# A REVIEW ON GREEN SYNTHESIS OF SILVER NANOPARTICLE, CHARACTERIZATION AND OPTIMIZATION PARAMETERS

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## Abstract

*Nanotechnology deals with the study of particles in the range of 1-100nm where they have unique properties which define their application. In recent years, green synthesis of silver nanoparticles is prominent with scientists and researches for its ease of availability, nonhazardous waste production and is economically viable too. It is seen that the green synthesis has over taken the chemical synthesis of nanoparticles as it is quick and easy. The methodology of synthesis along with various conditions like the temperature, time, pH, silver ion concentration, radiations also plays a vital role in the shape, size and yield of the nanoparticles produced. Optimization of the parameters for the better quality yield of silver nanoparticles enables us to apply in areas as microbiology, photography, catalysis, biological labeling, phototonics, optoelectronics, medical devices and healthcare products*

***Keywords:*** *Nanotechnology; silvernanoparticles; green synthesis; optimization*

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## 1. INTRODUCTION

In current scenario with a concern to protect the environment, green technology has got its own potential to overcome it. Metal nanoparticles for its own advantage of being used in various applications, the more economic and environment friendly way of producing it is a challenge. The applications of metal nanoparticles are in various field as in electronics as sensors, as an antimicrobial agent, as bio catalytic activity in various reactions, environmental remediation, physics, material science etc. Green synthesis has paved a way of more environmental and economic way of producing silver nanoparticles and with availability of lots of sources it has got its own specificity and application.

Characterization, play a vital role in estimating their nature of application in which the physical properties of the nanoparticles as size, shape, functional groups attached along with the optical properties are known.

The different parameters which influence the synthesis of nanoparticles are the pH, temperature, Silver ion concentration, concentration of the leaf extract used, time of reaction, radiations, pressure and so on. On optimizing these parameters maximum yield with desirable properties can be achieved. This paper discusses on the green synthesis methods of silver nanoparticles with all the characterization methods and the different optimization parameters.

## 2. GREEN SYNTHESIS METHODS

### 2.1 Polysaccharide Method

Reduction of silverions to nanoparticle is enabled by polysaccharide as reducing agent that can act as capping agent too. Synthesis of nanoparticle with Alpha D glucose and Beta D glucose in the presence of starch as a capping agent are also carried out. Significance of starch mediated silvernanoparticles is its easy integration into systems of biological and pharmaceutical applications. The interaction between starch and nanoparticles are week and are reversible at elevated temperatures enabling the separation of them (Ravendran et al 2003)

### 2.2 Tollens Method

The Tollens Synthesis method gives silver nanoparticles with controlled size in about one step process. The basic Tollens reaction involves the reduction of Tollens reagent ($Ag(NH_3)_2$) by an aldehyde. In the modified Tollens procedure $Ag^+$ ions are reduced by saccharides in the presence of ammonia yield a stable particle size where the ammonia concentration and the nature of the reductant play a major role in controlling the size of silver nanoparicle (Yu etal 2004)

### 2.3 Irradiation Methodology

Various studies indicate the successful production of silver nanoparticles by radiations.Silvernanoparticles of well defined shape and size can be produced by passing laser irradiation through an aqueous solution of Silver salt and surfactant. Also the microwave radiation of solution containing carboxymethyl cellulose sodium and silver nitrate produced uniform silvernanoparticles stable for 2 months. Stable nanoparticle is also synthesized by irradiating with gamma radiation and passing 6 MeV electrons beam. [26]

### 2.4 Polyoxometalates Method (POMs)

POMs have the capability of undergoing stepwise, multielectron redox reactions without disturbing their structure. POMs serve both as a photocatalyst, reducing agent and a stabilizer (Bogle etal 2004)

### 2.5 Biological Method

Extracts from microorganisms and plant, act both as reducing and capping agents in silver nanoparticle synthesis. The reduction process of silver ions takes place by biomolecules such as enzymes, proteins, aminoacid, polysaccharides and vitamins. Lot of researches are going on by using the extracts of various bacterias, fungi, Actinomycetes and also the plant extracts as this seem to be the safest and economical way of producing nanoparticle. Out of this green synthesis, using plant material as source is advantageous overall as they are abundantly available and easy to handle. Different plant sources that produce silver nanoparticles as listed out in Table1.

