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Abstract

Nanoparticles of noble metals, especially the silver nanoparticles, have been widely used in different fields of science. Their unique properties, which can be incorporated into biosensor materials, composite fibers, cosmetic products, antimicrobial applications, conducting materials and electronic components, make them a very important subject to be studied by chemistry, biology, healthcare, electronic and other related branches. These unique properties depend upon size and shape of the silver nanoparticles. Different preparation methods have been reported for the synthesis of the silver nanoparticles, such as electron irradiation, laser ablation, chemical reduction, biological artificial methods, photochemical methods and microwave processing. This chapter aims to inform the synthesis methods of the silver nanoparticles.

Keywords: silver nanoparticles, physical methods, chemical methods, green synthesis, different shape

1. Introduction

Silver has too much of modern industrial uses and is considered a store of wealth. However, the story of this legendary precious metal begins with its use by ancient civilizations. Silver has many attributes that made it so valuable to early peoples. It is malleable, ductile, lustrous, resilient, conductive, antibacterial, and rare. Also, it was used as a precious commodity in currencies, ornaments, jewelry, electrical contacts and photography, among others. Although bulk silver is widely known for their brilliant surfaces and colors, there is a drastic color difference when the metal reduces in dimensions. Even though the craftsmen did not know nanoparticles in that period, the mixing of the metal chlorides with molten glass led to the formation of metallic nanoparticles of different shape and size, therefore the physical formats of the metal nanoparticles had interesting interactions with light and produced visibly beautiful colors. The metal chlorides materialized
and formed nanoparticles in the molten glass before cooling, making art, one of the first uses for nanotechnology. Nowadays, the nanoparticles are an important field of the modern research dealing with design, synthesis, and manipulation of particle structures ranging from approximately 1 to 100 nm. Nanoparticle research is currently an area of intense scientific research, due to a wide variety of potential applications in fields such as healthcare, 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, and photo-electrochemical area. The silver nanoparticles have been widely used in the fields of chemistry and related branches due to their high surface to volume ratio and excellent conducting capability. From electrical switches, solar panels to chemical-producing catalysts and antimicrobial activity, the silver nanoparticle is an essential component in many industries. Its unique properties make it nearly impossible to substitute and its uses contain a wide range of applications. At the same time, many of the consumer products that claim to contain nanomaterials contain nanosilver. Examples of the consumer products that include nanosilver including computers, mobile phones, automobile appliances, food packaging materials, food supplements, textiles, electronics, household appliances, cosmetics, medical devices, imaging techniques, and water and environment disinfected. Most of these nanosilver-containing products are manufactured in North America, the Far East, especially in China, South Korea, Taiwan, Vietnam and India, the Russian Federation, and the Western Europe.

The knowledge of the silver nanomaterials synthesis methods is important due to an extensive application and area of use perspective. The main problem in synthesizing the silver nanoparticles is the control of their physical properties such as obtaining uniform particle size distribution, identical shape, morphology, nanoparticle coating or stabilizing agent, chemical composition or type and crystal structure. The methods can be classified and categorized that they follow common approaches and the differences such as reactants and the reaction conditions. Top-down versus bottom-up, green versus nongreen, and conventional versus non-conventional synthesis methods have been reported. The conventional synthesis methods contain the use of citrate, borohydride, two-phase systems (water-organic), organic reducers such as cyclodextrin, and micelles and/or polymer in the synthesis process. The unconventional methods contain laser ablation, radiocatalysis, vacuum evaporation of metal, irradiation, photolithography, electrodeposition and the electrocondensation. Top-down and bottom-up are the two synthesis approaches of metallic nanoparticles involving chemical, physical, and biological means. The common fabrication of the nanoparticles includes chemical and physical processes. The top-down approach uses macroscopic initial structures, which can be externally controlled in the processing of nanostructures. The nanoparticles synthesized by mechanical grinding of bulk metals and the addition of colloidal protecting agents are some examples of the top-down method. The bottom-up approaches contain the miniaturization of materials components (up to atomic level) with further self-assembly process. The reduction of metals, electrochemical methods, and decomposition are the examples of the bottom-up methods. In addition, the synthesis approaches can be classified as either green or non-green. Green synthetic systems use environmentally friendly agents such as sugars, plant extracts, bacteria and fungi to form and stabilize nanosilver.

