



## Green synthesized silver nanoparticles

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### ABSTRACT

Nanoparticles has been used in medicine for diagnosis and treatment of various diseases. The current review focuses on the eco-friendly approach to develop nanoparticles of metal, with a special emphasis green synthesized silver nanoparticles. Past few years, due to its good conductivity, chemical stability catalytic and antibacterial activity silver have gained much attention. The diversity and significance of their applications have generated an enormous interest in developing different methods to synthesize silver nanoparticles with well-defined and controlled properties. Various chemicals and physical methods are being explored for production of silver nanoparticles. In which, chemicals are used as reducing agents which subsequently become responsible for various biological risks due to their general toxicity. In addition to chemical and physical methods, a new simple and cheaper technique to synthesize silver nanoparticles utilizes biological tools such as bacteria, yeasts, fungi, and plants. Products from nature or those derived from natural products, such as extracts of various plants or parts of plant, have been used as reducing agent and as capping agents during green synthesis. This technique involved is simple, most stable, and generally one-pot processes compare to other methods. The green synthesis of nanoparticles has been proposed as a cost effective and environmental friendly alternative to chemical and physical methods.

**Keywords:** Silver nanoparticles, Green synthesis, Plant extracts, Eco-friendly.

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### INTRODUCTION

Nanotechnology has vigorously developed as vital field of modern research with potential effects in electronics and medicine [1]Nanoparticles are sub-Nano sized colloidal structures colloidal structures composed of natural, synthetic or semi synthetic polymers. Nanoparticles are structures ranging from approximately 1-100 nm. The International Organization for Standardization (ISO, 2008) defines the term *nanomaterial* as *material with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale*[2]Researches in the field of nanotechnology are finding that metal nanoparticles have all kinds of previously unexpected benefits. They are usually prepared from noble metals, that is silver, gold, platinum and palladium while silver nanoparticles being mostly exploited, because of its wide range of application in medicine, electronics, energy saving, environment, textile, cosmetics, biomedical, etc.[3]

Metal nanoparticles can be prepared by two routes, the first one is a physical approach that utilizes several methods such as evaporation/condensation and laser ablation. The second one is a chemical approach in which the metal ions in solution is reduced in conditions favoring the subsequent formation of small metal clusters or aggregates.[4] Biological method is commonly adopted for the synthesis of silver nanoparticles, use of plant extracts is widely studied due to its advantages over others[5].

### Types of Nanoparticles

Nanoparticles can be broadly grouped into two, organic nanoparticles and Inorganic nanoparticles. Organic nanoparticles include carbon nanoparticles (fullerenes) while the inorganic nanoparticles include magnetic nanoparticles, noble metal nanoparticles, (like titanium oxide and Zinc oxide). The increasing interest towards inorganic nanoparticles i.e of noble metal particles (Gold and Silver) as they provide superior material properties with functional versatility. Due to their size features and advantages over available chemical imaging drug agents and drugs, inorganic particles have been examined as potential tools for medical imaging as well as for treating diseases.

Silver nanoparticle has been used in olden days by humans. The first nanotechnologist ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Nanoparticles had been used in medicine for diagnosis and treatment of various diseases. Silver nanoparticles has used in development of targeted drug delivery system. Nanoparticles are synthesized by different methods like chemical, physical, etc. Physical and chemical methods may have adverse effect in the medical application. Nanoparticles are prepared by biological methods using microorganisms, enzymes, fungus and plant extracts. These methods have advantages as they were eco friendly approaches over the conventional methods. Green synthesis of nanoparticles using plant extract can prove advantageous over other biological processes by eliminating the elaborate processes of maintaining microbial cultures. The present work has focused on silver nanoparticles form herbal extracts. Therefore, this method can be eco-friendly, economical and rapid and in addition, the toxicity of the by-product would be lesser than the other.

