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Greener Techniques for the Synthesis of Silver Nanoparticles Using Plant Extracts, Enzymes, Bacteria, Biodegradable Polymers, and Microwaves

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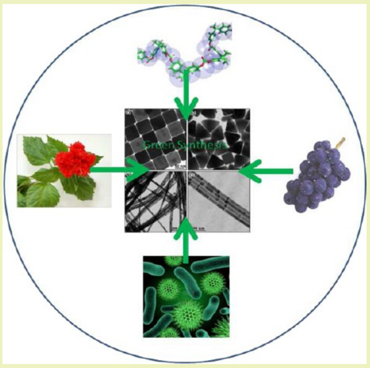
ABSTRACT: The use of silver nanoparticles (AgNPs) is gaining in popularity due to silver's antibacterial properties. Conventional methods for AgNP synthesis require dangerous chemicals and large quantities of energy (heat) and can result in formation of hazardous byproducts. This article summarizes recent activity in this general area where environmentally friendly synthetic techniques are currently being explored for the synthesis of "greener" AgNPs including the use of plant extracts, biodegradable polymers, and enzymes/bacteria and alternative energy input systems, such as microwave irradiation. Microwave heating enables efficient formation of nanostructures of uniform small sizes in shorter reaction times with reduced energy consumption; preventing agglomeration of ensuing nanoparticles is an additional attribute.



KEYWORDS: *Ag nanoparticles, Sustainable synthesis, Biomimetic processes, Microwaves*

USE OF PLANT EXTRACTS

Plant extracts are often environmentally and economically friendly materials and have been explored in the synthesis of silver nanoparticles (AgNPs). All parts of a plant bearing antioxidants or sugars, including leaves, fruits, roots, seeds, and stems, can be used in the synthesis process, replacing potentially hazardous chemicals like sodium borohydride ($NaBH_4$). The reason plant extracts work so well in the synthesis of nanoparticles is because they act as reducing agents as well as capping agents. Our group explored the use of tea leaf extracts to produce AgNPs;[1] the size of the nanoparticles formed could be controlled by varying the concentration of tea extract or epicatechin in the sample. Figure 1 shows various images of AgNPs produced at different epicatechin and tea extract concentrations. Ultraresolution microscopy was used to prove that the AgNPs had interactions with keratinocytes, the most common skin cells. Yet, after evaluating the mitochondrial function and using that to assess cell viability and membrane integrity, it was shown that the AgNPs produced by this method were nontoxic to humans.[1]

Green tea (*Camellia sinensis*) extracts can act as reducing and stabilizing agents in AgNP production. Colloidal systems of these particles exhibited highly efficient, single-photon induced luminescence, which could be manipulated by changing the silver ion concentration.[2] Furthermore, Nadagouda and Varma[3] investigated the use of not only tea extracts, but also coffee extracts. Figure 2 shows the particles produced using three different teas (a, c, and d) and three different coffees (b, e, and f). Generally, tea extracts produced larger particles than coffee extracts, according to this technique. Also, this method did not require the use of any surfactant, capping agent, or template. AgNPs produced ranged from 20 nm (coffee) to 60 nm (tea) and were in a face-centered cubic (fcc) symmetry when crystallized.[3]

Similar to tea leaf extracts, other plant leaf extracts can be used to produce nanosized silver particles in an eco-friendly way. *Capsicum annuum*, for example, is a species of pepper (bell and chili peppers) whose leaves can be used for nanoparticle synthesis. Proteins with amine groups reduced the silver ions and acted as a control during synthesis. After interacting with the silver ions, the protein's secondary structure was found to be altered. The crystalline phase of the NPs changed from polycrystalline to single crystalline and increased in size with increasing reaction time. A recognition-reduction-limited nucleation and growth model was suggested to explain the possible formation mechanism of silver NPs in *Capsicum annuum* L. extract.[4] *Argemone mexicana* is another plant that can be used to replace toxic chemicals as the capping and reducing agent. According to scanning electron microscope (SEM) and X-ray diffraction (XRD) analyses, cubic and hexagonal structured AgNPs were synthesized in the size range of 10−50 nm.[5] If a

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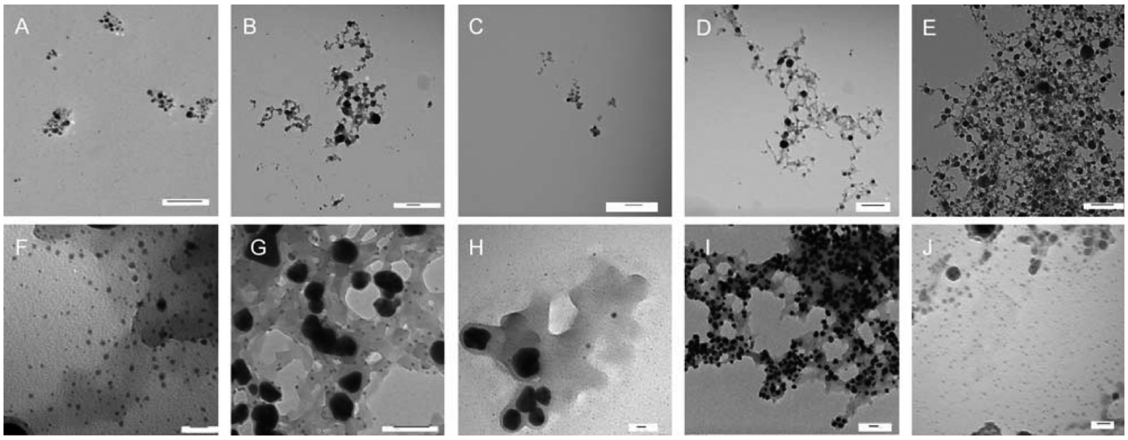

