



Manufacturing Techniques for Carbon Nanotubes, Gold Nanoparticles, and Silver Nanoparticles

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Abstract

Extensive research has been focused around organic and inorganic nanoparticles (NP) due to their unique and abundant benefits such as superior drug loading, biocompatibility, and role in drug delivery, biosensing, and theranostic. Among the organic NPs, carbon nanotubes (CNT), graphene NP, and fullerenes are widely explored, while gold and silver are extensively used for inorganic NP in biomedicine. The fabrication of CNT and its types like single-walled CNT (SWCNT) and double-walled CNT using conventional methods like arc discharge method, laser ablation, and chemical vapor deposition has been considered in detail. The traditional method of preparation of gold NPs (GNPs) is chemical reduction method which uses toxic chemicals or yields by-products which may compromise its inert characteristic. Thus, the current trend has been shifted toward the synthesis of GNPs using green method. In the last few decades,

incredible innovations have come up regarding the applications and methods of fabrication of silver nanoparticles (AgNPs). Similar to methods used for the fabrication of GNPs, AgNPs are also manufactured by various chemical methods such as reduction, light-mediated ion implant. The additional method which has been extensively explored is green synthesis of AgNPs using plants, bacteria, and fungi. This chapter provides an insight into the commonly used techniques as well as recently explored techniques in preparation of carbon nanotubes, gold NPs (GNP), and AgNPs.

Keywords

Manufacturing · Carbon nanotubes · Single-walled carbon nanotubes (SWCNT) · Gold nanoparticles · Silver nanoparticles · Green synthesis · Chemical synthesis

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1 Introduction

Carbon nanotubes (CNTs) are relatively new nanomaterials known to the public for nearly 20 years; however, their history is somewhat longer. CNTs were first discovered and identified by Radushkevich and Lukyanovich in 1952 (Radushkevich and Lukyanovich 1952) and then

observed by Oberlin et al. (1976) in 1976 as single (or double)-walled CNTs. In later history, the discovery of CNTs is credited to Iijima as the first scientist to depict preparation method of multi-walled CNTs (MWCNTs) after a random event during 1991 test of new arc evaporation technique for C60 carbon molecules (Iijima 1991). CNTs have attracted many researchers owing to their unique properties such as excellent electrical, mechanical, and thermal properties and larger surface area and a wide range of applications (Baughman et al. 2002). Nevertheless, in order to scale up at industrial level for increasing quantity and improving quality of the manufactured CNTs, it is necessary to develop new techniques for synthesis or improvement in the existing techniques. Generally, CNTs are divided into two types: single-walled CNTs (SWCNTs) and MWCNTs. SWCNTs are made up of a single sheet of graphene that is wrapped around itself forming a cylindrical tube. This is difficult to obtain, however they are unique because of higher stability and better mechanical properties. The SWCNTs possess a diameter in the range of 0.4–3 nm, and the length can be more than 10 mm, which can act as a good template for study in one-dimensional mesoscopic physics system (Dekker 1999). The MWCNTs are formed by two or more layers of concentric atoms, i.e., they are formed by two or more SWCNTs.

Gold nanoparticles in recent years have garnered significant interest due to their inherent optical and electrical properties when scaled down to nano-size which finally results in varied and diverse applications in biomedical field. These noble metals being inert in nature are devoid of significant toxicity in appropriate concentrations. Manufacturing techniques established previously were chemical reduction based which evolved through the years to explore different aspects like physical ablation techniques, sonochemical-based techniques, etc. The toxicity when preparing gold nanoparticles by chemical reduction often has increased due to the use of different chemicals and surfactants, and this has necessitated toward the use of green method-based synthesis of gold nanoparticles in recent years. The literature discussed here gives a brief

overview of different techniques explored over the years for preparation of gold nanoparticles.

There is recent focus on understanding the relationship between the physicochemical properties of nanomaterials and their potential risk to the human health and the surrounding environment day by day. Due to the growing popularity of silver nanoparticles (AgNPs) in consumer commodities, an effort has been placed to verify the safety of AgNPs along with the need to understand the mechanism of action for its antimicrobial effects. Due to unique properties of nanoparticles such as smaller particle size in nanoscale and higher surface area, which can significantly change physical, chemical, and biological properties, their significance has increased tremendously leading to numerous applications. One such application of surface-modified silver is in the field of antimicrobial effectiveness (Rai and Duran 2011). The beneficial effect of colloidal silver has been known for many years, but thorough studies on its outcome on the environment have recently begun. Preliminary studies have proved that AgNPs influence microbes and microbial cells principally due to the release of low concentration of silver ion from the nanoparticles.