**Table 1** Plant sources for the synthesis of silver nanoparticles with shape and sizes.

| Plant source | Part | Size | Shape | Reference |
|---|---|---|---|---|
| *Cinnanmon zeylanicum* | Bark | 31-40nm | Quasi spherical shaped and rod shaped | (Sathikumar 2009) |
| *Pelargonium graveolens* | Leaves | 16-40nm | Quasi linear superstructures | (Shanker et al 2003) |
| *Cinnammum camphora* | Leaves | 55-80nm | Triangular or spherical | (Huang et al 2007) |
| *Aloe vera* | Leaves | 50nm | Triangular | (Chandran et al 2006) |
| *Cycas* | Leaves | 2-6 nm | Spherical | (Philip et al 2001) |
| *Jatropha curcas* | Latex | 20 nm | Spherical | (Bar et al 2009) |
| *Jatropha curcas* | Seed | 15 to 50 nm | Rod shaped | (Bar et al 2009) |
| *Cynnamon zeylanicum* | Bark | 80 nm | Spherical | (Sathikumar 2009) |
| *Black Tea* | Leaves | 40nm | Spherical | (Begum et al 2009) |
| *Desmodium triflorum* | Leaves | 5-20nm | Spherical | (Ahmed etal 2010) |
| *Murraya koenigii* | Leaves | 20nm | Hexagonal and spherical | (Jha et al 2009) |
| *Citrus limon* | Leaves | 50nm | Spherical | (Prathnaa et al 2011) |
| *Coriandrum sativum* | Leaves | 26nm | Spherical | (Sathyavathi et al 2010) |
| *Capsicum annuum* | Leaves | 10-12nm | Triangular | (Li et al 2007) |
| *Medicago sativa* | Leaves | 2-20nm | Spherical | (Gardea et al 2003) |
| *Azadirachta indica* | Leaves | 5-35nm | Spherical, plate like, core shell structure | (Shankar et al 2004) |
| *Pelargoniumgraveolens* | Leaves | 16-40nm | Triangular | (Shankar et al 2003) |

### 2.6 Mechanism of Synthesis of Silvernnaoparticles through Plant Extracts

Main mechanism in which the silver nanoparticles are synthesized is through the reduction of silver ions in which the phytochemicals play a vital role in it. Phytochemicals such as terpenoids, flavones, ketones , aldehydes, amides and carboxylic acid play a vital role (Gluskar 1999). Mechanism of synthesis of silver nanoparticles involves three main phases. The first phase is called an activation phase in which the reduction of the silverions is carried out and nucleation of reduced metal ions are carried out. The second phase is called as a growth phase in which small adjacent nanoparticles spontaneously coalesce into particles of larger size (Oswald Ripening). During the growth phase the nanoprticles aggregates to form nanotubes, nanoprisms, nanohexadrons and variety other irregularly shaped nanoparticles. The third phase is called as a termination phase in which the final shape of nanoparticles are confined. Also the nanoparticles acquire most energetically favourable conformation. Plant extracts play a vital role to stabilize the metal nanoparticles (Si etal 2007).

### 2.7 Role of Plant Metabolites in Silver Nanoparticle Synthesis

Various plant metabolites including terpenoids, polyphenols, sugars, alkaloids, phenolic acids and proteins play an important role in reduction of metal ions which yields nanoparticles. FTIR spectroscopy reveals that Terpenoids are often associated with the nanoparticles. Terpenoids have strong antioxidant activity and was found to play an principal role in bio reduction of silver ions (Rai et al 2007). Flavanoids have various functional group which involves in silver nanoparticle formation. It is noted that the tautomeric transformation of flavanoids from the enol form to keto form may release a reactive hydrogen atom that can reduce metal ions to form nanoparticles.(Ahmed etal 2010) Flavanoids are also able to adsorbed on the surface of nascent nanoparticle. This means they are involved in stages of nucleation and further aggregation in addition to bio reduction stage.

