Review Article
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Syntheses, characterization and applications of silver nanoparticles

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Received on: 26/11/2021 Accepted on: 30/12/2021 Published on: 31/12/2021

ABSTRACT

Silver nanoparticles (Ag NPs) are prepared by green, biological, physical and chemical approaches. Their biosynthesis involves the use of fungi, yeast, bacteria, plants and algal extracts. Physical methods include evaporation, arc-discharge, condensation, direct current (DC), magnetron sputtering and energy ball milling method. Chemical methods involve the reduction of silver salt. FTIR, UV-Vis spectroscopy, X-ray diffractometry and X-ray photoelectron spectroscopy are used for their characterization. Ag NPs find various technological applications and also possess anticancer, antimicrobial, anti-angiogenesis, anti-inflammatory, antiplatelet, anti-proteolytic and antifungal activities and also used in lung cancer chemoprevention, food packing, soaps, toothpastes, shampoos, detergents and cosmetics.

Keywords: Silver nanoparticles; Synthesis; Characterization; Applications.

How to cite this article: Rafique S, Hussain S, Ahmad M and Amjad M (2021). Syntheses, characterization and applications of silver nanoparticles. J. Chem. Res. Adv., 02(02): 20-29.

Introduction

Nanoparticles (NPs) are vast class of materials that include small discrete mass of matter which have one particular range from 1-100nm (Laurent et al., 2008). They can be classified into many types i.e., lipid based nanoparticles, polymeric nanoparticles, semiconductor nanoparticles, ceramics nanoparticles, metal nanoparticles, carbon based nanoparticles *etc* (I. Khan et al., 2017). Material science is directly related to the nanotechnology which finds numerous applications in almost all the fields of everyday life (Duncan, 2011; Hughes, 2000; Qu et al., 2013; West & Halas, 2000). The investigations on nanomaterials are a field of interest in today's science (Hussain & Amjad, 2021; Hussain et al., 2020; Javed & Hussain, 2020; Raza et al., 2021). Silver nanoparticles (Ag NPs) find a broad range of applications especially in the medical field and material sciences(Abbas et al., 2016; Kim et al., 2007; Marin et al., 2015; Nosheen et al., 2021; Rehman et al., 2019). Keeping in view there greater importance, the current review focuses on their methods of syntheses, characterization and applications.

Synthetic Methodologies

The preparation of silver nanoparticles can be done by various green, biological, chemical and physical approaches. However the biological and green approaches are comparatively easier, less time consuming and eco-friendly(Panigrahi, 2013).The physical, biological and chemical methods involve the manufacture of poisonous byproducts which are harmful; furthermore, these techniques are highly expensive. The green biosynthesis is a novel method which has been recently developed and employsa variety of plant extracts to synthesize metal nanoparticles (M. Khan et al., 2018).

Green synthesis

The growing needs to develop eco-friendly products can be fulfilled by the method of biological approaches and green synthesis. Various metal nanoparticles are synthesized by using a variety of fungi and bacteria. However, the most adopted method is green synthesis which employs plant extracts; this method has as well a distinct benefit that the plants are easily available, widely distributed, act as source of several metabolites and much safer to handle(Kuntyi et al., 2019).

The silver nanoparticles (AgNPs) can effectively be produced from bio-reduction of silver nitrate solutions by using neem leaf extracts. In future, there will be a good valuable potential of neem leaf extracts for the production of silver nanoparticles owing to their stable and benign nature(Mallikarjuna et al., 2011). The green synthesis of silver nanoparticles can also be done by using many other plant sources.

The excellent bactericidal properties against a wide variety of microorganisms are shown by silver nano particles (Ag NPs). They are synthesized, frequently to investigate their physical or morphological properties and to apply in drugs, electronics, catalysis and in biological systems. Fungi, actionmycies, yeast, bacteria and plant extracts are involved in biogenic synthesis of Ag NPs(Siddiqi et al., 2018). With increasing motivation on green chemistry, natural compounds like chitosan, glucose, soluble starch and approximately microorganisms have been involved in considerable research as reducing, safer alternatives and stabilizing mediators to produce the silver nano-sphere. Due to the well-established therapeutic importance of medicinal plants, these are extensively used for the size and shape-controlled formation of silver nanoparticles (Amin et al., 2012).