Figure 1. Morphology of AgNPs: (A) 1:1 ratio of water to epicatechin (scale bar: 100 nm): (B) 2:1 ratio of water to epicatechin (scale bar: 100 nm); (C) 10:3 ratio of water to epicatechin (scale bar: 100 nm): (D) 10:1 ratio of water to epicatechin (scale bar: 100 nm): (E) 20:1 ratio of water to epicatechin (scale bar: 100 nm); (F) 1:1 ratio of water to tea extract (scale bar: 20 nm); (G) 2:1 ratio of water to tea extract (scale bar: 100 nm): (H) 10:3 ratio of water to tea extract (scale bar: 20 nm); (I) 10:1 ratio of water to tea extract (scale bar: 100 nm); (J) 20:1 ratio of water to tea extract (scale bar: 20 nm). Reproduced with permission from ref 1. Copyright 2010 Royal Society of Chemistry.

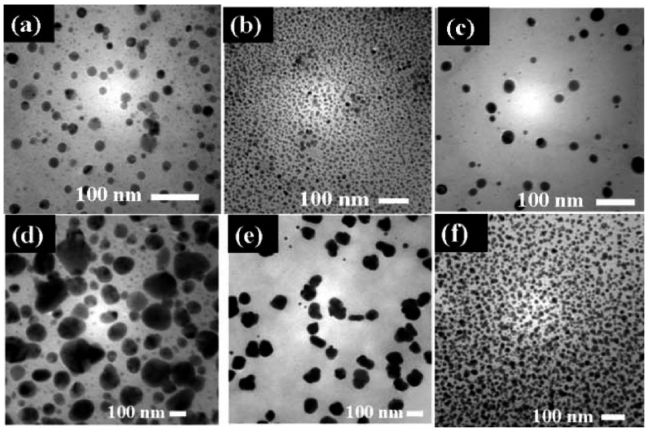

Figure 2. TEM image of silver nanoparticles synthesized using (a) Bigelow tea, (b) Folgers coffee, (c) Lipton tea, (d) Luzianne tea, (e) Sanka coffee, and (f) Starbucks coffee extract at room temperature in one step without using any hazardous reducing chemicals or nondegradable capping agents. Reproduced with permission from ref 3. Copyright 2008 Royal Society of Chemistry.

different extract is used, the nanoparticles formed can be of a more precise size. For example, using *Aloe vera* leaf extract as the reducing agent forms AgNPs 15.2 ± 4.2 nm.[6] Other leaf extracts that can be used in this process include *Nelumbo nucifera* Gaertn, *Eucalyptus hybrida*, *Helianthus annuus*, *Rosa sinensis*, *Acalypha indica*, and *Tinospora cordifolia* Miers.[7−12] The utilization of different leaf species results in different properties of the synthesized AgNPs. For example, *Rosa sinensis*, as seen in Figure 3, could be used to synthesize AgNPs, which can be seen in Figure 4. It was found that the variation of pH of the reaction medium consisting of silver nitrate and hibiscus leaf extract produced different shaped AgNPs. It was also determined that the stabilization occurred through carboxylate ions and the AgNPs.[10] *Acalypha indica* can generate AgNPs that inactivate waterborne bacterial pathogens like *E. coli* and *V. cholerae* within a half hour.[11] Jayaseelan et al.[12] investigated the application of "green" synthesized AgNPs for pediculocidal and larvicidal activity. *Tinospora cordifolia* Miers, a vine commonly found in India and Sri Lanka, was used as the reducing agent; AgNPs produced with this plant could be an effective and ecofriendly way to control head lice.[12]

Figure 3. Digital photograph of hibiscus leaf used in the synthesis. Reproduced with permission from ref 10. Copyright 2010 Elsevier.

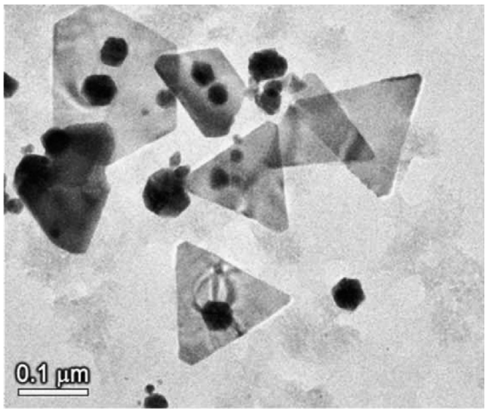

Figure 4. TEM image of AgNPs synthesized from hibiscus leaf. Reproduced with permission from ref 10. Copyright 2010 Elsevier.