In order to satisfy the requirements of AgNPs, a variety of approaches have been employed for the synthesis of nanoparticles. Generally, traditional physical and chemical methods are very costly and harmful. Interestingly, biologically prepared AgNPs from biological sources including bacteria, fungi, yeast, algae, or plants show superior yield, solubility, and good stability. Among numerous synthetic methods used for manufacturing AgNPs, biological methods seem to be less complicated, quick, nontoxic, and green approaches that can produce specific size and morphology under optimized conditions for research. A green chemistry approach promises the synthesis of AgNPs. Over the years, green nanotechnological advancements through biological resources have emerged significantly for synthesis and fabrication of metal nanoparticles (Gahlawat and Choudhury 2019). The methods of synthesis of AgNPs can be broadly divided into wet chemistry, ion implants, and biological sources.

2 Manufacturing Techniques for Carbon Nanotubes

2.1 Fabrication Methods for CNTs

Several methods have been evolved for the fabrication of CNTs, viz., chemical vapor deposition (CVD), laser ablation, arc discharge, electrolysis, and sonochemical/hydrothermal method. Each method has its own advantages and limitations. Fabrication methods for development of CNTs involve different mechanisms with varying levels of purity. The ultimate aim is to develop CNTs with greater purity and improve synthesis processes, which results in reduction of fabrication cost.

2.1.1 Arc Discharge Method

Iijima et al. utilized the arc method in the discovery of CNTs. This method involves the electric discharge of two electrodes (cathode and anode) of graphite inside a steel chamber, containing inert gas at high pressure (Sales 2003). In addition to this, in this method, helium/argon/methane gases are utilized, and the pressure is nearly 50–500 torr with temperature greater than 1700 °C with the catalyst Co and Fe in carbon, which has been confirmed first in SWCNT synthesis. This method causes the CNT expansion with fewer structural defects in comparison with other methods (Al Hasan 2019). The CNT-based quality produced by electric arc method is based on the quality and quantity of the catalyst, the pressure, the geometry of the system, inert gas nature, temperature, and electric current of the cathode and anode distancing during the process (Droppa Junior 2004; Teixeira 2010). The anode is composed of graphite and metals, such as Co, Ni, Pd, Pt, Ag, and Fe, and mixtures of Ni, Fe, and Co with other elements like Fe-NO, Ni-Cu, Co-Ni, Ni-Ti, Co-Cu, etc. The metal catalyst plays an important role in the process yield (Prasek et al. 2011). Iijima et al. fabricated SWCNTs with diameter of 1 nm (Iijima and Ichihashi 1993); however, Bethune et al. developed SWCNTs with a diameter of 1.2 nm by using co-evaporation of Co and carbon in an arc generator, and walls were made of single

thick atomic layer (Bethune et al. 1993). Additionally, Ajayan et al. also used co-catalyst for synthesis of SWCNTs with a diameter of 1–2 nm utilizing arc discharge in helium atmosphere. Ni is one of the most utilized catalysts in the synthesis of SWCNTs (Ajayan et al. 1993). Furthermore, Saito et al. fabricated single-layer CNTs involving platinum-group metals (Pd, Ir, Ru, Pt, Os, and Rh) using the arc discharge method. The results indicated that Pt, Pd, and Rh demonstrated catalytic activity for growing SWCNTs; however, other metals were not able to show the catalytic activity. The results demonstrated that the diameter size of core Rh-based CNTs was found to be 20–30 nm. However, the diameter size of core Pd-based SWCNTs was found to be 50–200 nm (Saito et al. 1996). Furthermore, Zhao et al. investigated the effect of catalysts in the fabrication of SWCNTs using modified arc discharge method. In this technique, helium buffer gas with a pressure of 500 torr, an arc current of 100 A, and a temperature of 600 °C was kept constant. Nevertheless, the chemical composition of catalysts such as Co-Ni, Ni-In, FeS-Ni-Mg + zeolite, FeS-Ni-Mg, La-Mg, Nb, La-Ni-Mg, Co-Mg, Ni-Y₂O₃, Ga-Mg, Co-Y₂O₃, and Mo-Co-Mg was varied in the experiment. All the aforementioned catalysts with a content of 3 wt% of mixture of powder graphite and catalyst were considered. The results indicated that the SWCNTs were produced at large scale using Co-Ni and Fe-Ni-Mg as the catalysts. However, instead of SWCNTs, the amorphous carbon on the soot was produced using Co-Mg, Ga-Mg, and La-Mg as catalysts. The rest of the catalysts were able to produce a very small amount of SWCNTs. From the results, it can be concluded that S and Fe or few transition metals can effectively initiate the growth of SWCNTs. However, bimetal powders of catalysts including Mg cannot activate the carbon clusters to form regular CNTs. In conclusion, it can be said that FeS and Ni or few transition metals as a catalyst can increase the production of SWCNTs. Therefore, suitable catalyst or a combination of catalysts plays a significant role in the production of SWCNTs (Zhao et al. 2019).

