

Recent Advances in Synthetic Methods and Applications of Silver Nanoparticles

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Abstract

Nanotechnology has recently advanced to a variety of applications in day-to-day life such as in Medicine, agriculture, water treatment, and in energy harvesting. A variety of preparation techniques have been reported for the synthesis of silver nanoparticles; notable methods include, chemical methods, Physical synthetic techniques, Green synthesis-biological synthetic methods. Characterization is performed by employing a form of completely different techniques like transmission and scanning microscopy (TEM, SEM), Fourier Transform Infrared chemical analysis (FTIR), and UV-Vis chemical analysis The aim of this review paper is to target about the synthesis methods of preparation of silver nano particles and their applications in the various fields.

Keywords: *Nanoparticles; Synthesis of silver nanoparticles; Chemical method; Physical synthetic techniques; Green synthesis; Transmission Electron Microscopy; UV-vis spectroscopy; SEM*

Introduction

Nanotechnology is defined as the study and use of structures between 1 nanometres and 100 nanometres in size and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. Nanoparticles are defined as the particles with the size range of 1 nm to 100 nm at least in one of the three dimensions. Nanoparticles correspond to the fundamental building blocks for various nanotechnology applications. Nanoparticles (NPs) have wide range of applications in fields such as health care, cosmetics, food and feed, environmental health, mechanics, optics, biomedical sciences, chemical industries, electronics, space industries, drug-gene delivery, energy science, optoelectronics, catalysis, single-electron transistors, light emitters, nonlinear optical devices, jewelry, metalcraft, vessels or containers for liquid, coins, shavings, foils, and photography (where photosensitive Ag halides are reduced) [1,2]. Nanosized metallic particles are unique and can considerably change physical, chemical, and biological properties due to their surface-to-volume ratio; therefore, these nanoparticles have been exploited for various purposes.

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Metal nanoparticles can be prepared by three ways , 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 are reduced in conditions which favour the subsequent formation of small metal clusters [3,4]. The third one is the biological methods mostly consist of green synthesis approaches, where extracts of different plants, prokaryotic bacterial cells, and eukaryotic fungi are used as reducing agents to reduce the metallic silver precursor for the preparation of AgNPs [5].

Nanoparticles stabilization is usually discussed in terms of two categories of stabilization, which are electrostatic and steric. Electrostatic stabilization is achieved by the coordination of anionic species, such as halides, carboxylates or polyoxoanions [6,7]. This results in the formation of an electrical double layer, which causes coulombic repulsion between the nanoparticles. Steric stabilization is achieved by the presence of bulky, typically organic materials, due to their bulk, block the nanoparticles from diffusing together. Polymers and large positive charged particles such as alkylammonium are examples of steric stabilizers. The choice of stabilizer also allows one to tune the solubility of the nanoparticles [8].

Silver is the noblest metal in the fabrication of nanoparticles due to its wide spectrum of bactericidal and fungicidal activities. Silver nanoparticles can coordinate with various ligands and macromolecules in the microbial cell. Silver has been widely used in the control of microbial proliferation as well as curing wound healing due to its anti-inflammatory effect. Silver has many modern industrial uses and it is considered a store of wealth [9]. This review targets about the synthetic methods of preparation of silver nanoparticles and their applications in various fields.

Materials and Methods

Methods to synthesize silver nanoparticles

Aquatic biota: Plankton

Basically, silver nanoparticles can be synthesized in three ways including physical, chemical, and biological methods. A general synthesis of silver nanoparticles is illustrated in (FIG. 1).

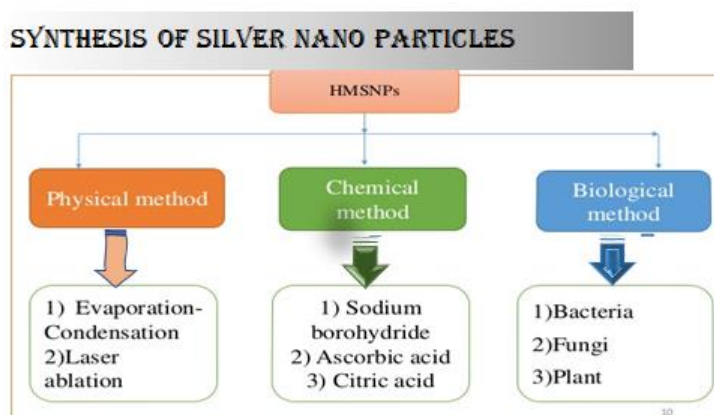


FIG. 1. Methods to synthesize silver nanoparticles.