Other than leaf extracts, fruit extracts can also be used, such as papaya fruit extract which can be a very cost efficient and ecofriendly method as well. The papaya fruit acts as a reducing and capping agent with the $AgNO_3$ solution. The average particle size synthesized is 15 nm, and the structure is typically cubic shaped. The nanoparticles synthesized using the papaya fruit extract were highly toxic against several multi drug-resistant human pathogens.[13] *Citrus sinensis* peel extract can serve as a reducing and a capping agent in the synthesis of silver nanoparticles; silver nanoparticles generated at 25 and 60 °C showed that the temperature difference produced variations in the ensuing AgNPs. UV−vis, Fourier transform infrared spectroscopy (FTIR), XRD, energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) analyses all confirmed that AgNPs were successfully formed as can be seen in Figure 5. TEM analysis proved that variation in temperature produced differently sized particles. The ensuing nanoparticles displayed antibacterial properties and activity against some bacteria like *Escherichia coli*, *Pseudomonas aeruginosa* (Gram-negative), and *Staphylococcus aureus* (Gram-positive).[14] *Tanacetum vulgare* fruit extract has also been explored as a means to produce AgNPs. Upon confirmation of successful synthesis, extract and silver ion concentrations, as well as temperature, were varied to examine the influence of the properties of AgNPs.[15]

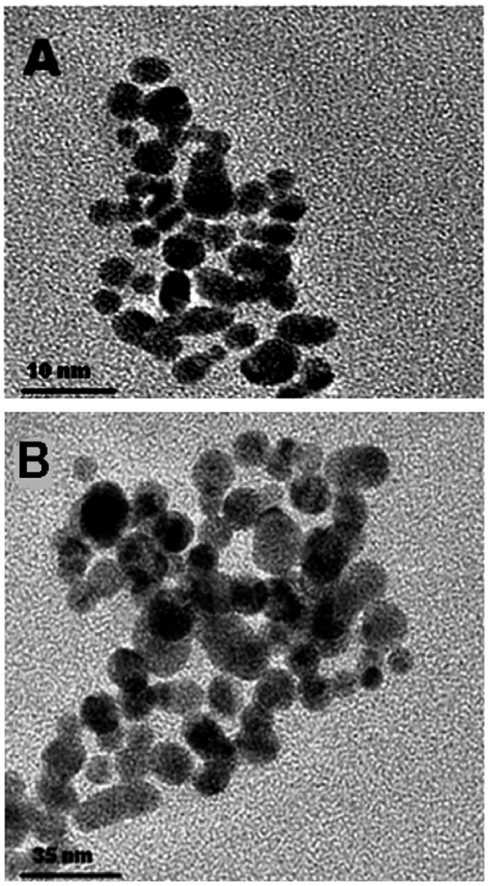

Figure 5. HRTEM images of the biosynthesized silver nanoparticles showing various particles sizes at (A) 60 and (B) 25 °C. Reproduced with permission from ref 14. Copyright 2011 Elsevier.

While leaves are the most common plant extracts studied for green AgNP synthesis, seeds, stems, roots, and bark extracts have been explored as well. *Trianthema decandra* root extract, which contains antioxidants that can act against diseases like atherosclerosis in humans, was studied. Particles produced with this plant were approximately 15 nm and cubic or hexagonal in shape.[16] Smaller nanoparticles could be formed from dried stems and roots of *Ocimum sanctum*, a plant in the basil family. The plant's broth acted as the reducing agent for the silver ions that were being synthesized into nanoparticles. UV−vis spectroscopy showed the formation of AgNPs, while TEM, selected area electron diffraction (SAED), and XRD analyses showed the morphology and crystalline phase of the nanoparticles. TEM showed that the size of the silver nanoparticles were in the range of 10 ± 2 nm if obtained from roots and 5 ± 1.5 nm if obtained from the stem. *Ocimum sanctum* is able to reduce silver ions to nanoparticles because of the presence of phytochemicals, while its chemical framework is effective at providing stability to avoid agglomeration.[17] *Phytolacca decandra*, a plant historically used in medicinal settings, was found to be useful. The homeopathic mother tincture, *Phytolacca decandra*, was used to synthesize AgNPs with the following standard procedure for forming AgNPs from a solution of silver nitrate ($AgNO_3$). A 100 mg portion of $AgNO_3$, 20 mL of Milli-Q water, and 5 mL homeopathic mother tincture of *Phytolacca decandra* (ethanolic root extract of *Phytolacca decandra*) were mixed together and stirred. The reduction occured in only about 10 min and was possible at ambient conditions. The colloidal solution formed was centrifuged to separate out the AgNPs. The size of each particle was approximately 91 nm. The particles exhibited both anticancer and antibacterial properties, though no antifungal properties were noticed.[18] The bark extract and powder of *Cinnamon zeylanicum* was found to be an effective agent in AgNP synthesis. The nanoparticles' surfaces were highly negative in charge as determined through zeta potential studies.[19] Finally, seed extract of *Jatropha curcas* was useful for synthesizing AgNPs. The particles formed using this method were spherical with diameters from 15 to 50 nm, depending on the initial concentration of $AgNO_3$.[20]

