SYNTHESIS OF SILVER NANOPARTICLES BY BIOLOGICAL AND CHEMICAL METHODS

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Abstract: Silver nanoparticles (NPs) preparation techniques have been reported for the synthesis of silver NPs; notable examples include, laser ablation, gamma irradiation, electron irra diation, chemical reduction, photochemical methods, microwave processing, and biological synthetic methods. The aim of this article is, to reflect on the current state and future prospects, and the potentials and limitations of the techniques for industries.

Keywords: Nanoparticle synthesis; Silver nano particles; Physical synthesis; Chemical synthesis; Biological synthesis

Introduction: Nanotechnology is an important field of modern research dealing with design, synthesis, and manipulation of particle structures ranging from approximately 1-100 nm. Nanoparticles (NPs) have wide range of applications in areas 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, and photo-electrochemical applications (1-2). Nano biotechnology is a rapidly growing scientific field of producing and constructing devices. An important area of research in Nano biotechnology is the synthesis of NPs with different chemical compositions, sizes and morphologies, and controlled dispersities. Nano biotechnology has turned up as an elementary division of contemporary nanotechnology and untied novel epoch in the fields of material science receiving global attention due to its ample applications. It is a multidisciplinary approach resulting from the investigational use of NPs in biological systems including the disciplines of biology, biochemistry, chemistry, engineering, physics and medicine. Moreover, the nanobio- technology also serves as an imperative technique in the development of clean, nontoxic, and eco-friendly procedures for the synthesis and congregation of metal NPs having the intrinsic ability to reduce metals by specific metabolic pathways (1-2). Nowadays, there is a growing need to develop eco-friendly processes, which do not use toxic chemicals in the synthesis protocols. Green synthesis approaches include mixed- valence polyoxometalates, polysaccharides, Tollens, biological, and irradiation method which have advantages over conventional methods involving chemical agents associated with environmental toxicity. Selection of solvent medium and selection of eco-friendly nontoxic reducing and stabilizing agents are the most important issues which must be considered in green synthesis of NPs. Silver NPs are of interest because of the unique properties which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic super- conducting materials, cosmetic products, and electronic components. Several physical and chemicalmethods have been used for synthesizing and stabilizing silver NPs (3, 4). The most popular chemical approaches, including chemical reduction using a variety of organic and inorganic reducing agents, electrochemical techniques, physicochemical reduction, and radiolysis are widely used for the synthesis of silver NPs. Most of these methods are still in development stage and the experienced problems are the stability and aggregation of NPs, control of crystal growth, morphology, size and size distribution. Furthermore, extraction and purification of produced NPs for further applications are still important issues (5-6). This review article presents an overview of silver nanoparticle preparation by physical, chemical, and green synthesis approaches.

Synthesis of silver NPs Physical methods: Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of NPs distribution are the advantages of physical synthesis methods in comparison with chemical

processes. Physical synthesis of silver NPs using a tube furnace at atmospheric pressure has some disadvantages, for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability. Moreover, a typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to reach a stable operating temperature (7,8). It was demonstrated that silver NPs could be synthesized via a small ceramic heater with a local heating area (9). The small ceramic heater was used to evaporate source materials. The evaporated vapor can cool at a suitable rapid rate, because the temperature gradient in the vicinity of the heater surface is very steep in comparison with that of a tube furnace. This makes possible the formation of small NPs in high concentration. The particle generation is very stable, because the temperature of the heater surface does not fluctuate with time. This physical method can be useful as a nanoparticle generator for long- term experiments for inhalation toxicity studies, and as a calibration device for nanoparticle measurement equipment (9).The results showed that the geometric mean diameter, the geometric standard deviation and the total number concentration of NPs increase with heater surface temperature. 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 6.2-21.5 nm and 1.23-1.88 nm, respectively. Silver NPs could be synthesized by laser ablation of metallic bulk materials in solution (10-11). The ablation efficiency and the characteristics of produced nano-silver particles depend upon many parameters, including the wavelength of the laser impinging the metallic target, the duration ofthe laser pulses (in the femto-, pico- and nanosecond regime), the laser fluence, the ablation time duration and the effective liquid medium, with or without the presence of surfactants (12-13). One important advantage of laser ablation technique compared to other methods for production of metal colloids is the absence of chemical reagents in solutions. Therefore, pure and uncontaminated metal colloids for further application scan are prepared by this technique (14). Silver nanospheroids (20-50 nm)were prepared by laser ablation in water with femtosecond laser pulses at 800 nm(15).The formation efficiency and the size of colloidal particles were compared with those of colloidal particles prepared by nanosecond laser pulses. As a result, The formation efficiency for femtosecond pulses was significantly lower than that for nanosecond pulses. The size of colloids prepared by femtosecond pulses were less dispersed than that of colloids prepared by nanosecond pulses. Furthermore, it was found that the ablation efficiency for femtosecond ablation in water was lower than that in air, while in the case of nanosecond pulses, the ablation efficiency was similar in both water and air.

