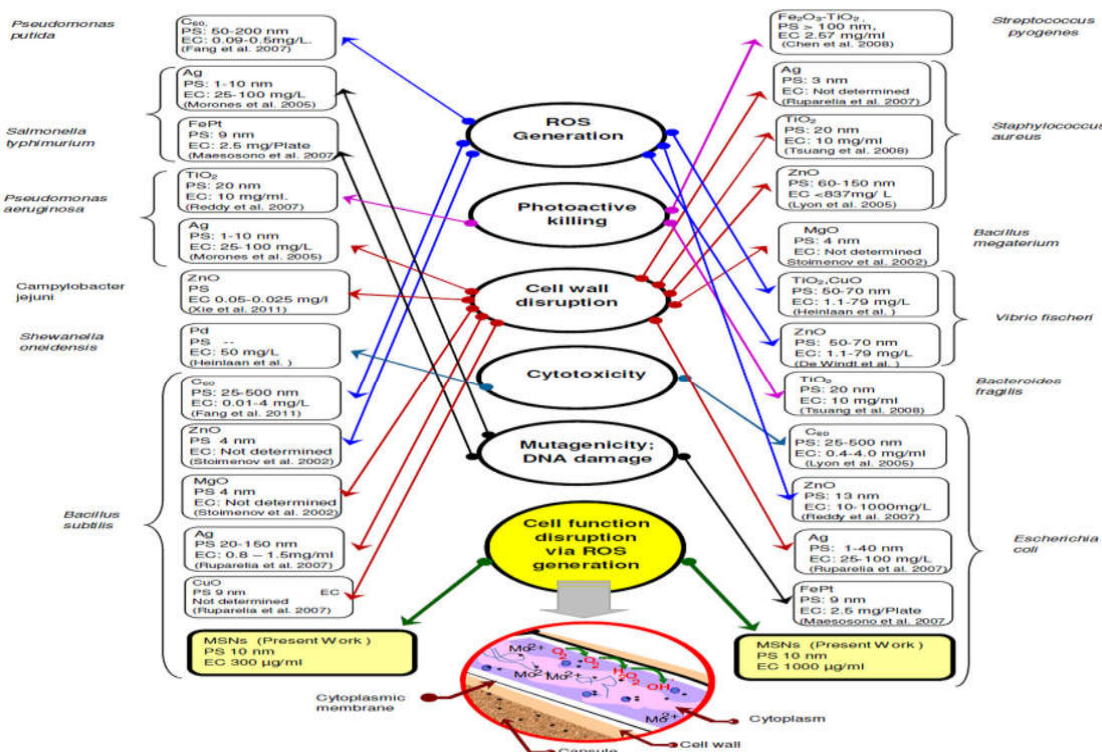


Fig. 4. Comparative illustration showing the antimicrobial effect of different NPs with MSNs on various gram-positive and gram-negative bacteria [45]

IV. CONCLUSIONS

The use of natural and biogenic resources for production of NPs is a green eco-friendly, sustainable, inexpensive and contaminant free process. The NPs synthesized in this manner from plants and microorganisms are more stable, controllable and effective in treatment against pathogens and are less toxic to humans and environment as compared with those produced by chemical methods.

Green NPs play a crucial role in all walks of life and find application in environmental remediation, nano-scale catalysis, treatment of water contaminated by toxic metal ions, water splitting, CO₂ sequestration, food and packaging, drugs and medicine, control and management of plant disease and also as effective fertilizers.

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