Compared to SWCNTs and MWCNTs, the fabrication methods for double-walled carbon nanotube (DWCNT) deposition are more complicated. However, a number of successful investigations have been carried out to produce DWCNTs using arc discharge method. For instance, Hutchinson et al. (2001) fabricated DWCNTs by arc discharge method using an atmosphere of hydrogen and argon mixture. Additionally, graphite rod was used as an anode with a diameter of 8.2 mm filled with catalysts. The mixture of Co, S, Ni, and Fe was utilized as a catalyst. With advancement, Sugai et al. (2003) developed DWCNTs with high quality by high-temperature pulsed arc discharge method using Y/Ni alloy catalysts. Furthermore, Huang et al. (2003) developed DWCNTs with high resistance to high-temperature (about 720 °C) oxidation in air without additional annealing even after acid treatment. This can be explained by in situ defect-healing effect of the bowl-like cathode and the absence of reactive gases during arc discharge.

The arc discharge method of MWCNTs is simple in case when all the growth conditions are ensured. With the approach of two electrodes, there is increase in the temperature, which is around 3000 °C to 4000 °C, following which there is a deposition of carbon in the form of black soot on the walls of the chamber and the negative electrodes, thus forming the MWCNTs. Moreover there is formation of some amount of amorphous carbon, fullerenes, and graphite sheets (Droppa Junior 2004; Teixeira 2010). The graphite usually water-cooled electrodes with diameters between 6 mm and 12 mm in a chamber filled with helium at subatmospheric pressure (Prasek et al. 2011). Additionally, direct current arc discharge technique is one of the most efficient techniques to fabricate carbon-based nanoplat-forms. Owing to its efficiency in fabrication and great commercial value, there was breakthrough in synthesis of C60 by direct current arc discharge method using helium atmosphere. This method can fabricate carbon-based nanoplat-forms like SWCNTs, MWCNTs, spherical carbon NPs, carbon nanohorns, and graphene. In this method, the aforementioned nanoplat-forms are collected from different positions. For exam-

ple, MWCNTs and graphene-based NPs are collected from anode deposit (Liang et al. 2014); however, SWCNTs are collected from cathode deposits (Liang et al. 2012). Additionally, Li et al. investigated that flow rate of H₂ buffer gas enhances or accelerates the growth process of graphene owing to which carbon-based nanomaterials deposit fast onto the chamber. The rapid flow of gas plays a significant role in separation and exfoliation of few-layer graphene to single-layer graphene (Li et al. 2014). Furthermore, Li et al. investigated that under N₂ atmosphere, the dimensions of carbon nanomaterials and the diameter and length of CNTs gradually decrease (Li et al. 2017). For instance, Zhang et al. investigated the controllable synthesis of carbon nanomaterials using direct current arc discharge method. The transmission electron microscopy (TEM) results indicated that spherical carbon NPs were obtained with size range of 30–80 nm under argon and nitrogen atmosphere as buffer gas. However, few graphene sheets were obtained when exposed to hydrogen atmosphere with a size ranging from 200 nm to 400 nm. The results indicated that atmosphere plays a significant role in controlling the morphology of carbon nanomaterials using direct current arc discharge technique. Furthermore, the researcher investigated the effect of gas pressure; the results indicated that spherical carbon nanomaterials produced were amorphous and aggregated under the argon atmosphere at 40 kPa and 50 kPa pressure due to low temperature gradient. However, when the argon pressure was increased to 70 kPa, the structure of carbon nanomaterials was clearly seen. In this case, long residence time of primary particles was responsible for aggregation. Increase in gas pressure leads to increase in temperature gradient, thereby facilitating carbon clusters to be deposited into the inner side of chamber by intense quenching (Zhang et al. 2019). However, many studies have utilized methane or hydrogen atmosphere in arc discharge method. Additionally, Wang et al. investigated the effect of various atmospheres on the morphology of CNTs. The researchers utilized direct current arc discharge of graphite electrodes in methane and helium. By evaporation under high arc current and high-pres-