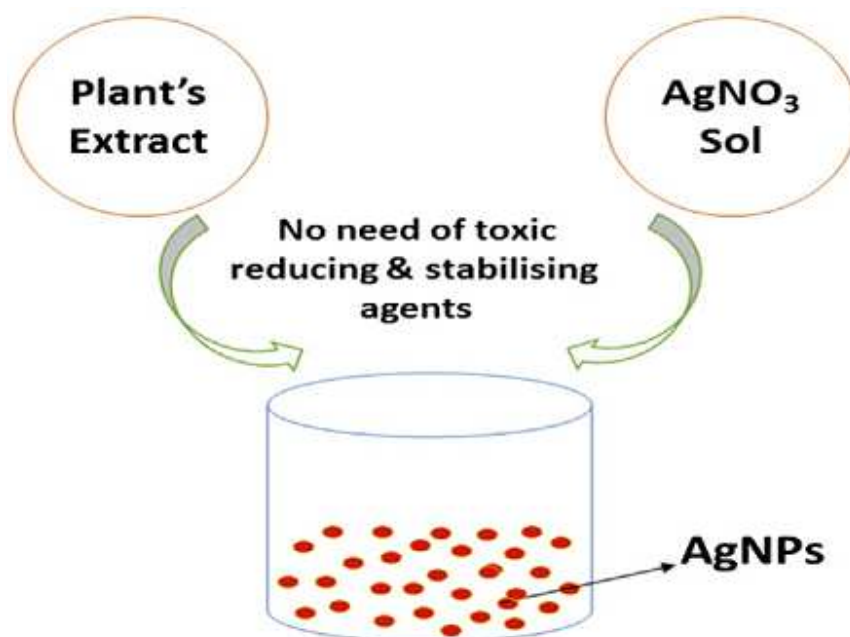


Figure 1: One pot green synthesis of silver nanoparticles

A single- step environmental friendly approach is employed to synthesize silver nanoparticles as shown in **Figure 1**. The environmental friendly synthesis of nanoparticles process is a revolutionary step in the field of nanotechnology. Silver nanoparticles have proved to be most effective as it has good antimicrobial efficacy against bacteria, viruses and other eukaryotic microorganisms. Silver is widely known as a catalyst for the oxidation of methanol to

formaldehyde and ethylene to ethylene oxide. Silver is a naturally occurring precious metal, most often as a mineral ore in association with other elements [6-7].

Silver nanoparticles have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaic to biological and chemical sensors. Examples include conductive inks, pastes and fillers which utilize silver nanoparticles for their high electrical conductivity, stability, and low sintering temperature [8]

A variety of techniques including physical and chemical methods have been developed to synthesis silver nanoparticles. Therefore, there is a growing need to develop environmental friendly nanoparticles synthesis processes that do not use toxic chemicals in the synthesis protocol.

#### **Physical method**

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of nanoparticles distribution are the advantages of physical synthesis methods in comparison with chemical processes. Physical synthesis of silver nanoparticles using a tube furnace at atmospheric pressure has some disadvantages. The physical method can be useful as a calibration device for nanoparticles measurement equipment. The results showed that the geometric mean diameter, the geometric standard deviation and the total number concentration of nanoparticles increase with heater surface temperature. Spherical nanoparticles without agglomeration were observed, even at high concentration with high heater surface temperature. The geometric mean diameter and the geometric standard deviation of silver nanoparticles were in the range of 6.2-21.5nm and 1.23-1.88nm respectively [9].

Silver nanoparticles could be synthesized by laser ablation of metallic bulk materials in solution. The ablation efficiency and the characteristics of produced nano-silver particles depend upon many parameters, including the wavelength of the laser impinging the metallic target, the duration of laser pulses, the ablation time duration and the effective liquid medium, with or without the presence of surfactants. One important advantages of laser ablation technique compared to other methods for production of metal colloids is the absence of chemical reagents in solutions. Therefore, pure and uncontaminated metal colloids for further applications can be prepared by this technique.

#### **Chemical method**

The most common approach for synthesis of silver nanoparticles is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride, elemental hydrogen, poly ethylene glycol are used for reduction of silver ions in aqueous or non-aqueous solutions. These reducing agents reduce Ag<sup>+</sup> and lead to the formation of metallic silver, which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles. Polymeric compounds such as poly vinyl alcohol, poly vinyl pyrrolidone, poly ethylene glycol and poly methacrylic acid have been reported to be effective protective agents to stabilize nanoparticles[10-12].