Biosynthesis

Due to its economical, simplicity, eco-friendliness and supportable methods, biosynthesis of metal nanoparticles is achieving more significance. It is an environment friendly and unexploited method to protect and improve the environment for bio-manufacturing of AgNPs by using leaf extract of plants(Singh et al., 2016). The exciting and emerging area of nanotechnology is green synthesis of AgNPs by using microorganisms and may have significant impression on auxiliary advances in nano-science(Abdelghany et al., 2018). The biological synthetic methods from microorganisms and/or herbal extract have several advantages over the physical and chemical synthetic methods of AgNPs. These biological routes are simple, cost-effective, eco-friendly, and easily scaled up for high production/yield. With the use of biological agents such as yeast, fungi, bacteria, plants and algal extracts, the biosynthetic methods are gaining popularity for the formation of metal and metal oxide nanoparticles(Singh et al., 2016). A strong antimicrobial activity is shown by biosynthesized AgNPs which cause a widespread inhibition of growth against numerous fungi as well as bacteria (grambacteria and gram negative). Fungal, bacterial and plant extract sources can be used for the production of nanosilver, this type of formation is very reliable, easy, and nontoxic in nature(Gudikandula & Charya Maringanti, 2016).

Physical methods

The toxic chemicals are not involved in physical methods and generally have fast processing time. They include condensation, evaporation, arc-discharge, direct current (DC) magnetron sputtering and energy ball milling method. The physical methods have additional advantages in the sense that the AgNPs are produced with a narrow size distribution(Wei et al., 2015). In a single process, large quantities of AgNPs samples can be produced by physical approach. This method is also most useful to produce AgNPs powder. But major expenses for investment of equipments should be measured(Natsuki et al., 2015).

Chemical synthesis

Sodium borohydride ($NaBH_4$) and trisodium citrate ($C_6H_5Na_3O_7.2H_2O$) are used for the reduction of silver salt for chemical preparation of silver nano-colloid solution. Ascorbic acid is a mild reducing agent which is used for the reduction of silver salt to prepare the triangular silver nano-plates(Rashid et al., 2013). The presence of nanoparticles in the solution is recommended by change in color of reaction mixture, silver ions are reduced in the aqueous solution and a UV-Visible spectrophotometer is used to measure the absorption spectrum(Punjabi et al., 2015).

The microwave synthesis involves the reduction of silver nanoparticles at a changeable rate under microwave radiations in contrast to the conventional heating technique. More rapid reaction can be done by this technique which provides a higher concentration of silver nanoparticles with the equivalent temperature and exposure. The different applications are found in micro-emulsion technique in biological and chemical field owing to their unique properties such as thermodynamic constancy, huge interfacial area, ultra-low interfacial tension and the capability to solubilize immiscible liquids. Micro-emulsion method is one of the flexible preparation technique which permits to organize the particle properties such as geometry, surface area, particle size control, homogeneity and mechanisms of morphology (Dargo et al., 2017).

Chemical reduction method

The synthesis of silver nanoparticles can be successfully done from aqueous silver nitrate in the presence of a reducing agent i.e., tri-sodium citrate. This is a simple and low-cost approach for the preparation of nanoparticles. The surface topography of AgNPs suggests that they are spherical in nature. In preparation of antimicrobial agents, this process is very useful and could be subjugated for advance biomedical application(Shekede, 2018). It was found that there is decrease in size of silver nanoparticles by increasing concentration of trisodium citrate while the opposite effects are shown by increasing the concentration of ascorbic acid. Furthermore, the synthesized silver nanoparticles are quasi-spherical in shape; furthermore, with increasing the concentration of trisodium citrate these particles will be more uniform. It has been observed that a slight change in particle shape from quasi-spherical to polygonal is reflected while increasing the concentrations of ascorbic acid (Suriati et al., 2014). Silver colloidal nanoparticles can be syntehsized by chemical reduction of silver ions using sodium borohydride in the presence of laponite. The AgNPs were found to be spherical with their mean sizes below 10 nm (Liu et al., 2007).