It is important to measure nanosilver concentration, size, shape, surface charge, crystal structure, surface chemistry, and surface transformation in nanoparticle synthesis. The characterization
and detection techniques for the nanosilver contain transmission electron microscopy (TEM), scanning electron microscopy (SEM), electrospay scanning mobility particle sizer (ESMPS), zeta size analysis, atomic force microscopy (AFM), dynamic light scattering (DLS), Brunauer-Emmett-Teller analysis (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, nuclear magnetic resonance spectroscopy (NMR), inductively coupled plasma mass spectroscopy (ICP-MS), thermal gravimetric analysis (TGA), and atomic absorption spectroscopy (AAS).

2. Physical methods

The most important physical methods for the synthesis of the silver nanoparticles are evaporation-condensation, laser ablation, electrical irradiation, gamma irradiation, and lithography. Kimura and Bandow examined the measurement of the optical spectra of many metal colloid solutions and presented new preparation methods of metal colloids inorganic solvents without the chemicals such as redox reagents, polymers, electrolytes, glue or other kinds of colloid stabilizers. Three different preparation methods as the matrix isolation method, the gas flow-cold trap method, and the gas flow-solution trap method, were used to examine the synthesis of silver NPs [1]. The laser ablation method, which has several types of different applications, is another method to study the synthesis of silver nanoparticles (Ag-NPs). The laser ablation technique is a new useful and efficient method to prepare and obtain metal colloids in absence of chemical reagents. This method helps to control particle size of colloids by changing the number of laser pulses [2]. Pyatenko et al. produced silver nanoparticles by irradiating an Ag target with a 532 nm laser beam in pure water. This technique is successfully applied to produce small nanoparticles with a narrow size distribution in pure water without using any chemical additives by using a high-power laser and small laser beam spot sizes [3]. Sadrolhesseini et al. prepared a new method for the fabrication of silver nanoparticles which are dispersed in graphene oxide using the laser ablation and thermal effusivity of nanocomposite. This environmentally friendly method, which does not require any chemical agents, polymeric or surfactant stabilizers, works by releasing the nanoparticles inside liquid solution [4]. Tsuji et al. studied to perform to prepare Ag-NPs by laser ablation of a silver plate in polyvinylpyrrolidone (PVP) aqueous solutions and laser irradiation onto prepared colloidal solutions. This technique is seen as a remarkable technique due to its procedural simplicity and a very high rate of obtainability of nanoparticles of various species and materials such as metals, metal oxides semiconductors, and organic materials by the irradiation of intense laser light onto those materials settled in solvents [5]. The pulsed photoacoustic (PA) technique is another method to study the synthesis of the Ag-NPs in ethanol by laser ablation and determine the production rate laser pulse and concentration of synthesized Ag-NPs [6]. Researchers have studied mechanisms and processes such as plasma formation, dynamics of the cavitation bubble [7, 8], and also the influence of laser parameters and solvents on nanoparticles [9, 10].

Nanosphere lithography (NLS) is a simple and inexpensive nanofabrication method to produce large variety of nanoparticle (NP) structures and well-ordered 2D NP arrays. Jensen et al. studied the effect of solvent on the optical extinction spectrum of periodic arrays of surface-confined
silver nanoparticles fabricated by NSL and four separate samples of NP arrays. Jensen et al. have investigated four separate samples of nanoparticle arrays; three samples were obtained nanoparticles that are truncated tetrahedral in shape but that differ in out-of-plane height and one sample have nanoparticles that are oblate ellipsoidal in shape [11]. Jensen et al. also demonstrated that the localized surface plasmon resonance extinction maximum of a single nanoparticle material system, silver, can be continuously tuned throughout the visible, near-infrared, and mid-infrared regions of the electromagnetic spectrum [12].

3. Chemical method

3.1. Chemical reduction of silver nanoparticles

The size, shape, and surface morphology play an important role in controlling the chemical, physical, optical, and electronic properties of nanomaterials. The chemical reduction is one of the most commonly used methods for the synthesis of silver nanoparticles by inorganic and organic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH₄), elemental hydrogen, polyol process, Tollens reagent, N,N-dimethylformamide (DMF), and poly(ethylene glycol)-block copolymers, hydrazine, and ammonium formate are used for the reduction of the silver ions (Ag⁺) in the aqueous or nonaqueous solutions.

3.2. Different shapes of silver nanoparticles synthesized with various chemical reductants

3.2.1. Synthesis of spherical silver nanoparticles

The spherical silver nanoparticles were synthesized using the reducing agents such as ascorbic acid, sodium citrate, NaBH₄, thiosulfate, and polyethylene glycol. In addition to that, the use of the surfactants such as citrate, polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), and polyvinyl alcohol (PVA) for interactions with particle surfaces can stabilize particle growth and protect particles from sedimentation and agglomeration [13–17].