#### **Need For Green Synthesis**

The biosynthesis of nanoparticles as the physical and chemical processes was costly. Often, chemical process includes some of the toxic chemical absorbed on the surface that may cause adverse effect in the medical applications. This is not an issue when it comes to biosynthesized nanoparticles via green synthesis route. Green chemistry to improve and/or protect our global environment is focal issues in many fields of research. The development of cost efficient and ecologically benign methods of synthesis of nano materials still remains a scientific challenge as metal nanoparticles are of use in various catalytic applications, via electronics, biology and biomedical applications, material science, physics, environmental remediation fields[13].

#### **Biological synthesis of silver nanoparticles**

Biological methods of green synthesis of nanoparticles and these have proven to be better methods due to slower kinetics; they offer better manipulation and control over crystal growth and their stabilization. Plant extracts as reducing and capping agents, has received special attention among others, due to maintaining an aseptic environment during the process. Medicinal plants having well established therapeutic importance are being widely used for the size and shape controlled synthesis of silver nanoparticles.

The use of microorganisms in the synthesis of nanoparticles emerges as an eco-friendly and exciting approach. Silver nanoparticles, like its bulk counterpart, are an effective antimicrobial agent against various pathogenic microorganisms. Though various chemical and biochemical methods are being explored for silver nanoparticles production, microbes are very much effective in this process [14].

Various microbes are known to reduce the metals, most of them are found to be spherical particles as reported earlier. The resistance conferred by bacteria to silver is determined by the 'sil' gene in plasmids. Plant mediated synthesis of nanoparticles is a green chemistry approach that interconnects nanotechnology and plant biotechnology [15]. The technique for obtaining nanoparticles using naturally occurring reagents such as plant extracts could be considered attractive for nanotechnology, because the complex process of maintaining cell cultures are removed in this technique and it is also suitable for large-scale synthesis of nanoparticles. Plant parts such as leaf, root, latex, seed, and stem are being used for nanoparticles synthesis. Nano capsulation has been investigated as a means of protecting palmitate structures against photo degradation by ultraviolet-visible spectrophotometry (UV-Visible) radiation [16-18]. Silver nanoparticles having a surface Plasmon resonance band created at 406nm. Biosynthetic methods employing both biological microorganism such as bacteria and fungus or plant extract, have emerged as a simple and viable alternative to more complex chemical synthetic procedures to obtain nano materials. Extract from plant may act both as reducing and capping agents in silver nanoparticles synthesis [18-19] is summarized in the

**Table 1**

**Table1: Green synthesized of silver nanoparticles from various plant extracts**

Plant extract as reducing/capping agents	Characterization, Observation & Particle size	Applications	References
<i>Sesbania grandiflora</i> leaf extract	spherical shaped nanoparticles in the size of 22 nm	Cytotoxic activity was also tested against human breast cancer (MCF-7) cells towards the development of anticancer agent	[20].
leaf broth of <i>Murraya paniculata</i>	The colour change in reaction medium from pale yellow to dark brown was observed during the incubation period.		[21]
<i>Alhagi maurorum</i> leaf ethanolic extract. Boiled, crushed	reaction mixtures turned dark brown, predominance of silver nanosized crystallites (14 – 29 nm) after short incubation period		[22]
<i>Solanum torvum</i>	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	Antimicrobial activity	[23]
<i>Azadirachta indica</i> (Indian Neem).	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	Antimicrobial activity of the synthesized silver nanoparticles was tested using both gram positive as well as gram negative bacteria i.e. <i>Staphylococcus aureus</i> and <i>Escherichia coli</i> , respectively	[24]
<i>Ocimum sanctum</i> leaf	Silver nanoparticles with size in the range 10-20 nm having symmetric SPR band centered around 409 nm are obtained		[25]
<i>Ocimum sanctum</i> , as reducing agent.	The absorption peak at 430 nm broadens with increase in time indicating the polydispersity nature of the nano particles.	antibacterial, antifungal	[26]
<i>Azadirachta indica</i>	Synthesized nanoparticles are characterized under UV-Vis spectroscopy at the range of 350-420 nm. The peak showed at 351 nm.	Green synthesized silver nanoparticle showed zone of inhibition against isolated Gram positive ( <i>Salmonella typhi</i> ) and Gram negative ( <i>Klebsiella pneumoniae</i> ) bacteria.	[27]
leaf extract of <i>Acalypha indica</i>	the formation of nanoparticles was observed within 30 min	antibacterial activity against water borne pathogens	[28]
<i>Ulva fasciata</i> crude ethyl acetate extract	nanoparticles are crystalline in nature, spherical in shape and poly-dispersed with size ranging from 28 to 41 nm	<i>Ulva fasciata</i> based bionanoparticles inhibited the growth of <i>Xanthomonas campestris</i> pv. <i>malvacearum</i> (14.00±0.58 mm Zone of inhibition),	[29]
extract of <i>Cleome viscosa</i>	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	The test cultures included in this study were <i>Staphylococcus aureus</i> , <i>E. coli</i> , <i>Pseudomonas</i>	[30]