Physical methods

In physical processes, metal nanoparticles are generally synthesized by evaporation-condensation, which could be carried out using a tube furnace at atmospheric pressure. The source material within a boat centered at the furnace is vaporized into a carrier gas. Nanoparticles of various materials, such as Ag, Au, PbS, and fullerene, have previously been produced using the evaporation-condensation technique [10-13]. Conventional physical methods including spark discharging and pyrolysis were used for the synthesis of AgNPs. The advantages of physical methods are speed, radiation used as reducing agents, and no hazardous chemicals involved, but the downsides are low yield and high energy consumption, solvent contamination, and lack of uniform distribution.

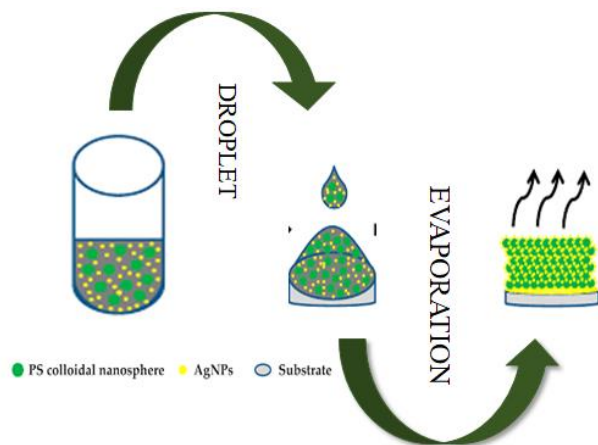


FIG. 2. Synthesis of silver nanoparticles by evaporation-condensation method.

The results showed that the geometric mean diameter, the geometric standard deviation, and the total number concentration of NPs increase with heater surface temperature (FIG. 2). Spherical NPs without agglomeration were observed, even at high concentration with high heater surface temperature. The geometric mean diameter and the geometric standard deviation of silver NPs were in the range of 6.2 nm-21.5 nm and 1.23 nm-1.88 nm, respectively [14,15].

Laser ablation

Laser ablation is a method for fabricating various kinds of nanoparticles which also includes semiconductor quantum dots, carbon nanotubes, nanowires, and core shell nanoparticles. In this method, nanoparticles are generated by nucleation and growth of laser-vaporized species with a background gas. The extremely rapid quenching of vapor is advantageous when production of high purity nanoparticles in the quantum size range (<10 nm) [16,17].

Chemical methods

The most common methods for nanoparticle synthesis is wet chemistry. It is the nucleation of particles within a solution. This nucleation occurs when a silver ion complex, AgNO_3 or AgClO_4 , is reduced to colloidal silver in the presence of a reducing agent [18-20]. When the concentration increases enough, dissolved metallic silver ions bind together to form a stable surface. The surface is energetically unfavourable when the cluster is small, because the energy gained by decreasing the concentration of dissolved particles is not as high as the energy lost from creating a new surface [21,22]. When the cluster reaches a certain size, known as the critical radius, it becomes energetically favourable, and thus stable enough to proceed to grow.



FIG. 3. Synthesis of silver nanoparticles by chemical method.

This nucleus then remains in the system and grows as more silver atoms diffuse through the solution and attach to the stable surface. When the dissolved concentration of atomic silver decreases enough, it is no longer possible for enough atoms to bind together to form a stable nucleus. At this nucleation threshold, new nanoparticles stop being formed, and the remaining dissolved silver is absorbed by diffusion into the growing nanoparticles in the solution.

Ion implantation

Ion implantation was used to create silver nanoparticles embedded in glass, polyurethane, silicone, polyethylene, and poly (methyl methacrylate). Particles are embedded in the substrate by means of bombardment at high accelerating voltages. At a hard and fast current density of the ionic beam up to a particular value, the dimensions of the embedded silver nanoparticles has been found to be monodisperse within the population, after which only an increase in the ion concentration is observed. A further increase within the ionic beam dose has been found to scale back both the nanoparticle size and density within the target substrate, whereas an ionic beam operating at a high accelerating voltage with a gradually increasing current density has been found to end in a gradual increase within the nanoparticle size. There are a couple of competing mechanisms that can end in the decrease in nanoparticle size; destruction of NPs upon collision, sputtering of the sample surface, particle fusion upon heating, and dissociation.