Plants and their extracts can be very useful when it comes to metal nanoparticle synthesis. The reason plant extracts work so well to synthesize silver nanoparticles is because antioxidants present in them act as reducing agents. By altering the concentration of $AgNO_3$ (the most common solution reduced to form AgNPs) and the concentration of the plant extract (leaf, fruit, seed, stem, root, or bark), the size and shape of synthesized AgNPs can be controlled to an extent. Thus, if a particular size/shape of AgNPs is required, it can be accomplished by altering concentrations or plant used. Plant usage is also beneficial because it eliminates the need to maintain cell cultures, as is common in other biological processes. Further experimentation is required for optimum AgNP synthesis, though. If nanoparticles are produced outside the cell, the biosynthesis would be more beneficial, and the amount of nanoparticles produced could be massive.[21]

■ MICROWAVE-ASSISTED SYNTHESIS

The conventional method of AgNP synthesis requires the reductive reaction to occur in an oil bath, which must be held at a constant temperature of ~80 °C for 5 h (on average). Due to excessive heating and extended reaction time, more eco-friendly means of AgNP synthesis are desired. An alternative green AgNP synthesis technique employs the use of microwaves. In general, microwave (MW) heating is better than a conventional oil bath when it comes to consistently yielding nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization.[22] Heating samples with microwaves is a practical method for the greener synthesis of nanomaterials. MW heating is advantageous as it has shorter reaction times, reduced energy consumption, and better product yields which prevents the agglomeration of the particles formed.[22]

Nadagouda and Varma[22] have discussed the production of silver nanostructures at length through a MW-assisted synthetic approach which shows that the one-pot synthesis of metallic nanostructures in solutions can be conducted efficiently via MW heating. Silver, gold, platinum, and gold–palladium nanostructures have been prepared through this method, which illustrates the generality of this approach. Through MW heating conditions, spherical nanoparticles can be prepared within a few minutes and single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites can also be formed. By altering some experimental parameters like the concentration of metallic precursors, surfactant polymers, and solvents, or the operational temperature, parameters like morphology and nanostructure size could be controlled.[22] Other than the elimination of the oil bath, MW-assisted techniques, in conjunction with benign reaction media, can also drastically reduce chemical wastes and reaction times in several organic syntheses and chemical transformations.[23]

Though it has been found that AgNPs can be produced by a vast amount of different synthesis techniques, the mass production of these nanoparticles is desired for industrial purposes. Nearly monodisperse silver nanoparticles can be synthesized in large quantities using a microwave-assisted chemistry method in an aqueous system. In these methods, amino acids act as reducing agents and soluble starch acts as a protecting agent. It is essential for the synthesis of consistently reproducible silver nanoparticles that amino acids with basicity like that of L-lysine or L-arginine, which have two amino groups per molecule, is present; large-scale synthesis can occur with this synthetic process. For example, an 80 mL microwave sealed vessel can be used for a reaction yielding 0.1 g of nearly monodisperse silver nanoparticles. When solvent, renewable reactants, and microwave irradiation are put together, there is practical potential for the green chemical synthesis of metal nanoparticles with controlled shapes and sizes.[24] Not only silver, but silver doped lanthanum chromites can also be synthesized with MW energy.[25] Several characterization techniques were used to examine these particles: FTIR revealed the oxygen bands and bending modes of the particles, XRD analysis showed peaks that corresponded with lanthanum chromite, and thermogravimetric analysis (TGA) proved the product to be stable. Particles ranged from 7–8 to 20–26 nm and were magnetic in nature.[25] Another example is the synthesis of nanopowder catalysts of Ag–Fe oxide. Analyses methods, such as XRD and TEM, clarified the change in the composition of the surface during catalysis. The patterns seen through XRD analysis showed that the temperature effect caused the particles to grow in size. The activity of the prepared catalysts was studied to obtain the effects of the catalyst composition and the preparation method on CO oxidation at low temperature.[26]

Microwave energy and thermal reduction can be coupled to synthesize silver nanoparticles that can be deposited on oxidized carbon paper (CP) electrodes. The AgNPs that are synthesized through this method maintain a uniform size between particles and are well-dispersed over the carbon paper substrate. The MW-synthesis of silver nanoparticles is made possible by depositing the silver catalysts on CP electrodes. Figure 6 illustrates the AgNP formation on CP substrates at different magnifications. This method can potentially be used in alkaline fuel cells because the synthesis occurs quickly, there is high activity, and the process is very simple.[27] Nanosized calcium deficient hydroxyapatites (CDHA) can be used to generate nanosized calcium deficient hydroxyapatite with a silver substitution (SCDHA) in three different concentrations by MW-assisted synthesis. This study showed that controlling the parameters of the MW process could influence the size of the crystals produced. It was shown that the MW power had more of an impact on the size of the particles than the length of time of the treatment. The ensuing powder product could be used in the field of medicine and biomedical engineering to make grafts and coating metal implants in addition to work against bacterial infections without the use of antibiotics. Ultimately, this technique could reduce medicinal costs and time of hospitalization.[28]