sure methane gas, thick NTs embellished with many carbon NPs were obtained. However, utilizing anode with a diameter of 6 mm, an arc current of 20 A, and a methane gas pressure of around 50 torr can lead to the formation of long and thin MWCNTs (Wang et al. 1996).

Generally, the production of CNTs is the presence of impurities that affects the final properties of CNTs as material that could be used in some special applications. Hence, there are different studies carried out by the researchers dealing with this problem. The purification of CNTs can be carried out using various methods such as oxidation, filtration, annealing, ultrasonication, and thermal and acidic treatment (Prasek et al. 2011).

2.1.2 Laser Ablation or Laser Vaporization Technique

The CNT synthesis using laser ablation was first reported by Gao et al. in 1995. This technique for the fabrication of CNTs is similar to arc discharge technique. Both techniques have a similar principle, i.e., both methods utilize the condensation of carbon atoms generated from the vaporization of graphite targets (Rakhi 2019). However, this method includes the use of light source, which is absent in arc discharge process. According to the literature, laser ablation method can produce SWCNTs with greater than 90% of purity. This method includes various factors and rate-limiting steps, viz., type of gas, temperature, target material, light sources, and pressure which regulates the production of CNTs. Both carbon atom and graphite rod can act as carbon feedstock for nanotube growth when suspended in surrounding atmosphere in reaction chamber. The growth of CNTs in the reaction zone can be tuned by supply of carbon feedstock to ensure pure and defect-free CNT formation (Scott et al. 2001). Additionally, in this method, during the synthesis of CNTs, there is formation of fullerenes as an intermediate which further degrades into lower fragments by laser effects, and this disintegrated fragments of carbon act as feedstock for further growth of CNTs (Das et al. 2016). As SWCNTs have to be collected from water-cooled chamber of laser ablation process, SWCNT formation occurs near/at graphite target in the proximity of

laser attack surface. Greater target ablation can be achieved by laser irradiation by maintaining the appropriate temperature in reaction chamber (Das et al. 2016). The hot plasma plume is generated owing to high-temperature ablation of target material which supports proper and fast growth of SWCNTs in gas phase (Journet et al. 1997; Su and Zhang 2015). In this method, the graphite target is placed in a quartz tube surrounded by a furnace at around 1200 °C. The carbon soot produced by the vaporization of graphite electrode by continuous or pulse laser is transferred to a water-cooled Cu collector with the help of a constant flow of inert gas (helium and argon) (Scott et al. 2001; Dillon et al. 2000; Braidy et al. 2002; Guo et al. 1995). Furthermore, the growth of CNTs can be explained by “scooter” mechanism (Thess et al. 1996). According to this mechanism, on the open edge of nanotubes, a single transition metal atom (Co, Fe, or Ni) gets chemisorbed. This metal atom circulates around the open end of the tube and absorbs small carbon molecules leading to the formation of graphite-like sheet. The metal atom must be highly effective in catalyzing the nanotube growth, and it must have a sufficient high electronegativity so as to prevent the formation of fullerenes. The growth of CNTs continues until many catalyst atoms aggregate on the end of the nanotube. These formed large catalyst clusters will either become over-coated with sufficient carbon to terminate the catalytic activity or get detached from the tip. The CNT tip will thus be terminated either with a fullerene-like cap or with a catalyst particle (Rakhi 2019).