Microemulsion techniques

Microemulsion includes a mixture of water, surfactant, and oil or a mixture of water, surfactant, co-surfactant, and oil. Synthesis of Silver Nanoparticles to form microemulsion, including anionic surfactants such as bis (2-ethylhexyl) sulfosuccinate, sodium dodecylbenzene sulfonate, and lauryl sodium sulphate, cationic surfactants such as cetyltrimethylammonium bromide, polyvinylpyrrolidone, and non-ionic surfactants such as Triton X-100, etc. The water droplets covered by surfactant molecules act as micro-reactors and offer a unique micro-environment for the formation of the nanoparticle.

Uniform and size controllable silver NPs can be synthesized using microemulsion techniques. The NPs preparation in two-phase aqueous organic systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. The interface between the two liquids and also the intensity of inter-phase transport between two phases, which is mediated by a quaternary alkyl-ammonium salt, affect the rate of interactions between metal precursors and reducing agents. Metal clusters formed at the interface are stabilized, due to their surface being coated with stabilizer molecules occurring in the non-polar aqueous medium and transferred to the organic medium by the inter-phase transporter. One of the major disadvantages is the use of highly deleterious organic solvents.

Thus, large amounts of surfactant and organic solvent must be separated and removed from the final product. For instance, Zhang and co-workers used dodecane as an oily phase (a low deleterious and even nontoxic solvent), but there was no need to separate the prepared silver solution from the reaction mixture [10,11]. On the other hand, colloidal NPs prepared in nonaqueous media for conductive inks are well-dispersed in a low vapor pressure organic solvent, to readily wet the surface of the polymeric substrate without any aggregation. The advantages can also be found in the applications of metal NPs as catalysts to catalyze most organic reactions, which have been conducted in non-polar solvents. It is very important to transfer metal NPs to different physicochemical environments in practical applications.

Green synthesis

Green synthesis of silver nanoparticles requires high radiation, highly toxic reductants, and stabilizing agents, mixed valence polyoxometalates, polysaccharides, Tollens, biological, and irradiation method which have advantages over conventional methods involving chemical agents associated with environmental toxicity which can cause pernicious effects to both humans and marine life. In contrast, green synthesis of metallic nanoparticles is a one pot or single step eco-friendly bio-reduction method that requires relatively low energy to initiate the reaction. This reduction method is also cost efficient.

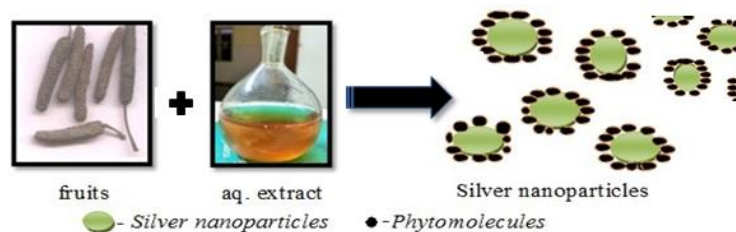


FIG. 4. Green synthesis of silver nanoparticles.

Extracts from bio-organisms may act both as reducing and capping agents in Ag NPs synthesis. The reduction of Ag^+ ions by combinations of biomolecules found in these extracts such as enzymes/proteins, amino acids, polysaccharides, and vitamins is environmentally benign, yet chemically complex. An extensive volume of literature reports successful Ag NP synthesis using bioorganic compounds. For example, the extract of unicellular green algae *Chlorella vulgaris* was used to synthesize single-crystalline Ag nanoplates at room temperature. Proteins in the extract provide dual function of Ag^+ reduction and shape-control in the nano silver synthesis. The carboxyl groups in aspartic and/or glutamine residues and the hydroxyl groups in tyrosine residues of the proteins were suggested to be responsible for the Ag^+ ion reduction. Carrying out the reduction process by a simple bifunctional tripeptide Asp-Asp-Tyr-OMe further identified the involvement of these residues. This synthesis process gave small Ag nanoplates with low polydispersity in good yield (N55%).

Bacterial and fungal synthesis of nanoparticles is practically applicable because bacteria and fungi are easy to handle and can be modified genetically easily. This provides a means to develop biomolecules that can synthesize AgNPs of varying shapes and sizes in high yield, which is at the forefront of current challenges in nanoparticle synthesis. Fungal strains such as *Verticillium* and bacterial strains such as *Klebsiella pneumoniae* can be used in the synthesis of silver nanoparticles. When the fungus/bacteria is added to the solution, protein biomass is released into the solution. Electron donating residues such as tryptophan and tyrosine reduce silver ions in solution contributed by silver nitrate. These methods have been found to effectively create stable monodisperse nanoparticles without the use of harmful reducing agents.