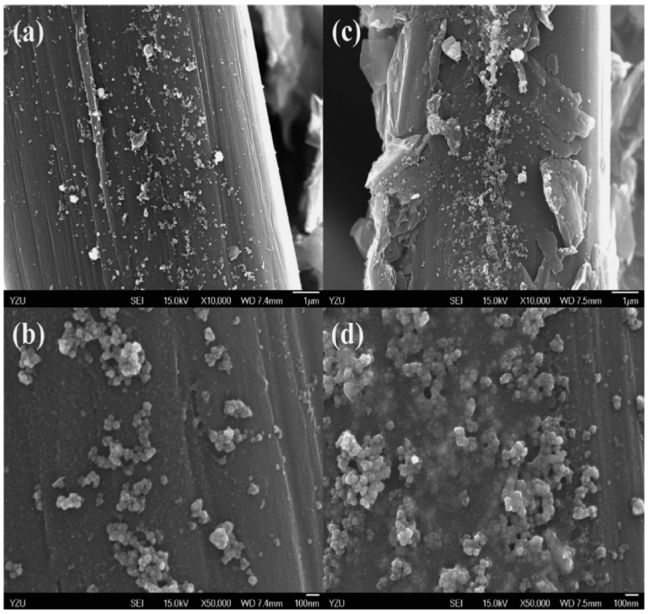

Figure 6. FE-SEM images of as-grown silver nanoparticles over oxidized CP substrates: Ag–CP–M at (a) low and (b) high magnification and Ag–CP–T at (c) low and (d) high magnification. Reproduced with permission from ref 27. Copyright 2011 Elsevier.

Another class of polymer (silver/polypyyrole (PPy)) based silver composites were produced using MW energy on the basis of interfacial polymerization. A water/chloroform interface was used under MW irradiation with no oxidizing agent. The silver nanoparticles produced were spherical, well-dispersed, and approximately 20 nm in size.[29] $AgNO_3$ provided Ag^+ ions for the thermal polymerization of pyrrole. The ions were converted to PPy/Ag nanocomposites. TEM images proved that the particles were about 5–10 nm in size. The PPy/Ag had a thick film, which could sense ammonia, hydrogen sulfide, and carbon dioxide at 100, 250, and 350 °C, respectively.[30] MW radiation and ethylene glycol can be used to synthesize Ag powders from $AgNO_3$ at temperatures of 100–200 °C. After 23 min of treatment, the powdered form was obtained in high yield (99%) with the diameters ranging from 0.15 to 1.8 μm; they grew in size and also aggregated. However, when polyvinyl pyrrolidone (PVP) was used in the mixture of $AgNO_3$, the particles ranged from 62 to 78 nm in diameter.[31] Another classic example is Fe–Ag bimetallic nanoparticles, which could be synthesized using MW heating and an oil-soluble silver salt.[32] The AgNPs were characterized through a series of tests, such as freeze-etching replication transmission electron microscopy (FRTEM), which revealed the nanoparticle diameter and distribution. Centrifuge tests (both normal and high speed) were conducted in order to determine the dispersion stability of the synthesized particles. The AgNPs were spherical in shape and had an average, uniform size of 30 nm.[33] Alcohols like ethanol coupled with PVP, at temperatures that exceed 120 °C, show that silver salts can be reduced into nanoparticles under MW irradiation. Hydrolysis of alkoxysilanes along with the silver salt, in the presence of MW irradiation, can produce Ag/SiO_2 composite sols, which displayed antimicrobial properties.[34]

Vongehr et al.[35] reviewed recent advances in the utilization of various water-based synthesis routes toward the shape-controlled synthesis of silver nanoparticles and microstructures. Several one-pot methods employing commercial MW ovens, inexpensive/low power ultrasound cleaners, or two-electrode electrochemistry were described. Synthesis of Ag nanostructures with various shapes in solution and their doping on unmodified silica and on/inside carbon spheres were investigated.[35] $AgNO_3$ in an ethanolic medium along with PVP under MW irradiation was used to synthesize AgNPs; a surface plasmon band at 416 nm indicated that silver nanoparticles have been produced within 5 s after being exposed to MW irradiation. The nanoparticles were spherical in shape and had a diameter of 10 ± 5 nm. Their fluorescence band was noticed at 491 nm.[36] MW synthesis was used to prepare different kinds of nanosilver colloids. $AgNO_3$ was mixed with sodium citrate and then split into five groups. Each group was heated for varying durations of time at different temperatures. TEM, absorption spectrum, and electrophoresis experiments were used to analyze the nanosilver colloids. It was determined that the nanosilver colloids had a negatively charged surface when heated for a long period of time and a positively charged surface when heated for a short period of time.[37] Carbon nanospheres were synthesized and functionalized before being covered with bimetallic particles of gold and silver. The particles were produced using MW-assisted methods. SEM studies revealed that the sizes of the particles produced were different and depended on the concentration of the hydrocarbon gas that was used. XRD analysis indicated that these particles were cubic in nature. Raman spectra presented that the higher the concentration of the bimetals on the surface, the better the degree of graphitization.[38] Silica−alumina can be used to synthesize silver nanoparticles with precursors like Ag_2O or $AgNO_3$. By coupling MW-plasma with fluidized bed technologies, the precursors could be decomposed and evaporated; the ensuing nanoparticles were spread over the support in a uniform manner. The particles were as small as 3 nm in diameter or as big as 50 nm. They were not oxidized, and the particles were well spread out.[39] Nanosilver/PVP composite materials were synthesized using the MW approach. The catalytic reduction of Ag^+ ions was discussed and UV−vis and XRD analyses were used to confirm the formation of silver nanoparticles. Their phase was found to be an fcc system. The nanoparticles ranged from 15−25 nm and were evenly spread out in the PVP matrix.[40]