## 3. CHARACTERIZATION

### 3.1 Reduction of Silverions

The reduction of silver ions is noticed by the colour change from pale green to dark brown colour which is observed within minutes after the addition of 1mM silver nitrate to the leaf extract. The formation of nanoparticles by different salts gives characteristic peak at different absorptions which can be monitored by UV/VIS spectroscopy. Silver nanoparticle formation from the silverions shows a characteristic peak at 450 nm.

### 3.2 Shape and Size

Various factors govern the size and shape of the nanoparticle. Estimation of the morphological features silvernanoparticle is by Transmission electron microscope (TEM). Determination of size and shape has a greater impact on its optical behaviour and surface plasmon effect. They can be in triangular, spherical or hexagonal in shape.

### 3.3 Functional Group

Sometimes the functional group gets attached to the nanoparticle formed. The functional groups attached depend on the source of nanoparticles. This might be also due to the improper purification step performed during synthesis of nanoparticles. The functional group attached to the silver nanoparticle has to be found to ensure its relevance to the application. Functional groups attached to the nanoparticle can be well analyzed by FTIR.

### 3.4 Crystalline Nature

The crystalline nature of silver nanoparticles can be confirmed by X-ray diffraction studies. The spectrum shows distinct peaks indexed to the reflection of the crystalline planes of face centred cube. Understanding the crystalline nature of silver nanoparticles enables its application in optical sensors and image analysis. The optical properties can be well studies by the addition of stabilizer and capping agent as polyvinylalcohol and glycerol during the synthesis of nanoparticles.

### 3.5 Size Distribution

Dynamic light scattering system (DLS) is generally used for analysis of the size distribution pattern of particles in suspension or solution which gives the hydrodynamic diameter of particles. The average size of particles in a suspension can be well analyzed by DLS.

### 3.6 Elemental Composition

Energy dispersive X-ray spectroscopy (EDX) determines the elemental composition. It is used to confirm that the nanoparticle suspension contains nothing but silver.

### 3.7 Stability Analysis

Zeta potential is an essential parameter for the characterization of stability in aqueous nano suspensions. This possibly gives the charge of the nanoparticles formed. The indication of positive or negative nature of nanoparticles enables its use in electronic devices.

### 3.8 Thermal Stability

Thermal stability of the nanoparticle formed can be monitored by Thermo Gravimetric Analysis (TGA). The change in weight of the subjected materials with respect to temperature range of 0-1000$^{o}$C can be carried out. The loss in weight might be related to the decomposition of surface coated phytochemicals, adsorbed water molecules and oxidation of silver nanoparticle upon increase in temperature.

### 3.9 Silver Ion Concentration Determination

Silver ion concentration can be analysed by Atomic Absorption Spectroscopy (AAS), which shows the conversion of $Ag^{+}$ ions to $Ag^{0}$ nanoparticles. The reaction time of complete conversion of $Ag^{+}$ to $Ag^{0}$ nanoparticles can be well noted by this method.

## 4. FACTORS INFLUENCING METAL NANOPARTICLE SYNTHESIS

### 4.1 Silverion Concentration

The concentration of silver nitrate solution used also has an effect on Silver nanoparticle formation. Experiments carried out by varying dilutions of silver nitrate solution also have an effect on the shape and size of the nanoparticle. It is seen that the increased dilution as 1:1 with the extract will give a comparatively bigger size of nanoparticle and lesser concentration gives a smaller sized one. The optimum silver ion concentration at most cases is reported as 1mM.

### 4.2 Effect of pH

pH has a great influence in formation of nanoparicle. pH has the capability in affecting the phytochemicals by a charge change in them. It also affects the ability to bind to each other during the termination phase and thereby affecting the shape, size and yield of the nanoparticles.