		aeruginosa, Vibrio cholerae, and Salmonella. The maximum inhibitory effect using 3mM silver nitrate against the microbes were obtained	
leaf extract of <i>Daturaalba</i> Nees.	aggregates silver nanoparticles and these were spherical in shape	Anti bacterial activity It was observed against <i>chlostridiumdiphtheria</i>	[31]
<i>Bacopa monniera</i> whole plant	From TEM analysis, the size of the silver nanoparticles was measured (10-30 nm).	antimicrobial activity of synthesized particles showed effective inhibitory activity against <i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , <i>Klebsiella pneumonia</i> and <i>Bacillus subtilis</i> .	[32]
The herbal leaves like <i>Ocimum sanctum</i> and <i>Vitex negundo</i>	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	antibacterial activities	[33]
the extract of <i>Trianthema decandra</i>	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD		[34]
<i>Solanum xanthocarpum</i> L	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	Being used in anti- <i>H. pylori</i> therapy.	[35]
papaya fruit extract	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD showed the average particle size of 15 nm as well as revealed their cubic structure	biologically synthesized nanoparticles were found to be highly toxic against different multi drug resistant human pathogens ( <i>Escherichia coli</i> and <i>Pseudomonas aeruginosa</i> ).	[36]
<i>Ocimum sanctum</i> (Tulsi)	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	antimicrobial activity	[37]
<i>Argimone mexicana</i> leaf extract	Nanoparticles were characterized using UV-Vis absorption spectroscopy, FTIR, XRD	antimicrobial activities.	[38]

### Mechanism of formation of green synthesized silver nanoparticles[39]

The metal ions bind to the reducing metabolites and stabilizing agents and are reduced to metal atoms. The resulting complex of the metal ion and metabolite interacts with similar complexes forming a small metal nanoparticle. Next step is the growth and coalescence of separate small particles into larger ones occurs through the coarsening process. This process continues until the particles assume a stable shape and size as shown in **Figure 2**.

### Applications of silver nanoparticles[40-42]

- Silver in ion or metallic can be exploited in medicine for burn treatment, dental materials, water treatment, sun-screen lotions, etc.
- The silver nanoparticles were also used for impregnation of polymeric medical devices to increase their antibacterial activity. Silver impregnated medical devices like surgical masks and implantable devices showed significant antimicrobial efficiency.
- Researchers have also recommended the use of silver and copper ions as superior disinfectants for waste water generated from hospitals containing infectious microorganisms.
- Silver nanoparticles can be used for the production of antimicrobial paints based on vegetable oil. The silver nanoparticles embedded drying oil is an excellent coating material and can be used to coat several kinds of surface such as wood, glass, polypropylene, poly (methyl methacrylate), polystyrene and building walls made of different materials.
- Silver has been used extensively for the treatment of burns, incorporated into bandages for use in large open wounds.
- Silver nanoparticles can be coated on common poly-urethane (PU) foams by overnight exposure of the foams to nanoparticles solutions. Repeated washing and air drying yields uniformly coated PU foam, which can be used as a drinking water filter where bacterial contamination of the surface water is a health risk. Nanoparticles are stable on the foam and are not washed away by water. The nanoparticle binding is due to its interaction with the nitrogen atom of the poly-urethane.
- Dressings have a part to play in the management of wounds, whether they are sutured or open, usually chronic wounds of many aetiologies which are healing by secondary intention. Nanocrystalline technology appears to give the highest, sustained release of silver to a wound without clear risk of toxicity.
- Silver zeolite is used in food preservation, disinfection and decontamination of products.
- Anti-microbial applications: air and water purification, films, food preservation