BIODEGRADABLE POLYMERS

Soluble starch, like plant extracts, can be used as reducing and stabilizing agents to synthesize AgNPs; such nanoparticles were stable for three months at room temperature. The nanoparticles size range was between 10 and 34 nm, as determined by a TEM. XRD analysis showed that the AgNPs have an fcc geometry. When excited at 380 nm, they produced a typical emission peak at 553 nm.[41] Silver nitrate, glucose, sodium hydroxide, and starch can be used, respectively, to serve as precursor, reducing agent, accelerator, and stabilizer for the reduction synthesis of AgNPs. The effect of NaOH on the synthesis of silver nanoparticles is investigated by looking at two reaction pathways. Changes in pH occur when different amounts of NaOH are added. If prepared at different pH values, the aqueous solution of AgNPs has different surface plasmon resonance (SPR).[42] Polyethylene glycol (PEG) was used to prepare stable silver colloids because it is another eco-friendly reducing agent as well as a stabilizer. The particles produced were monodispersed with a diameter of less than 10 nm. The colloids worked against bacteria and fungi that were Gram-positive and Gram-negative.[43] Biodegradable starch worked as a stabilizing agent to synthesize AgNPs. The analyses showed that the nanoparticles were coated with a layer of starch. The particles' diameters ranged from 5 to 20 nm. XRD analysis showed that the nanoparticles had an fcc structure.[44]

Polymers that have ion-exchangeable capacity can be used in many fields of science. The polymer often used contained phosphonic acid groups and had a low molecular weight. There was an initial complexation of the polymer to Ag^+, and then, the metal ions were reduced into nanoparticles. The AgNPs were stabilized in the presence of an ion-exchange polymer. The surface morphology indicated that cubes and rectangular prism structures were formed.[45] Copolymers like cyclodextrin, grafted with poly acrylic acid, can be used to produce nanosized silver particles where potassium persulfate was used as the initiator. The copolymer reduces and stabilizes the silver ions that yielded AgNPs, thus, these nanoparticles aggregated. The concentration of the alkali, $AgNO_3$, the copolymer, and the method of heating all played a role in determining the size of the gathered nanoparticles. Further experimentation proved that the nanoparticles had antibacterial properties.[46] Poly(methyl vinyl ether-co-maleic anhydride) (PVM/MA) could be used as a reducing and stabilizing agent as well. The nanoparticles synthesized were stable at room temperature for up to a month and had a 5−8 nm coat of PVM/MA surrounding them.[47]

Factors involved in the synthesis, like the acidity, initial concentrations of starting materials, and the molar ratio of the reactants were all varied. Some dispersing agents were used to keep the nanoparticles from accumulating and were analyzed for morphology, particle size, the elemental composition, etc. It was also determined that the nanoparticles were fcc structures, not aggregating, and very spherical in shape. The average particle was 10.2−13.7 nm in size, depending on what was used to reduce the ions (citrate or ascorbic acid). The zeta potential was from −40 to −42 mV and was influenced mainly by the nanoparticles acidity and size.[48] Formaldehyde, when reacted with ammonium hydroxide, forms a polymer that influences the way in which the silver attaches to the substrate, as well as the way it coats it. When there are no favorable conditions for the synthesis of the polymer, the nanoparticles formed will be concentric and will have a plasmon resonance between that of gold and silver which occurs at 498 nm. By knowing this, the amount of formaldehyde used can be drastically decreased, by 100 fold, which would lead to a more environmentally friendly synthesis.[49]

Gamma radiolysis was used to synthesize silver nanoparticles with the help of gum acacia, which acted as the protecting agent; a plasmon absorption peak at 405 nm confirmed the formation of AgNPs. The amount of radiation and the ratio of the gum acacia to the Ag ions influence the formation of various sizes. Dynamic light scattering was used to analyze the nanoparticles. It was determined that at very high doses of radiation, the nanoparticles were smaller than 3 nm. XRD analysis determined the nanoparticle to have an fcc structure.[50] Sarkar et al. examined the synthesis of Ag nanowires as well as AgNPs.[51] Through a polypol process, with the help of a polymer, Ag nanowires and AgNPs were formed; SEM, XRD, and UV−vis analyses showed that the nanoparticles were 60−200 nm and held prismatic and hexagonal shapes while the nanowires had diameters from 50 to 190 nm and lengths between 40 and 1000 μm. The reaction occurred at 210 °C when ethylene glycol was used as the solvent. The different photoluminescence (PL) emission from the nanoclusters spread out through the methanol and the ethylene glycol at room temperature. The excitation wavelengths were measured between 300 and 414 nm.[51] By changing the reducing and capping agents that are used to synthesize AgNPs, one can change the morphologies of the nanoparticles as well. The synthesis yielded nanoparticles that were spherical in shape and around 15−43 nm in size after being heated at 70 °C for 30 min; while at room temperature, the particles were only 8−24 nm. Sodium hydroxide reduced salt in ethylene glycol and cubes were formed upon some aggregation. By adding 5 wt % PVP to 1 wt % of starched solution (aq), mixtures of spherical and anisotropic structures were produced. The reaction took place at 70 °C for 1 h. Thus, a number of AgNP morphologies can be prepared by adjusting the capping and reducing agents.[52] Silver nanoparticles can be synthesized using sulfated polysaccharide which can be obtained from marine red algae, *Porphyra vietnamensis*. The AgNPs retrieved had a SPR with a center at 404 nm. The size of the particle was measured to be around 13 ± 3 nm. Further analysis showed that sulfate moiety from the polysaccharides was involved in $AgNO_3$ reduction. Zeta potential measurements of −35.05 mV showed that the anionic polysaccharide had indeed capped the nanoparticles' surfaces and contributed to the electrostatic stability. The nanoparticles were stable at a very broad pH range, from 2 to 10, and electrolyte concentration of 10^{-2} M; the antibacterial activity was noticed against Gram-negative bacteria (*Escherichia coli*).[53] AgNP synthesis techniques that are less detrimental to the environment include mixed-valence polyoxometallates, polysaccharides, Tollens method, irradiation, and biological methods. The first method, mixed-valence polyoxometallates, was conducted in water. $AgNO_3$ solutions, with glucose and starch resulted in AgNPs with starch-protected coats.