Characterization and properties of silver nano particles

At the nano scale, the behavior and properties of materials fluctuate significantly when compared to micro scale. The improved magnetic, electric and optical properties are shown by nanoparticles. Two basic factors are there which cause the different behavior of nano-materials as compared to the macro materials. These are quantum and surface effects (properties of surface atoms fraction). The chemical reactivity of materials is affected by these factors and they also control their optical, mechanical, magnetic and electrical properties(Khatoon & Ahmad, 2012).It is essential to understand the characterization of silver nanoparticles (AgNPs) for the applications and control of nanoparticles synthesis. For the determination of different parameters various techniques are used. With the use of scanning and transmission electron microscopy (SEM, TEM), the morphology of AgNPs can be obtained. Zetasizernano series analyzer is used to measure the size distribution of AgNPs. The Energy dispersive X-ray spectroscopy (EDS) can be used; it involves emission scanning electron microscope. Fourier transform infrared spectroscopy (FTIR),X-ray diffractometry (XRD),UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS) are used for characterization of the silver nanoparticles. The formation of AgNPs is confirmed by UV-Vis spectroscopy and crystallinity is determined by using XRD. To evaluate the electrical conductivity and volume resistivity, Loresta-GP MCP-T610 resistivity meter is used. For instance, during UV measurement, optical absorption peak is observed due to surface Plasmon resonance of AgNPs(Chou & Lai, 2004). Zeta potential is especially significant to express surface charge of nanoparticles because with the external medium, silver nanoparticles are interacted. It is frequently believed that the particles having value of zeta potential more negative than −30 mV or greater than +30 mV are usually stable owing to the electrostatic repulsion. Also ionic strength of the medium is a factor on which zeta potential measurements are dependent and in which nanoparticles are postponed. Various factors like composition of the medium, pH and temperature effect on the zeta potential(Zewde et al., 2016). Anti-bacterial effect of silver nanoparticles has been widely investigated against aerobic and anaerobic bacteria. It is harmless for human cell, if the concentration of silver nanoparticles is small but lethal for majority of bacteria and viruses. The toxicity of cell is reduced by silver nanoparticles (Ag NPs) deprived of affecting the antibacterial efficiency(Liu et al., 2007). High Anti-bacterial activity is shown by nano-particles because their surface is finely refined and they interrupt the intracellular processes by penetrating through membrane of the cell due to their small size. Because of the formation of free radicals on the surface of silver nanoparticles they possess higher antibacterial effect(Liu et al., 2007). On bacteria, there are various mechanisms for the inhibitory effects of Ag NPs. The high affinity of Ag NPs to sulphur and phosphorus results in their higher antibacterial effects. Sliver nanoparticles react with sulphur-containing amino acids of bacterial cell membrane and destroy the cell viability. In addition to their reaction with proteins containing sulphur, the silver ions from AgNPs may also react with phosphorous and thus cause stoppage of DNA replication and also cause inhibition of enzyme functions. Ag NPs also show anti-inflammatory properties(Kim et al., 2007). It is shown by some researchers that anti-bacterial activity is increased by using the composites of polymer with lower amount of AgNPs. Cationic chitosan is known as one of the polymer of silver nanoparticles. There is higher antibacterial effect in composites of chitosan with Ag NPs than chitosan and Ag NPs alones. The negatively charged surface of the bacteria captured by the positively charged matrix of chitosan hereafter causes holes which lead to catastrophic disintegration of bacteria (Nadworny et al., 2008).Silver nanoparticles show anti-bacterial activity which depend upon both shape and sizes (M. Banerjee et al., 2010).Antibacterial activity basically depends upon surface to volume ratio of particles and their penetrating ability. The big particles have lower antibacterial activity than smaller silver nanoparticles which show high penetrating ability(Pal et al., 2007).There has been studied a wide range of antibacterial activity of silver nanoparticles (Ag NPs)(Martinez-Castanon et al., 2008).