2.1.3 Chemical Vapor Deposition (CVD)

The synthesis of CNTs can also be fabricated by another method, i.e., CVD. CVD is the most intensively studied technique for the large production of various types of CNTs (Kumar et al. 2017; Ferreira et al. 2016). In this technique, the growth of the CNTs can be promoted by pyrolysis of hydrocarbons or heating the gaseous hydrocarbon sources, viz., methane, acetylene, ethylene, ethanol, and CO, to 600 °C to 1000 °C with transition metal catalysts such as Co, Fe, and Ni (Kohl 2001; Yaceman et al. 1993). CNTs

can be fabricated with controlled growth of nanotubes, good alignment, and production at larger scale using this method (Ren et al. 1999). Additionally, control over shell number and diameter can also be achieved (Hou et al. 2008). Several steps are involved in CVD. Firstly, substrates are coated with the help of catalyst metal particles. Secondly, the substrate is placed in the furnace where the catalyst metal particles are subjected to reduction treatment upon heating under NH_3 or H_2 . Then, the hydrogen gas or CO is let into a furnace. Hydrocarbon molecules are prone to catalytic decomposition which led to deposition of carbon on the catalyst particles at temperature ranging from $500\text{ }^\circ\text{C}$ to $1200\text{ }^\circ\text{C}$ (Rakhi 2019). The synthesis of SWCNTs requires higher temperature, i.e., $600\text{ }^\circ\text{C}$ to $1150\text{ }^\circ\text{C}$, in the presence of mixture of inert gases such as argon and H_2 , and the synthesis of MWCNTs requires lower temperature, i.e., $500\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$, in the presence of inert gas atmosphere (Kiselev et al. 2006). In this regard, the temperature required for the fabrication of CNTs using CVD is lower as compared to arc discharge method. The structure of MWCNTs obtained by arc discharge technique is significantly different from the structure generated from CVD. As compared to arc discharge, the CVD produces less crystalline MWCNTs and exhibits more defects in MWCNTs (Rakhi 2019). Depending on the catalyst, spiral growth of MWCNTs can occur in CVD. CVD can produce the MWCNTs with greater diameter with a particle size of 100 nm . This method involves the growth of nanotubes perpendicular to the substrate; thus, the length of MWCNTs can be determined easily (Grobert et al. 1999). There are several substrates utilized in this method such as stainless steel, Si, Ni, Cu, SiO_2 , glass or Ti/Cu/Si, tungsten foil, and graphite. Many studies also utilized mesoporous silica; it may show a templating role in guiding the initial growth of CNTs (Afolabi et al. 2011; Dumpala et al. 2011). CVD method is broadly classified into thermal enhanced CVD and plasma enhanced (catalytic) CVD, and is considered as the standard technique which is more feasible and economical for large-scale production of CNTs. There are several other methods used for the fabrication of CNTs, such

as microwave plasma CVD, oxygen-assisted CVD, radiofrequency CVD, and hot-filament CVD. In this technique, catalysts are responsible for decomposition of carbon source either via heat (thermal CVD) or plasma irradiation (plasma CVD) and its new nucleation to obtain CNTs (Prasek et al. 2011).

3 Manufacturing Techniques for Gold Nanoparticles

3.1 Chemical Reduction Technique

Turkevich method was one of the most widely accepted techniques that laid the foundation for further development in synthesis of gold nanoparticles. It is based on chemical reduction technique using sodium citrate under boiling conditions. Under boiling conditions, the sodium citrate was converted to dicarboxy acetone that played multiple roles as reducing agent, seeding agent, and stabilizing agent. The precursor chloroauric acid was boiled initially, and then the reducing agent was added to it. Briefly, in experimental setup, 95 ml of chloroauric acid solution (containing 5 mg of Au) was heated to the boiling point, and 5 ml of 1% sodium citrate solution was added to the boiling solution with good stirring. After about a minute, a very faint grayish pink or grayish blue tone appeared, and in a period of 5 min , it darkened to deep wine and red color (Turkevich et al. 1953).

Frens in 1973, during his study on different size-dependent phenomena like Brownian motion, light scattering, and sedimentation of particles, focused on synthesis of different sizes of gold nanoparticles by varying the concentration of citrate to reduce gold by using the traditional Turkevich method. As the ratio of reactants was changed, a change in nucleation and growth rate was expected. In the procedure described by Frens, 50 ml of 0.01% HAuCl_4 was heated to the boiling point, and 0.5 ml of 1% trisodium citrate was added. Initially, the solution turned bluish indicating nucleation, and then it turned wine red after 1 min . The formation of gold nanoparticles

completed after a period of 5 min. Neither prolonged heating after that period or increasing citrate concentration after that resulted in any change or formation of nanoparticles in suspension. The change in sizes was analyzed after adding different volumes of trisodium citrate after boiling (Frens 1973).