The Tollens method reduced $Ag(NH_3)^{+2}$ using the saccharides and formed particles measured between 50 and 200 nm. Several morphologies included cubes, triangles, wires, and aligned wires, as can be seen in Figure 7. The irradiation method of the silver ions does not need a reducing agent. Bio-organisms with protein are used to act as reducing and capping agents to form stable nanoparticles that are consistent in structure. Polymer−Ag and TiO_2−Ag were also used in metal nanoparticle synthesis. The AgNPs showed high antimicrobial activity against both Gram-positive and Gram-negative bacteria.[54] Ag^+ ions can be reduced in $AgNO_3$ and chitosan solutions. It is a simple, inexpensive, and fast method to prepare chitosan films consisting of AgNPs. The polymer, chitosan, is natural and is a good agent for chelating and stabilizing, thus making this an eco-friendly approach. Several analyses like TEM, XRD, and TGA were used to confirm the presence of the Ag nanoparticles.[55] $AgNO_3$ can be reduced using a surfactant like absolute alcohol using PVP to synthesize silver nanoparticles with varying morphology and size of the nanoparticles. Both of these properties varied according to the concentration of metal salts, the reaction time, and the ratios of the surfactants deployed. Since no toxic chemicals were used and the solvents were environmentally friendly, this may be a practical method to synthesize AgNPs.[56]

■ ENZYMES AND BACTERIA

Silver nanoparticles can be synthesized through a novel biological method using the fungus *Verticillium*. Exposing the Ag^+ ions to the fungal biomass resulted in the reduction of the silver ions and formation of nanoparticles with dimensions of 25 ± 12 nm. Most likely the enzymes in the cell wall membrane reduce the silver ions. This was deduced after an electron microscopy analysis of the fungal cells showed that the silver particles' formation was concentrated below the cell wall surface. After the biosynthesis of the silver nanoparticles, the fungal cells still continued to grow, which shows that they are not toxic.[57] Another fungal species investigated was *Trichoderma asperellum*, one of the most common culturable fungi found in soil. UV−vis spectroscopy helped analyze the kinetics of the reaction. The analysis also shows an SPR band at 410 nm, and TEM and XRD analyses showed that the size of the nanoparticle was between 13 and 18 nm. The silver nanoparticles stay at a constant shape and size even after 6 months of being stored. FTIR and Raman spectroscopy were used as complementary tools to characterize the silver nanoparticles.[58] Bacterial strains could be used as well as fungal strains.

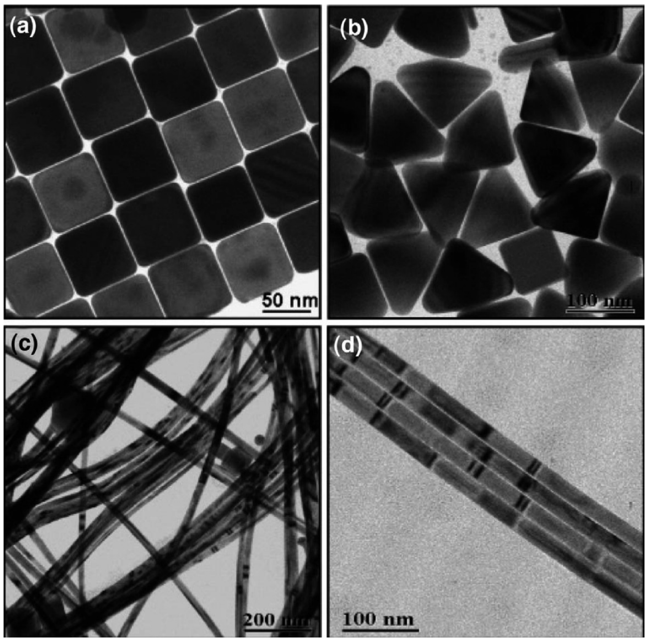

Figure 7. TEM images of silver nanoparticles: (a) cubes; (b) triangles; (c) wires; (d) an alignment of wires. Reproduced with permissin from ref 54. Copyright 2009 Elsevier.

