



A Review on Green Synthesis and Antibacterial Activity of Silver Nanoparticles

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Received: 20-06-2017; Revised: 09-08-2017; Accepted: 25-08-2017.

ABSTRACT

Nanotechnology is a broad interdisciplinary field of science that represents the design, synthesis, characterization and application of materials at nano scale level. Nanoparticles (NPs) are viewed as fundamental building blocks of nanotechnology. The term "nano scale" is generally referred to a scale between 1-100 nm. Nowadays, synthesis of NPs has been the subject of a lot of studies due to its commercial demands and wide applicability in various fields such as chemistry, biology, physics, material science, engineering, medicine etc. Silver nanoparticles (AgNPs) can be synthesized using chemical methods, physical methods, and biological methods. Green synthesis of AgNPs is efficient, fast, cheap, non-toxic, simple and eco-friendly than commonly used physicochemical methods. Green chemistry processes led to eco-friendly method of synthesis and safe process as compared to other methods. In this review, a cheap and environment friendly technique for synthesis of AgNPs by green chemistry approach was explained. Also antibacterial activity of AgNPs has been reviewed.

Keywords: Antibacterial activity, Green synthesis, Silver nanoparticles.

INTRODUCTION

Nanotechnology is concerned with the development of experimental processes for the synthesis of NPs with controlled sizes, shapes and disparity of materials at the nanometer scale and their potential use for human well being¹.

Owing to the wide range of applications offered by NPs in different fields of science and technology, different protocols have been designed for their synthesis. NPs can be synthesized using chemical methods, physical methods, and biological methods². Chemical methods have various drawbacks including the use of toxic solvents/surfactants, more expensive, generation of hazardous by-products, high energy consumption, and all which pose potential risks to human health and to environment³.

Green methods of synthesis make use of the vast bioresources naturally available like plants, bacteria, fungi, yeast, enzymes and others. Green synthesis of AgNPs provides advancement over chemical and physical methods as it is cost effective, eco-friendly, easily scaled up for large scale synthesis and also there is no need to use high energy, temperature and toxic chemicals⁴.

Metal NPs have been extensively studied due to their specific characteristics such as catalytic, optical, electronic, antimicrobial and magnetic properties⁵. Among noble metals, silver is the metal of preference in the field of biological systems, living organisms and medicine⁶.

In most respects, AgNPs have appeared as prospective alternatives for overcoming antibiotic resistance

problems because AgNPs utilize multivalent mechanisms to exert its antibacterial activities. AgNPs show potential antibacterial effects against infectious micro-organisms like *E. coli* and *S. aureus*⁷.

Nanoscience and Nanotechnology

Nanoscience is the study of phenomena and manipulation of materials at atomic and molecular levels, where properties are remarkably different from those at larger scale⁸. It is inter-disciplinary science which cuts across the areas of physics, chemistry, biology, and medicine⁹.

The term nanotechnology was first defined by Tokyo science university Professor Norio Taniguchi in 1974 as "Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule"¹⁰. Nanotechnology (sometimes shortened to "nanotech") is the science which deals with the synthesis, characterization, exploration and application of nano-sized materials for the development of science¹¹. Nanotechnology, and alongside nano structured materials, play an ever increasing role in science, research, economy, every days life, as more and more products based on nano structured materials are introduced to the market¹².

Nanobiotechnology is a field that has emerged as an intersection between biotechnology and nanotechnology for developing new biosynthetic devices and eco-friendly technology for the synthesis of nanomaterials¹³.

Green Nanoscience

Green nanoscience/nanotechnology involves application of green chemistry principles to the design of nanoscale



products, development of nano material production methods, and application of nanomaterials. Incorporation of green chemistry principles into nanotechnology is of great interest which has gained much attention over the past decade¹⁴. Green chemistry is the development, implementation, design of chemical products and processes to eliminate or reduce using/generation of hazardous substances on the environment and human health¹⁵.

AgNPs can be synthesized by physical and chemical methods, these techniques are either expensive or involve the use of hazardous chemicals, which pose an environmental risk¹⁶. Utilization of non-toxic chemicals, environmentally benign solvents, low energy consumption, moderate operation conditions and renewable materials are some of the key issues that merit the important consideration in a green synthesis strategy¹⁷.