3.2.2. Synthesis of silver nanorods

Zhang et al. prepared silver nanorods by photoinduced synthesis (Figure 1). At first step, monodisperse spherical seed nanoparticles were prepared by irradiating silver nitrate, bis(p-sulfonatophenyl)-phenolphosphine dihydrate dipotassium salt (BSPP), trisodium citrate, and sodium hydroxide solutions with 254 nm light. Then, Silver nanorods were grown in the solution with the injection of silver seeds at the growth medium containing silver nitrate and sodium citrate and then irradiated for 24 h using a halogen lamp and a bandpass filter to selectively tune. This photomediated method provided an elegant method for controlling the architectural parameters of the resulting silver nanostructures [18]. Ojha et al. mixed the solution of AgNO₃ and citrate and added NaOH into the solution. Then solution of ice cold of NaBH₄ was added while stirring. To synthesize Ag nanorods of at three different aspect
ratios, three stock solutions of AgNO$_3$, ascorbic acid, and the surfactant cetyltrimethylammonium bromide (CTAB) were prepared separately. These stock solutions were mixed at certain quantities properly. Thereafter, 1.0, 0.5, and 0.25 ml of synthesized seed solution were added to set one, two and three, respectively, and at the end, NaOH solution was also added to each set. The color of each nanorod solutions depends on the seed concentrations added in the final solution [19]. Ajitha et al. prepared the aqueous solution containing AgNO$_3$ with sodium citrate dihydrate as stabilizer. Then, sodium borohydride (reducing agent) solution was injected to the above solution all at once while stirring vigorously. The solution color was changed to light yellow. The entire solution was heated under continuous stirring on magnetic stirrer. CTAB solution was prepared through heating stirring on a magnetic stirrer for dissolution of CTAB. Then, AgNO$_3$ and ascorbic acid solution were added. And then, the seed solution was added and at last, few drops of NaOH were added to maintain constant pH and stirred well. The synthesis temperature was varied from 30 to 70°C [20].

3.2.3. Synthesis of silver nanowires

Sun et al. studied silver nanostructures that could be varied from nanoparticles and nanorods to long nanowires by adjusting the reaction conditions, including the ratio of PVP to silver nitrate, reaction temperature, and seeding conditions. They found that the large-scale synthesis of silver nanowires with diameters ranged from 30 to 40 nm, and lengths up to ~50 μm.
Li et al. demonstrated that the diameter of Ag nanowires produced by a polyol synthesis could be controlled by adjusting the concentration of bromide. The silver nanowires with diameters of 20 nm and aspect ratios up to 2000 have been obtained by adding 2.2 mM NaBr into AgNO₃ solution [22]. Gebeyehu et al. synthesized silver nanowire using a simple polyol method (Figure 2). They used polyvinylpyrrolidone as stabilizing and capping agent combined with sodium chloride and potassium bromide salts, ethylene glycol was used as both solvent and a reducing agent, and silver nitrate was used as a silver precursor. They determined that the diameter and uniformity of silver nanowires can be controlled by adjusting the concentration of AgNO₃ and [PVP] to [AgNO₃] molar ratio keeping the other parameters constant. AgNWs with diameters of 20 nm and aspect ratios >1000 were obtained by adding 30.5 mM AgNO₃ to a silver nanowire synthesis [23].

3.2.4. Synthesis of cubic silver nanoparticles

The synthesis of cubic silver nanoparticles was achieved by the reduction of silver nitrate using ethylene glycol in the presence of polyvinylpyrrolidone (PVP). In polyol process, ethylene glycol containing hydroxyl groups have functional structure as both solvent and reducing agent. Polyvinylpyrrolidone as capping agent was used to constitute the cubic shape. Molar ratio of the PVP and silver ions determines the shape of the product [24–26]. Siekkien et al. performed a faster method for synthesis of cubic silver nanoparticle by adding a trace amount of sodium sulfide (Na₂S) or sodium hydrosulfide (NaHS) to the conventional polyol synthesis (Figure 3). The reduction agent is important for the synthesis of NPs with different chemical compositions, sizes and morphologies, and controlled dispersities [27].