Proteus mirabilis PTCC 1710 is a bacterial strain that can be used to synthesize AgNPs. The particles could be synthesized either in an intracellular or extracellular way. Different analyses methods such as UV−vis spectroscopy, TEM, EDS, and atomic absorption spectrometer (AAS) were used. The UV−vis spectroscopy revealed that a maximum absorbance occurred at approximately 400 nm. The nanoparticles were spherical in shape and had approximate diameters of 10−20 nm. If the bacterial cells were incubated in Muller-Hinton broth medium, there was a higher extracellular synthesis of the silver nanoparticles. Tryptic soy broth increased the synthesis of the nanoparticles that were being formed through intracellular methods. This method was easy, inexpensive, and uncomplicated. The use of the bacteria is a very practical method to synthesize silver nanoparticles in an environmentally friendly manner.[59]

The application of AgNPs' antibacterial properties was explored by Hebeish et al.[60] After synthesizing 6−8 nm AgNPs using hydroxypropyl starch (HPS) as both the reducing and stabilizing agent, the particles were applied to cotton fabrics. SEM analysis proved that the AgNPs were successfully deposited on the fabric surface. Once properly deposited, the particles' antibacterial properties were explored. It was determined that the AgNP containing fabrics successfully inactivated both Gram-positive (*Sraphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacterium. Results proved beneficial regardless of AgNP concentration and after up to 20 washing cycles.[60] Titania (TiO_2) is another chemical that, like silver, has antimicrobial properties. Modification of TiO_2 using Ag particles (forming a nanocomposite) could be accomplished for the enhanced removal of prokaryotic cells like *E. coli*. Biological applications and advanced instrumentation use were also researched to better explain AgNPs' antibacterial effects.[61] Ramanathan et al.[62] investigated AgNP synthesis using *Morganella psychrotolerans*, a silver-resistant psychrophilic bacterium. It was discovered that the growth kinetics of bacteria can be used to control the nanoparticle's shape during biological synthesis. After exposing the silver ions to the bacterial cells, some electrochemistry experiments were conducted, which provided insights about the mechanistic aspects of bacterial Ag reduction.[62] Li et al.[63] explored the green synthesis of AgNPs by using fungal species. *Aspergillus terreus*, a mold frequently used for the production of organic acids, was used in this study; stable and spherical AgNPs from 1 to 20 nm were synthesized at room temperature in 2−4 h. Nicotinamide adenine dinucleotide hydrate (NADH), a coenzyme found in all living organisms, was determined to be the key reducing agent. Thus, it was speculated that AgNP formation may be an enzyme-mediated extracellular process.[63]

CONCLUSION

In conclusion, the greener alternatives for the synthesis of silver nanoparticles are desirable in view of the environmental issues associated with conventional AgNP preparative methodologies. Conventional methods for the generation of AgNPs require dangerous chemicals (borohydrides or hydrazine as reducing agents) and large quantities of energy and can result in the formation of hazardous byproducts. Thus, the use of polyphenols or sugars from plant extracts, biodegradable polymers, bacteria, and enzymes for the synthesis of AgNPs under ambient conditions or the use of an alternate energy source, microwaves, for the synthesis of uniformly small-size nanoparticles can be employed for sustainable synthesis. Specific size and shape-controlled Ag nanorods can be obtained using PEG[64] and Ag-based carboxymethyl cellulose (CMC) composites,[65] exhibiting luminescent properties, can be readily prepared using MW irradiation. Simple use of vitamins such as vitamin B_2,[66] B_1,[67] C,[68] can generate nanoparticles in aqueous medium and at ambient temperature. Additionally, some of the biodegradable and non-toxic byproducts from biodiesel production such as glycerol can be utilized for the sustainable production of Ag nanowires of controlled diameters[69] and other noble nanometals.[70] While these new biomimetic techniques have proven beneficial, there are still some areas of inherent safety concerns. Some properties of the nanoparticles, especially their fate in terms of degradation and movement in the environment, may be altered depending on the type of coating (capping) used. Also, toxicological studies should be carried out to ensure that the nanoparticles obtained via these greener methods are, truly, less toxic than those obtained by conventional methods. These newer techniques for greener AgNP synthesis using biorenewable materials appear promising as they do not have any toxic materials deployed during the reduction of silver salts or capping processes. In view of these findings, it appears that nanoparticles may be formed readily in nature from the available inorganic salts in the presence of antioxidants or polyols.

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Notes

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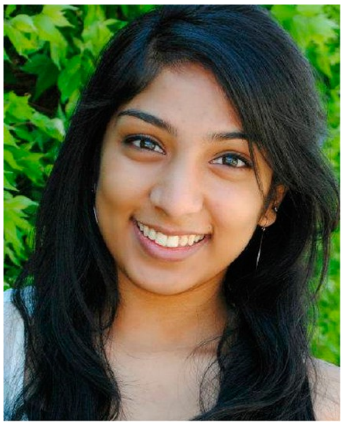
Biographies



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