Nanoparticles

The prefix nano is derived from Greek word nanos meaning “dwarf” or extremely small¹⁸. Nano-sized materials, known as NPs, possess unique and improved properties because of their larger surface area to volume ratio. NPs can be broadly grouped into two, namely, organic NPs and inorganic NPs which include noble metal NPs (like silver and gold), semi-conductor NPs (like titanium oxide and zinc oxide)¹⁹.

Synthesis of Silver Nanoparticles

AgNPs can be prepared by an enormous variety of methods which usually are categorized in two main synthetic routes which are the top-down and the bottom-up approaches²⁰.

Top-down approach

In the top-down (physical) approach, AgNPs are obtained from their bulk materials using different methods and techniques like thermal decomposition, irradiation, laser ablation, arc discharge etc.

Bottom-up approach

In bottom-up (chemical and biological) approach, AgNPs are obtained from their basic building blocks which react to generate AgNPs of the desired shape and size.

Chemical approach

Generally, chemical synthesis of AgNPs employs the following three main components²¹: (i) metal precursors, (ii) reducing agents and (iii) stabilizing/capping agents. The problems associated with chemical methods are extensive use of toxic chemicals, non-ecofriendly nature of the process, need expensive chemicals with high energy input, requirement of sophisticated instrumentation and further lead to the presence of some toxic chemicals adsorbed on the surface that could produce intolerable toxicity to humans and adverse effects in biomedical applications²².

Chemical method requires chemical reducing, capping and stabilizing agents which are mostly toxic, flammable, cannot be easily disposed off due to environmental issues, low material conversions, and high energy requirements²³. The most commonly used organic and inorganic reducing agents are (sodium citrate, ascorbate, sodium borohydride, Tollens reagent etc) for the reduction of Ag⁺ ions in aqueous solutions²⁴. Capping agents play a very pivotal and versatile role in AgNPs synthesis. AgNPs can be functionalized and stabilized using capping agents to impart useful properties by controlling morphology, size and protecting the surface thereby preventing aggregation.

Green synthesis of silver nanoparticles

Green synthesis refers to the recruitment of biogenic matter including plant extracts, biopolymers and microbial sources like bacteria, fungi, algae, and yeast for nanomaterials fabrication. Development of biocompatible, non-toxic and eco-friendly methods for the synthesis of AgNPs is a topic of concern in green chemistry²⁵.

The advancement of green synthesis of AgNPs is progressing as a key branch of nanotechnology; where the use of biological entities like micro-organisms, plant extract or plant biomass for the production of AgNPs could be an alternative to chemical and physical methods in an eco-friendly manner²⁶. In case of biological synthesis of AgNPs the reducing agent for reducing Ag⁺ ions and the stabilizing agents for preventing the aggregation of AgNPs are replaced by molecules produced by living organisms. Green synthesis of AgNPs possesses the following advantages over traditional chemical methods. (i) Green synthesis is simple and usually involves a one-pot reaction; (ii) it is amenable to scale up; (iii) the toxicity associated with hazardous chemicals are eliminated, (iv) green biological entities can be used as reducing and capping agents, and (v) finally, the process is cost-effective, require little intervention or input of energy, uses renewable resource, environmental friendly method and it is not necessary to use high pressure, energy, temperature and toxic chemicals²⁷.

The green synthesis of AgNPs involves three main steps based on green chemistry perspectives²⁸: (i) selection of a biocompatible and non-toxic solvent medium, (ii) selection of environmentally benign reducing agents, and (iii) selection of non-toxic capping and stabilizing agent for stabilization of AgNPs, which prevents aggregation of AgNPs.

Biosynthesis of AgNPs as an emerging highlight of the intersection of nanotechnology and biotechnology has received increasing attention due to a growing need to develop environmentally benign technologies in material synthesis and development of efficient green chemistry methods employing natural reducing, capping, and stabilizing agents to prepare AgNPs with desired morphology and size have become a major focus of



researchers. The use of environmentally benign materials like plant leaf extract for the synthesis of AgNPs offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemicals for the synthesis protocol and the particle's surface does not contain toxic chemicals²⁹.