Chemical methods: The most common approach for synthesis of silver NPs is chemical reduction by organic and inorganic 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 are used for reduction of silver ions (Ag+) in aqueous or non-aqueous solutions. These reducing agents reduce Ag+ and lead to the formation of metallic silver (Ag0), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles (16-17). The presence of surfactants comprising functionalities (*e.g.*, thiols, amines, acids, and alcohols) for interactions with particle surfaces can stabilize particle growth, and protect particles from sedimentation, agglomeration, or losing their surface properties.

Silver NPs with a size of 17 ± 2 nm were obtained at an injection rate of 2.5 ml/s and a reaction temperature of 100 °C. The injection of the precursor solution into a hot solution is an effective means to induce rapid nucleation in a short period of time, ensuring the fabrication of silver NPs with a smaller size and a narrower size distribution. Zhang and coworkers (18) used a hyper branched poly (methylene bisacrylamide aminoethyl piperazine) with terminal dimethylamine groups (HPAMAM-N(CH3)2) to produce colloids of silver. The amide moieties, piperazine rings, tertiary amine groups and the hyper-branched structure in HPAMAMN(CH3)2 are important to its effective stabilizing and reducing abilities. Chen and colleagues (19) have shown the formation of monodispersed silver NPs using simple oleylamine-liquid paraffin system. It was reported that the formation process of these NPs could be divided into three stages: growth, incubation and Ostwald ripening stages.

Microemulsion techniques: 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 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 (20). One of the major disadvantages is the use of highly deleterious organic solvents.

UV-initiated photo reduction: A simple and effective method, UVinitiated photoreduction, has been reported for synthesis of silver NPs in the presence of citrate, polyvinylpyrrolidone, poly (acrylic acid), and collagen. For instance, Huang and Yang produced silver NPs via photo reduction of silver nitrate in layered inorganic laponite clay suspensions which served as stabilizing agent for prevention of NPs aggregation. The properties of produced NPs were studied as a function of UV irradiation time. Bimodal size distribution and relatively large silver NPs were obtained when irradiated under UV for 3h.

Photo induced reduction: Silver NPs can be synthesized by using a variety of photoinduced or photo catalytic reduction methods. Photochemical synthesis is a clean process which has high spatial resolution, convenience of use, and great versatility. Moreover, photochemical synthesis enables one to fabricate the NPs in various mediums including cells, emulsion, polymer films, surfactant micelles, glasses, etc. Nano sized silver particles with an average size of 8 nm were prepared by photo induced reduction using poly (styrene sulfonate)/poly (ally amine hydrochloride) polyelectrolyte capsules as micro reactors (21). Moreover, it was demonstrated that photo induced method could be used for converting silver Nano spheres into triangular silver Nano crystals (nanoprisms) with desired edge lengths in 30-120_nm range (22). Particle growth process was controlled using dual-beam illumination of NPs. Citrate and poly (styrene sulfonate) was used as stabilizing agents. In another study, silver NPs were prepared through a very fast reduction of Ag+ by α-aminoalkyl radicals generated from hydrogen abstraction toward an aliphatic amine by the excited triplet state of 2- substituted thioxanthone series (TX-O-CH2- COO^- and TX-S-CH2-COO^-). Quantum yield of this prior reaction was tuned by substituent effect on thioxanthones, and led to a kinetic control of conversion of silver ion (Ag+) to silver metal (Ag0) (23).

Electrochemical synthetic method: Electrochemical synthetic method can be used to synthesize silver NPs. It is possible to control particle size by adjusting electrolysis parameters and to improve homogeneity of silver NPs by changing the composition of electrolytic solutions. Polyphenylpyrrole coated silver Nano spheroids (3-20 nm) were synthesized by electrochemical reduction at the liquid/liquid interface. This Nan compound was prepared by transferring the silver metal ion from aqueous phase to organic phase, where it reacted with pyrrole monomer (24). In another study, monodisperse silver nanospheroids (1-18 nm) were synthesized by electrochemical reduction inside or outside zeolite crystals according to silver exchange degree of compact zeolite film modified electrodes (25).

Irradiation methods: Silver NPs can be synthesized by using a variety of irradiation methods. Laser irradiation of an aqueous solution of silver salt and surfactant can produce silver NPs with a well-defined shape and size distribution (26). Furthermore, laser was used in a photosensitization synthetic method of making silver NPs using benzophenone. At short irradiation times, low laser powers produced silver NPs of about 20 nm, while an increased irradiation power produced NPs of about 5 nm. Laser and mercury lamp can be used as light sources for production of silver NPs (27).