There is a strong interaction of silver nanoparticles with electromagnetic radiation. The silver nanoparticles have first application in glass and fabrication ceramics to prepare the pigments. Ag NPs show optical properties which depend on the composition of individual particles, their sizes and shapes, presence and structure of adsorption layers &their environment(Lara et al., 2010).The image obtained by SEM exhibited that silver nanoparticles (AgNPs) are uniformly distributed on the surface in the ranges of 5-40nm and their shape is spherical(Midha et al., 2016).The AgNPs may possess a wide band in the IR range, near UV and visible ranges. The resulting band is called Plasmon resonance. The highest surface Plasmon resonance band intensity is shown by Ag NPs as compared to any other metals like gold and copper. The SPR band is formed due to the releasing of conduction of electrons when light strikes on the surface of silver nanoparticles (AgNPs)(Popov et al., 2006). The formation of oscillating dipole takes place when the diameter of silver nanoparticles AgNPs is greatly less than the wavelength of incident light. If the dipole is formed adjacent to the surface then this is known as surface Plasmon. The different orientation of silver nanoparticles is not equivalent with respect to incident wave if the particles are notspherical. The reason for this is the presence of two SPR band of cylindrical particles across and along its cylindrical axis. The polarization is caused by regions of positive and negative charge of dipole due to which amplitude and frequency of oscillation of dipole and long wavelength SPR band is obtained(Moores & Goettmann, 2006).With increasing the medium's dielectric permeability, this effect will also be increased. There are two parts of dielectric permeability of the medium known as imaginary part and real part. The lowest dielectric permeability is shown by imaginary part of AgNPs that lowers the overindulgence of electric field energy; therefore SPR band of the AgNPs has highest efficiency(Sherry et al., 2005).

Applications of silver nanoparticles

There are various technological applications of silver nanoparticles (AgNPs) because of their specific magnetic, chemical, electronic and optical characteristics which are entirely different from the characters of the bulk metals. A strong anti-microbial activity is shown by biosynthesized AgNPs which initiate a complete inhibition of growth for a wide range of fungi as well as Gram negative and Gram positive bacteria(Natsuki et al., 2015).The unique properties are found in silver nanoparticles(AgNPs)such as catalytic and optical properties which are dependent on shape and size of the synthesized nanoparticles(Khodashenas & Ghorbani, 2015). Their unique properties can be incorporated into the composite fibers, conducting materials, biosensor materials, cosmetic products, electronic components and they are considered as a very significant subject to be studied by healthcare, biology, electronic, chemistry and other related branches. These unique properties of silver nanoparticles (AgNPs) are shape and size dependent(are IntechOpen, 2018).Especially, due to their antimicrobial and physiochemical properties, silver nanoparticles (AgNPs) are very significant as they assist in therapies, used in molecular diagnostics and in devices for medical procedures(Ghaffari-Moghaddam et al., 2014).

Medical Uses

Today, the nanoparticles made from noble metals are most effectively studied, specifically palladium, platinum, silver and gold. In the field of medicine, silver nano particles play major role than others. The medicinal leaf extract of green synthesized silver nanoparticles show antimicrobial activity. A potent antimicrobial effectis exhibited by green synthesized silver nanoparticles to treat infectious disease.

Silver nanoparticles find the following uses(Panigrahi, 2013).

- Treatment of acne and ulcerative colitis
- Varnish of hospital material (face mask and surgical gowns)

- Isolated laser light persuaded opening of microcapsules
- Silver nano-composite for cell labeling
- Enhanced ramanscattering spectroscopy(SERS)
- Recognition of viral structures (SERS & Silver nano-rods)
- Anti-microbial effects against infectious organisms
- Molecular imaging of malignancy
- Orthopedic stocking
- Additive in bone cement. Implantable material using clay-layers with starch stabilized (AgNPs)
- Hydrogel for wound bandage

In history, major therapeutic agent in medicine has been known as silver, particularly to treat infectious disease as well as surgical infections(Alexander, 2009).The enhanced and unusual biomedical applications, non-toxic nature, biological functionality and high antimicrobial efficiency are extensively explored by silver nanoparticles (AgNPs)(He et al., 2016).Their important features are chemical stability, good conductivity, outstanding therapeutic potential and relative lower toxicity and they possess anticancer, antimicrobial,anti-angiogenesis,anti-inflammatory,antiplatelet,anti-proteolytic and antifungal activities(P. Banerjee et al., 2014; He et al., 2016).They also find applications in pharmaceutical products, soaps, toothpastes, shampoos, detergents and cosmetics(Firdhouse & Lalitha, 2015).If the silver is used in colloidal form, it is considered as effective in treatment of dacrocystitis, infected corneal ulcers, interstitial keratitis, blepharitis, acute epididymitis, staphylococcal sepsis, infectious diseases, puerperal sepsis and tonsillitis.