Characterisation of Silver Nanoparticles

Characterization of nanoparticles is important to know and to manage nanoparticle synthesis and applications. Characterization is performed by employing a form of completely different techniques like transmission and scanning microscopy (TEM, SEM), Fourier rework infrared chemical analysis (FTIR), and UV-Vis chemical analysis [20].

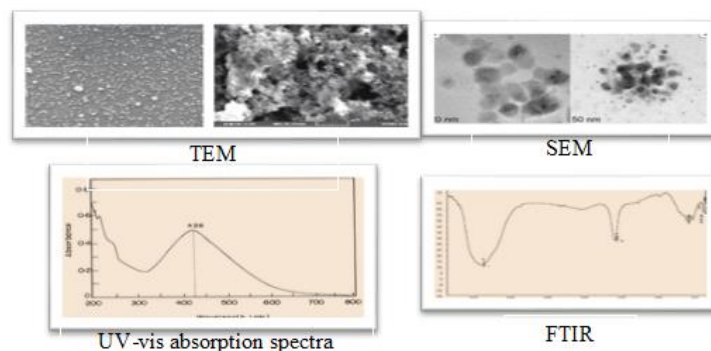


FIG. 5. Sample analysis of silver nanoparticles by TEM, SEM, UV-vis spectroscopy, FTIR.

These techniques are used for the determination of various parameters like particle size, shape, crystallinity, form dimensions, pore size, and surface area. Moreover, orientation, interval, and dispersion of nanoparticles and nanotubes in nanocomposite materials may be determined by these techniques. Moreover, dynamic lightweight scattering is employed for the determination of particle size distribution. Moreover, diffraction is employed for the determination of crystallinity, whereas UV chemical analysis is employed to confirm sample formation by showing the plasmon resonance [15,16].

Applications of Silver Nanoparticles

The silver nanoparticles are exceptional due to their excellent optical, thermal, catalytic, electromagnetic, adsorbent, and antimicrobial properties, which differ from the properties of silver present in volumetric sizes. This is due to the reduction in size which produces an increase in the surface area in relation to the volume, as well as the shape of the nanoparticle. AgNPs are extensively used as anti-bacterial agents within the health business, food storage, textile coatings and a variety of environmental applications. The product created with AgNPs are approved by a spread of authorized bodies, together with the USA authority, US EPA, SIAA of Japan, Korea's Testing and analysis Institute for industry, and FITI Testing and analysis Institute [5]. As anti-bacterial agents, AgNPs were applied in a very big selection of applications from disinfecting medical devices and residential appliances to water treatment (Gupta and Silver Li et al., 2008). Moreover, this inspired the textile business to use AgNPs in several textile materials. during this direction, silver nanocomposite fibres were ready containing silver nanoparticles incorporated within the material. The cotton fibres containing AgNPs exhibited high antibacterial drug activity against Escherichia. General applications of silver nanoparticles is illustrated below.

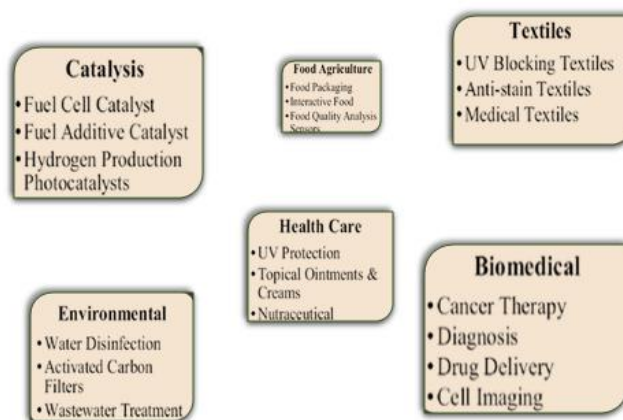


FIG. 6. Applications of silver nanoparticles.