The use of medical plant parts like stem, root, leaf, flower, fruit, seed, bark, etc for the synthesis of AgNPs is a quite novel method leading to truly green chemistry compared to other methods like chemical and physical methods³⁰. In biosynthesis method, plant extract has been used as reducing, capping and stabilizing agents for the synthesis of AgNPs due to their reducing properties³¹.

The main mechanism considered for the green synthesis of AgNPs process is plant assisted reduction due to phytochemicals present in extracts³². Biomolecules like

alkaloids, flavonoids, terpenoids, amino acids, tannins, saponins, phenols carbohydrates etc are present in the plant material can acts as reducing, capping and stabilizing agents³³.

Plant mediated synthesis of AgNPs is advantageous over other methods such as micro-organism by eliminating the elaborative and complicated processes for maintaining micro-organism cultures³⁴. Microbe mediated synthesis of AgNPs is not of industrial feasibility (more tedious and time taking process) due to the requirements of highly aseptic conditions, more steps in maintaining cell culture, longer incubation time for the intracellular reduction of Ag⁺ ions and requires more purification steps. So many reports related to the synthesis of bioactive AgNPs using several plants extracts have been already documented in various approaches as given in Table 1^{35,36}.

Table 1: Green synthesis of silver nanoparticles using plant extracts

Plant	Plant part used	Particle size (nm)
<i>Acalypha indica</i>	Leaf	20-30
<i>Aloe vera</i>	Leaf	20
<i>Alternanthera sessilis</i>	Leaf	20-30
<i>Argemonem axicana</i>	Leaf	30
<i>Artemisia capillaris</i>	Leaf	29.71
<i>Artemisia nilagirica</i>	Leaf	70-90
<i>Boswellia ovali foliolata</i>	Leaf	30-40
<i>Camelia sinensis</i>	Leaf	30-40
<i>Cacumenplatycladi</i>	Leaf	18.4±4.6
<i>Carica papaya</i>	Fruit	15
<i>Cassia fistula</i>	Leaf	50-60
<i>Catharanthus roseus</i>	Leaf	30±2, 27±2
<i>Chenopodium murale</i>	Leaf	30-50
<i>Citrus sinensis</i>	Peel	35-10
<i>Cinnamomum camphora</i>	Leaf	55-80
<i>Clerodendrum inerme</i>	Leaf	5-60
<i>Coleus aromaticus</i>	Leaf	44
<i>Cymbopogon citratus</i>	Leaf	32
<i>Cynodon dactylon</i>	Leaf	8-10
<i>Dioscorea bulbifera</i>	Leaf	35-60
<i>Eclipta prostrate</i>	Leaf	35-60
<i>Eucalyptus hybrid</i>	Leaf	50-150
<i>Eichornia crassipes</i>	Leaf	10-50
<i>Garcinia mangostana</i>	Leaf	35
<i>Gelidium acerosa</i>	Leaf	22
<i>Leucas aspera</i>	Leaf	29-45
<i>Mangifera indica</i>	Leaf	20
<i>Mentha piperita</i>	Leaf	90

<i>Mimusopselengi</i>	Leaf	55-83
<i>Morindacitrifolia</i>	Leaf	10-60
<i>Moringaoleifera</i>	Leaf	57
<i>Ocimum sanctum</i>	Leaf	157.2
<i>Ocimum tenuiflorum</i>	Leaf	25-40
<i>Piper betle</i>	Leaf	3-37
<i>Rosmarinus officinalis</i>	Leaf	60
<i>Rosa rugosa</i>	Leaf	30-60
<i>Sesbania grandiflora</i>	Leaf	10-25
<i>Solanum nigrum</i>	Leaf	56.6
<i>Sesuvium portulacastrum</i>	Leaf	5-20
<i>Swieteniam ahogani</i>	Leaf	20
<i>Syzygium cumini</i>	Leaf	29-92

Antibacterial Properties of Silver Nanoparticles

Meanwhile, in recent years, noble metal NPs have been the subject of research interest because of their unique properties, such as electronic, optical, mechanical, magnetic and chemical properties are significantly different from the bulk material³⁷. The physical and chemical properties of NPs are function of their size/shape and are therefore different as compared to size independent constant physical properties of bulk material. Properties of AgNPs are significantly different from bulk silver metal. These are large surface to volume ratio leading to large fraction of surface atoms, high surface energy, spatial confinement, and reduced imperfections³⁸. The size, shape, and surface morphology of AgNPs play a vital role in controlling their properties.