Figure 2. FE-SEM images of AgNWs synthesized at different [PVP] to [AgNO₃] molar ratio: (A) 2:1, (B) 4:1, (C) 6:1, (D) 8:1, (E) 10:1, and (F) 12:1 [23].
3.2.5. Synthesis of triangular silver nanoparticles

Zhang et al. prepared silver triangular bipyramids using the photoinduced reduction of 0.3 mM silver nitrate in aqueous solutions containing 1.5 mM sodium citrate, 0.3 mM bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP), and 0.005 M NaOH for 8 h using a 150 W halogen lamp and a bandpass filter (Figure 4). The samples were irradiated in the excitation wavelength range (500 ± 20, 550 ± 20, 600 ± 20, 650 ± 20 nm) [28]. Métraux and Mirkin used the chemical reduction method for the fabrication of silver nanoprisms. They synthesized silver nanoprisms at room temperature by using a mixture of AgNO₃/NaBH₄/polyvinylpyrrolidone/trisodium citrate/H₂O₂ in an aqueous solution as reagents [29].

3.3. Microemulsion techniques

Microemulsion includes a mixture of water, surfactant, and oil or a mixture of water, surfactant, co-surfactant, and oil. Many surfactants are available for the formation of the microemulsion in the preparation of the silver nanoparticles. Generally, many surfactants can be used
to form microemulsion, including anionic surfactants such as bis(2-ethylhexyl)sulfosuccinate, sodium dodecyl benzene sulfonate, and lauryl sodium sulfate, cationic surfactants such as cetyltrimethylammonium bromide, polyvinylpyrrolidone, and nonionic 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 nanoparticle [30–35].

3.4. Microwave-assisted techniques

The microwave synthesis methods provide the reduction of the silver nanoparticles with changeable rate microwave radiation in comparison to the conventional heating technique. Microwave-assisted technology, by accelerating chemical reactions from hours or days to minutes, provides quick results. Also, microwave irradiation provides uniform heating for the preparation of metallic nanoparticles and aids the ripening of these materials without aggregation [36–39].

4. Green synthesis

Biosynthesis of the nanoparticles has received considerable attention due to the growing need to develop environmentally beneficial technologies in material synthesis. To illustrate, a great
deal of effort has been put into the green synthesis of inorganic materials, especially metal nanoparticles using microorganisms and plant extracts. While microorganisms such as bacteria [40], algae [41], yeast [42], and fungi [43] are continued to be examined so far for the intra and extracellular synthesis of metal nanoparticles, the use of parts of the whole plant in analogous with nanoparticles synthesis methodologies is an exciting possibility which is newly explored. In the literature, various bacterial strains such as *Bacillus amyoliquefaciens* [44], *Acinetobacter calcoaceticus* [45], *Pseudomonas aeruginosa* [46], *Escherichia coli* [47] and *Bacillus licheniformis* [48] were used effectively for the synthesis of silver nanoparticles.

The benefits of using plants for the synthesis of the nanoparticles are that the plants are easily available and possess a large variety of active functional groups that can promote the reduction of silver ions. Most of the plant parts like leaves, roots, latex, bark, stem, and seeds are being used for the nanoparticle synthesis. Major compounds that ensure the reduction of the nanoparticles are biomolecules such as polysaccharides, tannins, saponins, phenolics, terpenoids, flavones, alkaloids, proteins, enzymes, vitamins, amino acids, and alcoholic component. The procedure for the nanoparticle synthesis of plants requires the collection of the part of the plant of interest from the available sites is done and then it is washed thoroughly several times with tap and distilled water to remove impurities of plants; followed with sterile distilled water to remove related wastes if any. Then, plant is dried clean and dry place in the shade for 10–15 days and then pulverized using a blender. For the plant broth preparation, an approximate amount of the dried powder is boiled with deionized distilled water. The resulting extract is then filtered thoroughly until no insoluble material appears in the broth. Then a few mL of the plant extract is added to the silver nitrate solution whose concentration is kept at 1 mM. The reduction of Ag$^+$ to Ag$^0$ is confirmed by the color change of the solution. Its formation is confirmed by using UV-visible spectroscopy and transmission electron microscopy or scanning electron microscopy. The most important plants like *Alternanthera dentate* [49], *Cymbopogon citratus* [50], *Argyria nervosa* [51], phlomis [52], *Aloe vera* [53], *Carica papaya* [54], *Nelumbo nucifera* [55], *Moringa oleifera* [56], *Ziziphus tenuior* [57], *Centella asiatica* [58], *Vitex negundo* [59], *Sweietenia mahagoni* [60], *Boerhaavia diffusa* [61], *Cocos nucifera* [62], *Brassica rapa* [63], *Melia dubia* [64], *Pogostemon benghalensis* [65], *Garcinia mangostana* [66], *Psoralea corylifolia* [67], *Portulaca oleracea* [68], *Trachyspermum ammi* [69], *Eclipta prostrata* [70], *Vitis vinifera* [71], *Thevetia peruviana* [72], *Calotropis procera* [73], *Premna herbacea* [74], *Ficus carica* [75], *Abutilon indicum* [76], *Terminalia chebula* [77], *Acorus calamus* [78], *Tinospora cordifolia* [79], *Ocimum tenuiflorum* [80], bamboo hemicelluloses [81], *Strechnos potatorum* [82], *Pine, Persimmon, Ginkgo, Magnolia, and Platanus* [83] used by researchers in green synthesis.