Water Treatment

The fresh leaf extract of Anac-ardium occidentale is used to synthesize stable silver nanoparticles(AgNPs) at 80°C as well as in unique analysis for detecting chromium(VI) ions in tap-water. The population of bacteria is decreased as the time of incubation increases(Singh et al., 2016). A wonderful photo catalytic activity is exhibited by the biosynthesized silver nanoparticles in contrast to dye molecules and might be exploited in water purification systems(Gudikandula & Charya Maringanti, 2016).

Wound Dressings

In diabetic foot care organization, wound dressings play a significant role. For the treatment of diabetic wounds, nano-crystalline silver ion dressing is a newer modality. Since from ancient time, silver and its compounds have been extensively used for the treatment of wound infections especially in patients of serious burns and for the treatment of bacteria. It is a cost effective selection with improved consequences as compared to the conformist saline dressings in diabetic foot ulcer management(Benelli & Lukehart, 2017). Owing to appearance of new therapeutic agents, the custom of silver compounds has been deteriorated(Gupta et al., 2018).

Agricultural Uses

The applications of nanoparticles are increasing in the field of agriculture day by day. However, there is dire need to establish its proper guidelines in this regard which are under investigations. Nanotechnology has made possible the controlled delivery of agrochemicals to improve plant growth enhancement, break disease resistance and nutrient consumption. The benefit of more targeted and effectual use of pesticides, insecticides and herbicides is shown by nano-encapsulation which is ecofriendly for the environment. The nanotechnology has improved the solubility of active ingredient and thus caused an increase of drug/pesticide effectiveness to many folds; the inherent property of active ingredient in terms of activity can be used in targeted areas (Benelli & Lukehart, 2017). It is projected that AgNPs could be used as an economical and broad spectrum antimicrobial agent for the protection of numerous crops (Singh et al., 2016).

Applications in Cancer Therapy

Silver nanoparticles have cytotoxic effects in MCF-7 breast cancer cells which are dose dependent caused by induction of apoptosis, with a concentration of 50% cell evolution inhibition LD100 of 14 ng/mL and LD50 of 3.5 ng/mL. Furthermore, it was found by Guru Nathan that silver nanoparticles (AgNPs) brought MDA-MB-231 cell death from side to side DNA fragmentation, activation of caspase 3 and ROS generation.

Advance work also specified that cytotoxic effects are shown by single-crystalline AgNPs with apoptotic features(Punjabi et al., 2015).There are promising therapeutic molecules recognized by silver nanoparticles (AgNPs) and are encompassing their use in therapy and in cancer diagnosis. The green-synthesized AgNPs show anti-tumor activity in lung cancer in *vivo* and in *vitro*. Silver nanoparticles exhibit anti-cancer properties which suggest that they might act as potential beneficial molecules in chemotherapy, especially for early-stage intervention and in lung cancer chemoprevention. This is the unique method for the destruction of cancerous cells(Siddiqi et al., 2018).

Applications in Food Packaging

In recent years, there have drawn a great interest of nanomaterials due to their astonishing properties which make them significant in food packing applications due to their antimicrobial, mechanical, catalytic and optical properties(Wei et al., 2015). Polymer entrenched metal nanoparticles showed to be highly effective due to the combination of organic–inorganic moieties. The definite use of AgNPs in food packaging is controlled by USA and EU food safety authorities in a judicious way, owing to the incapability to make convincing declarations on their toxicity. Consequently, their custom is assessed in terms of Ag+ immigration into the packed food(Bumbud sanpharoke et al., 2015).

Catalytic Degradation of Organic Dyes

Metal nanoparticles are gaining extra reputation by biosynthesis due to sustainable, simplicity and economical route of their syntheses. The AgNPs were producedby using leaf extract of *Raphanus sativus*and characterized by UV-spectroscopy and transmission electron microscopy (TEM). The biosynthesized AgNPs were found to be effective in water purification systems (Gudikandula & Charya Maringanti, 2016).