- Optical applications: solar cells, medical imaging, surface enhanced spectroscopy.
- Conductive applications: conductive adhesives, high-intensity LEDs, touch screens, LCDs
- Chemical and thermal applications: chemical vapour sensors, catalysts

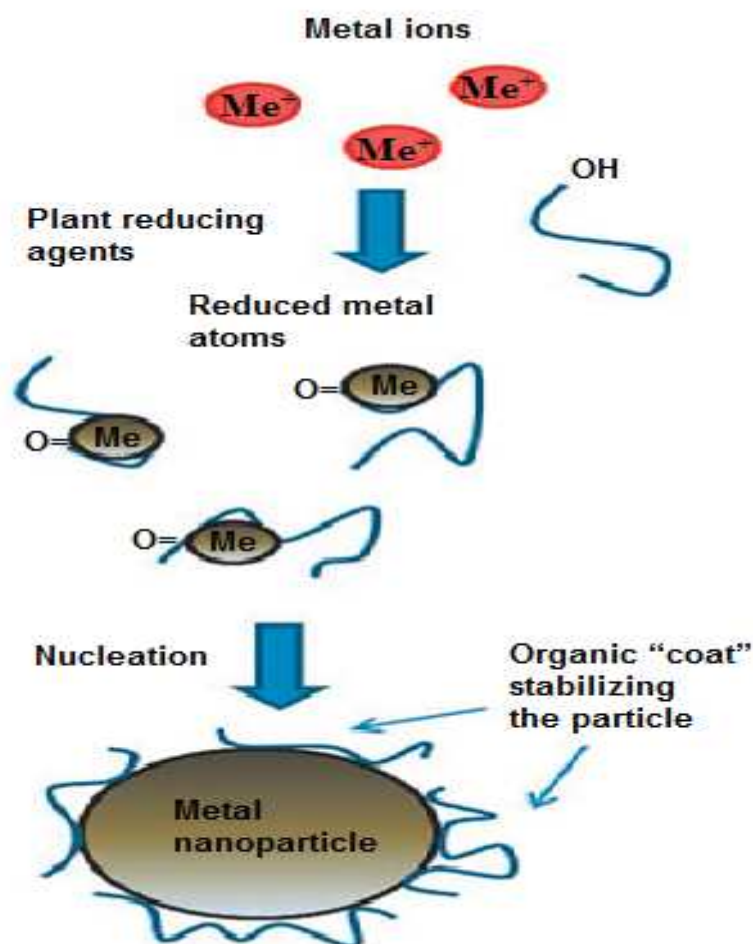


Figure 2: A schematic representation of metal nanoparticle synthesis in presence of a plant extract

### Silver nanoparticles optical properties

There is growing interest in utilizing the optical properties of silver nanoparticles as the functional component in various products and sensors. Silver nanoparticles are extraordinarily efficient at absorbing and scattering light and, unlike many dyes and pigments, have a colour that depends upon the size and shape of the particle. The strong interaction of the silver nanoparticles with light occurs because the conduction electrons on the metal surface undergo a collective oscillation when excited by light at specific wavelengths. Known as surface Plasmon resonance (SPR), this oscillation results in unusually strong scattering and absorption properties<sup>(43)</sup>.

Silver nanoparticles can have effective extinction (scattering + absorption) cross sections up to ten times larger than their physical cross section. The strong scattering cross section allows for sub 100nm nanoparticles to be easily visualized with a conventional microscope. When 60nm silver nanoparticles are illuminated with white light they appear as bright blue point source scatters under a dark field microscope. The bright blue colour is due to an surface Plasmon resonance that is peaked at a 450nm wavelength. A unique property of spherical silver nanoparticles is that this SPR peak wavelength can be tuned from 400nm (violet light) to 530nm (green light) by changing the particle size and the local refractive index near the particle surface. Even larger shifts of the SPR peak wavelength out into

the infrared region of the electromagnetic spectrum can be achieved by producing silver nanoparticles with rod or plate shapes.