Bio-based methods: Bio-based protocols could be used for synthesis of highly stable and well characterized NPs when critical aspects, such as types of organisms, inheritable and genetically properties of organisms, optimal conditions for cell growth and enzyme activity, optimal reaction conditions, and selection of the biocatalyst state have been considered. Sizes and morphologies of the NPs can be controlled by altering some critical conditions, including substrate concentration, pH, light, temperature, buffer strength, electron donor (*e.g.,* glucose or fructose), biomass and substrate concentration, mixing speed, and exposure time. In the following section, we discussed the synthesis of NPs using microorganisms and biological systems.

Bacteria: The bacteria have been explored in the synthesis of silver NPs. It was reported that highly stable silver NPs (40 nm) could be synthesized by bio reduction of aqueous silver ions with a culture supernatant of nonpathogenic bacterium, *Bacillus licheniformis* (28). Moreover, well-dispersed silver nanocrystals (50 nm) were synthesized using the bacterium *B. licheniformis* (29). Saifuddin and coworkers (30) have described a novel combinational synthesis approach for the formation of silver NPs by using a combination of culture

supernatant of *B. subtilis* and microwave irradiation in water. They reported the extracellular biosynthesis of mono dispersed Ag NPs (5-50 nm) using supernatants of *B. subtilis*, but in order to increase the rate of reaction and reduce the aggregation of the produced NPs, they used microwave radiation which might provide uniform heating around the NPs and could assist the digestive ripening of particles with no aggregation. Silver nanocrystals of different compositions were successfully synthesized by
Pseudomonas stutzeri AG259 (31). The silver-resistant bacterial strain, *P. stutzeri* AG259, isolated from a silver mine, accumulated silver NPs intracellularly, along with some silver sulfide, ranging in size from 35 to 46 nm (32). Larger particles were formed when *P. stutzeri* AG259 challenged with high concentrations of silver ions during culturing, resulted intracellular formation of silver NPs, ranging in size from a few nm to 200 nm (8,111). *P. stutzeri* AG259 detoxificated silver through its precipitation in the periplasmic space and its reduction to elemental silver with a variety of crystal typologies, such as hexagons and equilateral triangles, as well as three different types of particles: elemental crystalline silver, monoclinic silver sulfide acanthite (Ag2S), and a further undetermined structure (31). The periplasmic space limited the thickness of the crystals, but not their width, which could be rather large (100-200 nm) (5). In another study, rapid biosynthesis of metallic NPs of silver using the reduction of aqueous Ag+ ions by culture supernatants of *Klebsiella pneumonia*, *Escherichia coli*, and *Enterobacter cloacae* was reported (33). The synthetic process was quite fast and silver NPs were formed within 5 min of silver ions coming in contact with the cell filtrate. It seems that nitroreductase enzymes might be responsible for bioreduction of silver ions. It was also reported that visible-light emission could significantly increase synthesis of silver NPs (1-6 nm) by culture supernatants of *K. pneumoniae* (34). Monodispersed and stable silver NPs were also successfully synthesized with bioreduction of [Ag (NH3)2] + using *Aeromonas* sp. SH10 and *Corynebacterium* sp. SH09 (35). It was speculated that [Ag (NH3)2] + first reacted with OH− to form Ag2O, which was then metabolized independently and reduced to silver NPs by the biomass. *Lactobacillus* strains, when exposed to silver ions, resulted in biosynthesis of NPs within the bacterial cells (36, 37). It has been reported that exposure of lactic acid bacteria present in the whey of buttermilk to mixtures of silver ions could be used to grow NPs of silver. The nucleation of silver NPs occurred on the cell surface through sugars and enzymes in the cell wall, and then the metal nuclei were transported into the cell wherethey aggregated and grew to larger-sized particles. Korbekandi and colleagues (37). Demonstrated the bioreductive synthesis of silver NPs using *L. casei* subsp. *casei* at room temperature. Researchers have reported qualitative production of silver NPs by *Lactobacillus sp.,* but they did not optimize the reaction mixture. Biosynthesized silver NPs were almost spherical, single (25-50 nm) or in aggregates (100 nm), attached to the surface of biomass or were inside and outside of the cells. demonstrated the bioreductive synthesis of silver NPs using *L. casei* subsp. *casei* at room temperature. Researchers have reported qualitative production of silver NPs by *Lactobacillus sp.,* but they did not optimize the reaction mixture. Biosynthesized silver NPs were almost spherical, single (25-50 nm) or in aggregates (100 nm), attached to the surface ofbiomass or were inside and outside of the cells. Kumar and coworkers (38) have demonstrated enzymatic synthesis of silver NPs with different chemical compositions, sizes and morphologies, using α NADPHdependent nitrate reductase purified from *F. oxysporum* and phytochelatin, *in vitro*.