Cosmetic Products

The application of nanomaterials and nanotechnology can be found in numerous cosmetic products comprising make up, sunscreen, hair care products and moisturizer. Most commonly used chemicals give protection and now being used in leading cosmetics products. A AgNP is broad spectrum antimicrobial agent with high effect. The silver nanoparticles depending upon the particle size are safe to be used in cosmetics. The nanosilver can be used for healing agent, anti-acne, anti-scaring and anti-dandruff *etc* in cosmetic formulation(Carbone et al., 2016).

As Drug Delivery Vehicle against Infections

In vindictiveness of the development of pharmaceutical and medical sciences, there is still a major problem in chemotherapy for drugs delivery to a particular site of concern against numerous life-threatening infectious diseases. High toxicity is present in most of drugs which lead to various side effects and dropping the quality of life. The conventional microbicides are used against the infections which are associated with inadequate therapeutic index, development of multiple drug resistance, low drug bioavailability and adverse systemic side effects. There is a concern of silver nanoparticles in antimicrobial activity as potent efficient agent against infections because of their increased reactivity with active functional structures, ultra-small controllable sizes and higher surface area. The silver nanoparticles are coated on the surface of ligandamalgamated with drug as drug delivery vehicle instructs its continual release through reduced side effects when directed into the body. Silver nanoparticles are similarly used for biochemical analysis in blood and Immuno-toxicity(Carbone et al., 2016).

Catheters

The bioactive AgNPs are used to coat the plastic catheters. A coating method has been developed by the researchers which yield silver nanoparticles with thin (~100 nm) layer on the surface of the catheters. The catheters coated by nanoparticles are nontoxic, biocompatible and have ability to release specific and sustained discharge of silver at the establishment site. In these catheters, the risk of infection is highly reduced owing to significant in-*vitro* antimicrobial action(Sardar, 2017).

Antifungal Action

Antifungal activity isexhibited by AgNPs against several fungi. Behind the anti-fungal activity, there is no fully actual mechanism. The disorderly structure of the cell membrane is caused by destructing membrane reliability, thus the inhibition of the budding process has been credited to be accountable for the antifungal action of AgNPs against *C. Albanians* species. The significant effect on the anti-microbial activity is the shape of the AgNPs(Kuntyi et al., 2019)**.**

Conclusions

The green biosynthesis is the latest and eco-friendly technique for the production of Ag NPs. Biosynthesis involves the use of biological agents such as yeast, fungi, bacteria, algae and plant extracts. Physical methods include evaporation, arc-discharge, condensation, direct current (DC) magnetron sputtering and energy ball milling method. Sodium borohydride and trisodium citrate are used for preparation of silver nano-colloid solution while ascorbic acid is used to prepare triangular silver nano-plates. The use of a reducing agent i.e., tri-sodium citrate is low-cost and simple approach for the production of nanoparticles. The formation of AgNPs can be confirmed by transmission and scanning electron microscopy (TEM, SEM) to evaluate the morphology, Zetasizer Nano Series analyzer to measure the size distribution, Fourier transform infrared spectroscopy (FTIR) to know about the functional groups, X-ray diffractometry (XRD) to determine the crystallinity, Loresta-GP MCP-T610 resistivity meter to measure the electrical conductivity and UV-Vis spectroscopy. AgNPs find various technological applications due to their specific magnetic, chemical, electronic, optical and photo-catalytic properties. They possess anticancer, antimicrobial, anti-angiogenesis, anti-inflammatory, antiplatelet, anti-proteolytic and antifungal activities. They can be used as healing agent, anti-acne, anti-scaring and anti-dandruffetcagents in cosmetic formulation and also for lung cancer chemoprevention, water purification, food packing, soaps, toothpastes, shampoos, detergents and cosmetics. They can stop the DNA replication and have the ability todestroy the cell viability of bacteria and stop the DNA replication and inhibit the enzyme functions. The catheters coated by AgNPs nanoparticles are nontoxic, biocompatible and have ability to release specific and sustained discharge of silver at the establishment site.

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