Sivaraman et al. modified the Turkevich process by reversing the order of addition of sodium citrate. The molar ratio (MR) was such that sodium citrate was at least five times more than HAuCl_4 . Keeping the overall reaction volume to 25 ml, sodium citrate of 5.2 mM of 24.75 ml was prepared and kept for boiling. To this 0.25 ml, 25.4 mM HAuCl_4 was added to get an overall concentration of 0.254 mM. This resulted in formation of monodisperse 10 nm gold colloids at less than 2 min as compared to standard addition where it took up to 10mins. It is essential that MR is at least 5, or else reversing the addition does not have any significant affect (Sivaraman et al. 2011).

3.2 Two-Phase System-Based Reduction

Brust and Schiffrin used a two-phase system to synthesize thiol decorated gold nanoparticles. Phase transfer from aqueous to organic phase was employed to get monodisperse gold nanoparticles. Initially, aqueous tetrachloroaurate solution was prepared and mixed with organic phase toluene containing tetraoctylammonium bromide (TOAB), which acted as a phase transfer agent. This was mixed thoroughly till tetrachloroaurate was transferred to organic phase to which dodecanethiol was added. To this, aqueous organic phase containing sodium borohydride was added that acted as a reducing agent. The organic phase was subsequently evaporated and recrystallized with ethanol (Brust et al. 1994).

3.2.1 Electro spray-Assisted Chemical Reduction

The effects of method of addition of precursor to the reducing agent solution were studied by Soliwoda wherein gold(III) chloride hydrate

was reduced with the help of octadecyl amino methanol (ODAM). ODA M here played the role of both reducing agent and stabilizer. The precursor solution of gold(III) chloride hydrate was prepared in isopropanol, and this was added to reductive solution consisting of ODA M in cyclohexane and formaldehyde prepared separately. The addition of precursor solution to reductive solution was done either by electro-spray method in which the precursor solution was sprayed as fine mist, or by capillary technique in which the precursor solution was added to reductive solution as a continuous flow. The gold nanoparticles produced by capillary method showed a polydisperse sample, and that produced by electro spray technique had a monodisperse and much smaller particle size (Soliwoda et al. 2015).

3.3 Surfactant-Aided Preparation of Gold Nanoparticles

Gold nanoparticles can be prepared using surfactant to get nanorods using electrochemical technique or seed-mediated technique. Electrochemical technique yields higher amount of gold nanorods as compared to seed-mediated growth method.

3.3.1 Seed-Mediated Growth Method

Seed-mediated growth method employs formation of seed solution initially, which is subsequently added to growth solution to allow the nanoparticles of required dimensions to grow. Nikoobakht et al. prepared seed solution of CTAB and HAuCl_4 in reducing agent solution NaBH_4 at room temperature. After this, HAuCl_4 was added in the growth solution consisting of CTAB and AgNO_3 and mixed. To this solution, a mild reducing agent (ascorbic acid) was added and mixed till color changed from dark yellow to colorless. To this solution, finally, the seed solution was added, which resulted in preparation of nanorods after 20mins of mixing at room temperature. The nanorods formed had an aspect ratio of length to width of 4.7 and had plasmon bands less than 850 nm.

In the same study, another approach to prepare nanorods of plasmon width more than 850 nm was utilized. A mixture of surfactants consisting of benzyldimethylhexadecylammonium chloride (BDAC) and CTAB was used to which AgNO_3 was added. Following this, HAuCl_4 was added and mixed gently, and to this solution, the mild reducing agent ascorbic acid was added. To this solution, the seed solution was added that resulted in completion of growth of nanorods after 1 h. The preparation by this method resulted in obtaining nanorods having plasmon width more than 850 nm and lesser nanospheres in the solution (Nikoobakht and El-Sayed 2003).