Chemical Applications of Silver Nanoparticles

Catalytic activities of nanoparticles take issue from the chemical properties of the majority of materials. as an example, Köhler et al. showed that the bleaching of the organic dyes by application of atomic number 19 peroxy disulphate in solution at temperature is increased powerfully by the applying of silver-containing nanoparticles [19]. what is more, AgNPs was found to catalyse the luminescence from luminol-hydrogen peroxide system with chemical action activity higher than Au and atomic number 78 mixture [20]. Moreover, silver nanoparticles supported halloysite nanotubes (Ag/HNTs), with a silver content of regarding 11% to catalyze the reduction of 4-nitrophenol with NaBH_4 in base-forming liquid solutions. The optical properties of an aluminous nanoparticle rely in the main on its surface plasmon resonance, wherever the plasmon refers to the collective oscillation of the free electrons at intervals the aluminous nanoparticle. it's documented that the plasmon resonant peaks and line widths are sensitive to the dimensions and form of the nanoparticle, the aluminous species, and therefore the close medium. as an example, nanoclusters composed of 2-8 silver atoms can be the premise for a brand-new kind of optical knowledge storage. Moreover, fluorescent emissions from the clusters may double even be utilized in biological labels and electroluminescent displays. the chemistry properties of AgNPs incorporated them in nanoscale sensors which will provide quicker response times and lower detection limits. as an example, the conductor posited AgNPs onto corundum plates gold micro-patterned electrode that showed high sensitivity to oxide [15].

Physical Applications of Silver Nanoparticles

The silver nanoparticles, especially, are exceptional because of their excellent optical, thermal, catalytic, electromagnetic, adsorbent, and antimicrobial properties, which differ greatly to the properties that silver presents in volumetric sizes. this is often because of the reduction in size which produces a rise in the surface area in relevance the quantity, also as the shape of the nanoparticle. The optical properties of nanoparticles strongly depend upon the particle size and therefore the refractive index of the medium. The dependencies of those properties with respect to particle size are often of two kinds, because of the increase in energy caused by the quantum confinement of the system or by the resonance of the surface plasmon. The surface plasmons are defined as the collective oscillation of conduction electrons on the surface of the particle, as a result of the interaction with the electrical field of electromagnetic radiation.

Biological Applications of Silver Nanoparticles

The use of silver nanoparticles in *in vitro* and *in vivo* applications is rapidly increasing. In addition to silver nanoparticle-based ultrabright fluorescent labeling and Surface Enhanced Raman Spectroscopy (SERS) nanotags, other applications for silver nanoparticles include their use as thermal sources for hyperthermia and thermally modulated drug release from particle surface coatings. Silver nanoparticles can even be incorporated into core/shell constructs. An amorphous silica shell grown uniformly onto silver nanoparticle cores can have a spread of functional groups conjugated into the shell, providing a method for electrostatic or other interactions between the shell and a molecule. Fluorophores, drug molecules, or other high molecular weight organic molecules are often integrated within the shell for *in vitro* or *in vivo* labeling or drug delivery applications.

Discussions

The morphological parameters of nanoparticles can be modulated by varying the concentrations of chemicals and reaction conditions. Despite all beneficial uses for nano silver, its impact on the environment is concerning [12]. These synthesis methods may require the use of different raw materials and yield reaction by using toxic products or wastes. But in recent years, also known as “green chemistry”, an environmental-friendly approach has become a new option in chemistry, consisting of reduction and elimination of dangerous substances for the design of products in the environment [15]. However, as seen, there are numerous studies for the synthesis methods (green or no green) of the nano silver in literature but the most used methods in the industry are not yet known. For this reason, we suggest that researchers should be directed to work on the methods of synthesizing nano silver used in the industry.

The flexibility of silver nanoparticle synthetic methods and facile incorporation of silver NPs into different media have encouraged researchers to further investigate the mechanistic aspects of antimicrobial, antiviral, and anti-inflammatory effects of the nanoparticles. Shape, size, and size distribution of silver NPs can be controlled by adjusting the reaction conditions such as reducing agent, stabilizer, or employing different synthetic methods. Therefore, it is important to elucidate the effects of reaction conditions on the morphology and size of NPs.

In the true world, it is desirable that the properties, behavior, and types of nanomaterials should be improved to meet the points. On the other hand, these limitations are opening new and great opportunities in this emerging field of research.

Conclusion

A variety of preparation techniques have been reviewed for the synthesis of silver nanoparticles. Notable methods include, Wet chemical method, Ion implantation Microemulsion techniques, Green synthesis, Biological synthetic methods, and Characterization of silver nanoparticles. The synthetic methods of preparation of silver nano particles and their applications in the various fields is reviewed. UV chemical analysis is employed to confirm sample formation by showing the plasmon resonance. The unique optical properties and broad-based antimicrobial properties of silver nanoparticles have led to a rapid rise in the incorporation of silver nanoparticles in biological applications. The high level of control that is available for controlling the size, shape, and surface of silver nanoparticles provides a powerful library for not only generating functional materials for biological applications but also for understanding the fundamental mechanisms of transport and interaction of nanoparticles in biological systems. This understanding, coupled with the construction of more complex multifunctional silver nanocomposites, will enable the next generation of silver nanoparticle-based probes, devices, and therapeutics.

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