Many different plant extracts have been used in the synthesis of silver nanoparticles with the aim of producing Ag-NPs presenting different morphologies. TEM and SEM studies have shown that the presence of reducing agent in a plant-mediated synthesis of Ag-NPs, where the plant extract acts as reducing agents, shapes the nanoparticle during its growth. The use of medicinal plants in the synthesis of Ag-NPs is not only used for size and shape control, but also for providing plant antimicrobial properties to Ag-NPs. Tippayawat et al. reported a one-step hydrothermal method to prepare silver nanoparticles which is effective against gram-positive (*Streptococcus epidermidis*) and gram-negative (*Pseudomonas aeruginosa*). Reduction of Ag$^+$ ions to Ag$^0$ nanoparticles was performed in a medium of *Aloe vera* extract.
in which no extra reducing agent was used. The silver nanoparticle sizes were found to be in a range of 70.70–192.02 nm and controllable by varying temperature and time conditions of the hydrothermal process (Figure 5) [53]. Kagithoju et al. achieved an economic and environmentally friendly green synthesis of silver nanoparticles using an aqueous leaf extract of *Strychnos potatorum* from 3 mM silver nitrate solution. The XRD and SEM analysis have shown the average particle size of nanoparticles as 28 nm as well as revealed their (mixed, i.e., cubic and hexagonal) structure. These nanoparticles have shown bactericidal activity against multidrug-resistant human pathogenic bacteria [82].

Song and Kim compared their extracellular synthesis of metallic silver nanoparticles by using five plant leaf extracts (Pine, Persimmon, Ginkgo, Magnolia, and Platanus). Magnolia leaf

![Figure 5. SEM images of Ag-NPs were obtained at (A) 100°C for 6 h, (B) 150°C for 6 h, (C) 200°C for 6 h, (D) 100°C for 12 h, (E) 150°C for 12 h, and (F) 200°C for 12 h [53].](image-url)
broth was the best reductive agent for the synthesis and conversion of the silver nanoparticles. More than 90% of the conversion was completed in 11 min by using Magnolia leaf broth at 95°C of reaction temperature. The average size of the nanoparticles, which was analyzed by TEM and SEM, ranges from 15 to 500 nm. The particle size was controlled by changing the reaction temperature, leaf broth concentration, and AgNO$_3$ concentration [83]. Roy et al. prepared four different shapes (spherical, oval, rod and flower shape) of silver nanoparticles (Ag-NPs) using pomegranate juice as a novel reducing agent via microwave-assisted synthesis. The Ag-NPs were characterized by UV-vis spectroscopy, XRD, SEM and TEM analysis. The synthesized Ag-NPs have shown a very rapid, effective, shape-specific and dose-dependent bacteriostatic/bactericidal effect towards four different bacterial strains. Among the four different shaped AgNPs, the flower shape AgNPs exhibited the best results and led to the fastest bactericidal activity against all the tested strains at similar bacterial concentrations (Figure 6) [84].

5. Conclusions

Silver nanoparticles can be obtained by physical, chemical, and biological synthesis methods. Hundreds of research articles reporting different synthesis methods for Ag-NP are published every year. Throughout this chapter, we have reviewed only some of the most
relevant works, dealing mostly with physical, chemical, and biological methods. In literature, all known applications for metallic silver may involve the use of nanosilver in place of silver to take advantage of nanosilver’s unique properties. Despite all beneficial uses for nanosilver, its impact on the environment is concerning. 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 substantives for the design of products in the environment. However, as seen, there are numerous studies for the synthesis methods (green or nongreen) of the nanosilver in literature but the most commonly 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 nanosilver used in the industry.

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