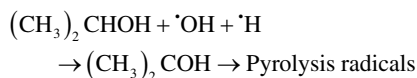
3.3.2 Electrochemical Method of Preparation

Electrochemical method of preparation employs the use of cathode and anode plates in an electrolyte solution. Yu et al. utilized gold plates as anode and platinum plates as cathode in an electrolyte surfactant solution hexadecyltrimethylammonium bromide (CTAB), which was cationic in nature. CTAB played the role of cationic electrolyte solution, rod-shaped inducing agent, and stabilizer of formed nanoparticles. A current of 3A for a time of 30 min was employed to produce electrolysis that resulted in conversion of bulk gold from anode to gold nanoparticles in the interface of cathode and electrolyte solution. The synthesis was carried out under ultrasonication at 38 °C. Acetone was added as cylinder-shape inducing agent in the micellar structure of CTAB that resulted in formation of Au nanorods (Yu et al. 1997).

3.4 Sonochemical-Assisted Reduction of Gold Nanoparticles

Sonochemical technique is based on the use of ultrasound to create microbubbles and cavitation in them due to high temperature leading to generation of radicals. In water, it leads to formation of H^+ and OH^- ions. The radicals reduce the Au^{3+} to Au^0 to form the gold nanoparticles. Okitsu

et al. found that the use of organic solvents in such conditions accelerated the formation of gold nanoparticles. The formation of gold nanoparticle was achieved by reducing NaAuCl_4 in the presence of 2-propanol. The ultrasonic bath was maintained at constant temperature at 200 kHz and 200 W. 2-Propanol is converted to reducing radical generated by pyrolysis in the presence of ultrasonic conditions (Okitsu et al. 2001).



These pyrolysis radicals reduce the Au^{3+} :

$$\begin{aligned} \text{gold(III)} + \text{reducing radical} &\rightarrow \text{gold(II)} \\ \text{gold(II)} + \text{reducing radical} &\rightarrow \text{gold(I)} \\ \text{gold(I)} + \text{reducing radical} &\rightarrow \text{gold(0)} \end{aligned}$$

3.4.1 Sonochemical-Assisted Chemical Reduction Using Ionic Liquid

Jin et al. used sonochemistry-based acoustic cavitation phenomenon to produce gold nanoparticles with the aid of H_2O_2 as a reducing agent in the presence of ionic liquid that acted as a gold capturing agent. Ionic liquids which have the ability to become miscible with organic as well as aqueous solution due to their dual characteristic to change their cationic and anionic character acted as green solvent. The thiol-linked ionic liquids could produce gold nanoparticles in the size range of 2–5 nm. Briefly, thiol-functionalized ionic liquid [1-(2', 3'-dimercaptoacetoxypropyl)-3-methylimidazolium, 3''-mercapto-1''-propanesulfonic acid (TFIL)] was treated with aqueous solution of HAuCl_4 (0.25 mM, 5 ml) at different concentrations corresponding to the Au/S molar ratio of 2:1, 1:1, 1:2, 1:4, and 1:8, respectively. After stirring for 5 min, reducing agent H_2O_2 was added to the ionic liquid solution containing precursor HAuCl_4 acid. Subsequently, the solution was placed in ultrasonic bath with circulating water at 25 °C. Sonochemical treatment of 40 KHz and 80 W was provided that resulted in the change of color of solution from light yellow to red. The prepared AuNP stayed stable for several weeks without precipitation. Characterization using TEM analysis revealed the least particle size was obtained in an Au/S

ratio of 1:2 wherein the size of particles was around 3 nm (Jin et al. 2007).

3.5 Green Method–Based Reduction

Metal ions of iron, silver, gold, etc., have been reduced using extracts of plants like *Jasminum sambac*, *Rosa rugosa*, *Magnolia kobus* and *Diospyros kaki*, *Ocimum sanctum*, *Aerva lanata*, *Coriandrum sativum*, *Phyllanthus*, and henna. The secondary metabolites present in these plants serve as both reducing agent and stabilizing agent after the AuNP is formed. In a particular study by Yulizaret al., the *Polyscias scutellaria* leaves acted to reduce precursor gold solution. Initially, the *Polyscias scutellaria* leaves were extracted in a mixture of organic and aqueous solvents. Different fractions of extract were then used to reduce H_{AuCl}₄ solution in the presence of UV radiation (Yulizar et al. 2017).