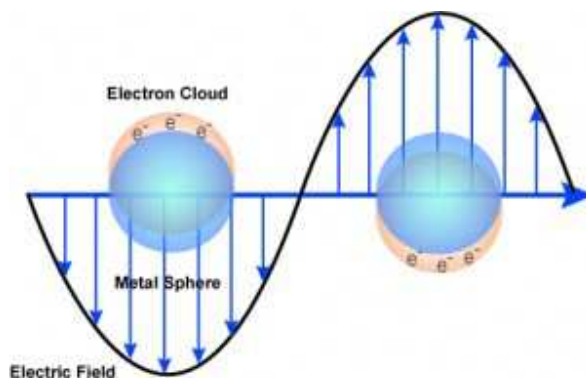


Figure 2: Image of surface Plasmon resonance, dark field microscopy

### Silver nanoparticles characterization

The size and shape of metal nanoparticles are typically measured by analytical techniques such as TEM, scanning electron microscopy (SEM) or atomic force microscopy (AFM). Measuring the aggregation state of the particles requires a technique to measure the effective size of the particles in solution such as dynamic light scattering (DLS) or analytical disc centrifugation. Unique optical properties of silver nanoparticles, a great deal of information about the physical state of the nanoparticles can be obtained by analyzing the spectral properties of silver nanoparticles in solution[44].

The spectral response of silver nanoparticles, as the diameter increases the peak Plasmon resonance shifts to longer wavelength and broadens. At diameters greater than 80nm, a second peak becomes visible at a shorter wavelength than the primary peak. The secondary peak is due to a quadrupole resonance that has a different electron oscillation pattern than the primary dipole resonance. The peak wavelength, peak width, the effect of secondary resonances yield a unique spectral fingerprint for a plasmonic nanoparticles with a specific size and shape

UV-Visible spectroscopy provides a mechanism to monitor how the nanoparticles change over time. When silver nanoparticles aggregate, the metal particles become electronically coupled and this coupled system has a different surface Plasmon resonance than the individual particles. Multi nanoparticles aggregate, the Plasmon resonance will be red-shifted to a longer wavelength than the resonance of an individual nanoparticle, and aggregation is observable as an intensity increase in the red/infrared region of the spectrum. For silver nanoparticles solutions that have not agglomerated and have a spectral shape that is identical to the as-received suspension, the UV-Visible extinction spectra can be used to quantify the nanoparticles concentration.

### Silver nanoparticles surface chemistry

When nanoparticles are in solution, molecules associate with the nanoparticles surface to establish a double layer of charge that stabilizes the particles and prevents aggregation<sup>[44]</sup>. Citrate based agent was selected because the weakly bound capping agent provides long term stability and is readily displaced by various other molecules including thiols, amines, polymers, antibodies and proteins. Nanoparticles synthesis and the study of their size and properties are of fundamental importance in the advancement of recent research. It is found that the optical, electronic, magnetic and catalytic properties of metal nano particles depend on their size, shape and chemical surroundings. In nanoparticles synthesis is very important to control not only the particle size but also the particle shape and morphology as well.

## CONCLUSION

A green synthesis route has been used for silver nanoparticles synthesis. This reaction is occurred at ambient temperature. The present review reveals that several plant biomass or plant extracts have been successfully used for extracellular biosynthesis of silver nanoparticles. And also analytical techniques, such as ultraviolet-visible spectroscopy (UV-vis), X-ray powder diffraction (XPD), transmission electron microscopy (TEM) and zeta

potential measurements can be applied to characterize the nanoparticles morphology. Silver nanoparticles based diagnostics and therapeutics hold great promise because multiple functions can be built onto the particles. The potential applicability of these silver nanoparticles in the present technique is simple, sensitive and selective for the versatile applications related to diagnostics and therapeutics. The usage of silver nanoparticles is safe to consumer health and environment.

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