The antibacterial properties of AgNPs are associated with its oxidation and liberation of Ag⁺ ions to the environment making it an ideal biocidal agent³⁹. It is expected that the large surface area to volume ratio and high fraction of surface atoms of AgNPs lead to high antimicrobial activity as compared with bulk silver metal⁴⁰. Moreover, the small size of AgNPs facilitates the penetration through cell membranes to affect intracellular processes from inside. Additionally, excellent antibacterial properties exhibited by AgNPs are due to their well-developed surface which provides maximum contact with the environment.

The formation of free radicals from the surface of the AgNPs may be considered to be another mechanism by which the cells die⁴¹. Free radicals have the ability to damage the cell membrane and make it porous which can ultimately lead to cell death. Gram-positive bacteria are made up of thick cell wall containing peptidoglycon, so that AgNPs did not affect easily. AgNPs easily penetrate into Gram-negative bacteria due to structure of cell wall that contains thin lipid layer, so AgNPs easily enter into the cell and disturb it⁴².

Antibacterial Applications of Silver Nanoparticles

AgNPs are of interest because of the unique properties which can be incorporated into antimicrobial applications,

biosensor materials, composite fibers, cosmetic products, wound healing, textile industry etc. AgNPs play a significant role in the field of biology and medicine due to their antimicrobial actions on pathogens⁴³.

Silver has been used as an antimicrobial agent for centuries; the recent resurgence in interest for this element particularly focuses on the increasing threat of antibiotic resistance, caused by the abuse of antibiotics⁴⁴. Antibacterial properties of the AgNPs may be due to their interactions with the cell wall of bacteria which results in the pore formation in cell walls where the AgNPs get deposited that causes change in permeability of the cell membrane⁴⁵.

Antibacterial effect of AgNPs has been widely described; their mechanism of action is yet to be fully elucidated. Most common mechanisms of toxicity proposed to date are^{46, 47}: (i) the surface area to volume ratio increases in the smaller size material compared with the bulk material, which provide opportunities for interactions with bacteria cell, (ii) AgNPs can cause cell breaking down, changes in the cell membrane permeability, inhibition of the ATP synthesis, (iii) AgNPs attach the surface of the cell membrane, penetrating in bacteria and disturb the cell function, (iv) interactions of AgNPs with amino acids and enzymes: bonding with amino acids (especially to -SH group), (v) obstructions in energy recruitment: influence on electron movement in the respiratory chain, inhibition of cytochromes; (vi) interaction with DNA and RNA, and (vii) generation of ROS.

Cells are majorly made up of sulfur and phosphorus which are soft bases and DNA has sulfur and phosphorus as its major components; AgNPs can act on these soft bases and destroy the DNA which would definitely lead to cell death^{48, 49}.

CONCLUSION

Different physical, chemical and biological methods have been developed for synthesis of AgNPs. Biological methods using plant extracts have advantages over other methods because of their



systems are single step in nature, environment friendly (green chemistry), cost effective, safe, compatibility for pharmaceutical applications, no need for (hazardous chemicals, high pressure, energy, power) and simply scaled up for large-scale synthesis. More than 100 different biological sources for synthesizing AgNPs are reported in the past decade by various authors. Many plants are becoming probable sources for reducing and stabilizing agents for green synthesis of AgNPs. The biological agents for synthesizing AgNPs cover compounds produced naturally in plants. AgNPs have shown great attention because of their unusual physical, chemical, electronic, catalytic, magnetic antibacterial and biological activities. From the technological point of view AgNPs have potential applications in the biomedical field.

Acknowledgement: The authors wish to thank Arba Minch College of Teachers Education, S.N.N.P.R, Ethiopia for the financial support towards the success of the research work.

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Source of Support: Nil, Conflict of Interest: None.