It is well noted that the better yield of nanoparticles are obtained at alkaline pH where is acidic pH low yield or no nanoparticle formation in noticed in different studies.

**Table 2** Effect of pH on yield of nanoparticle

| pH | Yeild % | Reference |
|---|---|---|
| <3 | Agglomerates, No yield | (Shankar etal 2003) |
| 3-5 | less yield | (Sathikumar 2009) |
| 6 | 52.3 | (Jiang et al 2009) |
| 7 | 69.8 | (Prathna et al 2011) |
| 8 | 88.7 | (Huang et al 2007) |
| 9 | 86.2 | (Gluskar et al 1999) |
| *10* | 80.3 | (Jiang et al 2009) |

### 4.3 Effect of Temperature

Temperature elevation can increase the reaction rate and efficiency of synthesis. Most studies are carried out at room temperature as it is the simplest and natural way of synthesizing the nanoparticle. As the temperature increases the time of reaction decreases and 95% conversion into nanoparticle is obtained at $95^0$C within 10 minutes. The temperature greatly influence on the shape of the nanoparticle too. Nanoparticles which give spherical shape at $60^0$C are giving triangular shape at $90^0$C.

**Table 3** Effect of temperature on nanoparticle formation

| Temp. | Shape | Plant species | Reference |
|---|---|---|---|
| $40^0$C | Triangular | *M.sativa* | (Shankar et al 2003) |
| $50^0$C | Spherical | *Cassia fistula* | (Prathna et al 2011) |
| $60^0$C | Spherical | *Coriandrum sativum* | (Li et al 2007) |
| $70^0$C | Spherical, | *C. aromaticus* | (Gluskar et al 1999) |
| $80^0$C | Spherical | *Nyctanthes arbortristis* | (Prathna et al 2011) |
| *$90^0$C* | Triangular | *Pelargoniumgraveolens* | (Shankar et al 2003) |

### 4.4. Effect of Time on Reaction

The reduction reaction and formation of nanoparticles starts immediately after the addition of silvernitrate with the plant extract which is noted by the colour change from light green to brown colour. But, it is seen that the particle size increases with increase in time and stabilize at a particular time. For instances studies reveal that seconds after the addition of the plant extract the size was 7nm and further increasing the time nucleation process has proceeded and became stable before 30mins were the size was 20nm.

### 4.5 Effect of Radiation

It is seen that the radiations have an impact on the silver nanoparticle synthesis. Studies are done on different radiation as Sunlight, Microwave, laser and UV radiation. The radiations induce the synthesis of nanoparticles also contributes on the shape. The sunlight is proved to give greater yield in comparison with other radiation. Studies reveal that the laser radiation produces triangular shaped nanoparticle whereas the microwave radiation has the ability to produce spherical shaped particles.

### 4.6 Effect of Extract Amount

As the amount of extract added increases the formation of silver nanoparticles increases. The reductase present in the leaf extract enables the synthesis of silver nanoparticles by reduction reaction with silver ions. The ideal concentration is in 1:1 ratio with silver ions. Increase in amount of extract results in the production of larger size nanoparticles.

### 4.7 Effect of Electron Donor

Glucose (56 mM) acts as an electron donor and has positive effects on nanoparticle synthesis. In absence of electron donor, electron reservoirs in reaction mixture for the recovery and revival of cofactors after a short time are finished and reaction declines.

## 5. CONCLUSION

Green synthesis of nanoparticles paves a way for future for economical synthesis without any harmful byproduct. Although there are different methods of green synthesis, the biological method using the plant extract serve as the widely used amongst all. It is seen that the source plays a vital role in contributing the shape and size of nanoparticles. As plants serves as a source for nanoparticle production there might be possible contaminations associated with the nanomaterials. Proper purification steps helps in overcoming the contamination. The synthesis of nanomaterials are associated with different factors affecting it such as pH, temperature, reaction time, radiations, silver ion concentration and plant extract. Each factor contributes to the size and shape. The yield can also be increased by optimising certain parameters. Hence it is essential to optimize the synthesis of silver nanoparticles for the better application of the same.

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