Algae: A few reports are available regarding gold accumulation using algal genera including cyanobacteria as biological reagent. Cyanobacteria and eukaryotic alga genera such as *Lyngbya majuscule*, *Spirulina subsalsa*, *Rhizoclonium heiroglyphicum*, *Chlorella vulgaris*, *Cladophora prolifera*, *Padinapavonica*, *Spirulina platensis*, and *Sargassum fluitans* can be used as cost effective means for biorecovery of gold out of the aqueous solutions, as well as the formation of gold NPs (39-40). Marine algae like *Chaetoceros calcitrans*, *Chlorella salina*, *Isochrysis galbana* and *Tetraselmis gracilis* can also be used for reduction of silver ions and thereby synthesis of Ag NPs (33). Marine cyanobacterium, *Oscillatoria willei* NTDM01 has been used for synthesis of silver NPs (100- 200 nm). Silver nitrate solution incubated with washed marine cyanobacteria changed to a yellow color from 72 h onwards, indicating the formation of silver NPs. When *Spirulina platensis* biomass was exposed to 10−3 M aqueous AgNO3, extracellular formation of spherical silver NPs (7-16 nm) has been resulted in 120 h at 37 °Cat pH 5.6 (41).

Plants: Synthesis of NPs using plants is very cost effective, and thus can be used as an economic and valuable alternative for the large-scale production of NPs (15). Plant extracts from alfalfa (*Medicago sativa*), lemongrass (*Cymbopogon flexuosus*), and geranium (*Pelargonium graveolens*) have served as green reactants in silver nanoparticle synthesis. Moreover, a high density of extremely stable silver NPs (16-40 nm) was rapidly synthesized by challenging silver ions with *Datura metel* leaf extract (38). The leaf extracts of this plant

contains biomolecules, including alkaloids, proteins /enzymes, amino acids, alcoholic compounds, and polysaccharides which could be used as reductant to react with silver ions, and therefore used as scaffolds to direct the formation of silver NPs in the solution. Song and colleagues elucidated the fact that *Pinus desiflora*, *Diospyros kaki*, *Ginko biloba*, *Magnolia kobus* and *Platanus orientalis* leaf broths synthesized stable silver NPs with average particle size ranging from 15 to 500nm, extracellularly. In the case of *M. kobus* and *D. kaki* leaf broths, the synthesis rate and final conversion to silver NPs was faster, when the reaction temperature was increased. But the average particle sizes produced by *D. kaki* leaf broth decreased from 50 nm to 16 nm, when temperature was increased from 25°C to 95°C (39). The researchers also illustrated that only 11 min was required for more than 90% conversion at the reaction temperature of 95°C using *M. kobus* leaf broth (39).Spherical silver NPs (40-50 nm) were produced using leaf extract of *Euphorbia hirta*(40). These NPs had potential and effective antibacterial property against *Bacillus cereus* and *Staphylococcus aureus*. *Acalypha indica* (Euphorbiaceae) leaf extracts have produced silver NPs (20-30 nm) within 30 min (41). These NPs had excellent antimicrobial activity against water borne pathogens, *E. coli* and *V. cholera* (minimum inhibitory concentration (MIC)=10 μg/ml). Studying synthesis of silver NPs with isolated/purified bio-organics may give better insight into the system mechanism. Glutathione (γ-Glu-Cys-Gly) as a reducing /capping agent can synthesize water-soluble and size tunable silver NPs which easily bind to a model protein (bovine serum albumin) (42).

CONCLUSION

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 these NPs. Different methods have been developed to obtain silver NPs of various shapes and sizes, including laser ablation, gamma irradiation, electron irradiation, chemical reduction, photochemical methods, microwave processing, and thermal decomposition of silver oxalate in water and in ethylene glycol, and biological synthetic methods. Biosynthetic methods of NPs provide a new possibility of conveniently synthesizing NPs using natural reducing and stabilizing agents. As possible environmentally and economically friendly alternatives to chemical and physical approaches, biosynthesis of metal and semiconductor NPs using organisms has been suggested. Mono dispersity and particle size and shape are very important parameters in the evaluation of NPs synthesis. Therefore, the efficient control on the morphology and monodispersity of NPs must be explored. Well- characterized NPs can be obtained by synthesis rates faster or compatible to those of chemical and physical approaches. This eco-friendly method can potentially be used in various areas, including pharmaceuticals, cosmetics, foods, and medical applications.

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