Dzimitrowicz et al. utilized plants of *Lamiaceae* family, *Mentha piperita*, *Salvia officinalis*, and *Melissa officinalis*, which are members of the *Nepetoideae* subfamily, to prepare extracts in the synthesis of gold nanoparticles. Components like hydroxyl group of phenolic compounds, secondary amines, and nitriles of the extract play the role of a reducing agent in reducing Au⁺³ to Au⁰. The leaves of the plants were extracted in double distilled water, and then the precursor solution H_{AuCl}₄ was treated with it. Further reduction in size of AuNP was anticipated by the use of direct current atmospheric pressure glow micro-discharge (dc-APGD). Discharge system was constructed of argon nozzle microjet which acted as anode and a flowing liquid as cathode which was the AuNP solution treated with plant extract. But the use of dc-APGD resulted in rise in particle size.

Apart from this, research on the use of several other plants and their extracts in production of gold nanoparticles has been carried out

(Table 18.1), with a perspective of obtaining a safe and biocompatible final product.

3.6 Physical Techniques to Prepare Gold Nanoparticles

Physical techniques are majorly top-down techniques that synthesize nanoparticles from larger sized bulk gold. Laser ablation is the most frequently employed technique to get AuNP from bulk gold. Unlike wet chemistry, initially, prepared gold nanoparticles were without surfactant, which led to highly polydisperse and aggregated nanoparticles. Mafune et al. synthesized sodium dodecyl sulfate stabilized laser-irradiated gold nanoparticles. Laser ablation at 1064 nm was employed in a surfactant SDS solution containing gold plate of 99.9% purity. The laser fluence used was of the power of 800 mJ/pulse/cm² that led to the formation of gold nanoparticles of 8.0 nm. This was further subjected to laser-induced fragmentation in which a laser irradiation of 532 nm was employed. The photons of this laser interacted with the electrons of the nanoparticles which led to heating of the nanoparticle to its boiling point. This leads to formation of fragments that allow the growth of nanoparticles (Mafuné et al. 2002).

Gold nanoparticles have also been prepared by similar laser ablation technique in pure water. Gold plates were exposed to laser wavelengths of 532 nm with different optical energy of 10–250 J/cm² and 5–40 J/cm² and then further exposed to laser of 532 nm and 266 nm. The laser implication on gold plate resulted in ablation-induced plume formation of gold atoms and clusters over the surface of the plate. These atoms and clusters tend to form embryonic nanoparticles and subsequently grow into nanoparticles. Gold nanoparticles having size less than 15 nm could be achieved by this process in pure water without the use of surfactants (Tarasenko et al. 2006).

Table 18.1 Gold nanoparticles synthesized by green method

Sr. no	Source	Description	Size of AuNP	Shape of AuNP	References
1	<i>Plumeria alba</i> flower extract (PAFE)	Aqueous extract of 1% PAFE and 5% PAFE was utilized in which the amine groups of the phytoconstituents acted as reducing agents.	Size with 1% PAFE = 28 ± 5.6 and size with 5% PAFE = 15.6 ± 3.4 nm	Spherical	Mata et al. (2016)
2	Fructus Amomi (cardamom)	Aqueous extract of Fructus Amomi and its constituents like phenols, tannins, and terpenoids were responsible for reduction and capping of gold nanoparticles.	269.9 nm	Spherical	Soshnikova et al. (2018)
3	Thermophilic filamentous fungi	The cell-free protein extracts, mycelia of the fungi were used for reduction of gold.	1–80 nm	Spherical and hexagonal	Molnár et al. (2018)
4	<i>Staphylococcus warneri</i>	The intracellular protein extract of <i>Staphylococcus warneri</i> was utilized to reduce the precursor gold solution.	81 nm	Spherical	Nag et al. (2018)
5	Marine red algae	Carrageenan oligosaccharide (CAO) from red algae acted as reducing agent and stabilizing agent on formed AuNP.	35 ± 8 nm	Ellipsoidal shape	Chen et al. (2018)
6	Hyperbranched polymers	Hyperbranched polyethylenimine-terminal isobutyramide (HPEI-IBAm) acted as a template and its amine group as reducing agent. Overall HPEI-IBAm also acted as a stabilizing agent for gold nanoparticles.	–	Spheroid shape	Liu et al. (2018)
7	Marine red seaweed <i>Gracilaria verrucosa</i>	Aqueous extract of <i>G. verrucosa</i> which contained various protein, phenolic, and aromatic constituents was responsible for reducing and stabilizing AuNP.	73.12 nm	60% spherical shapes and 20% triangular shapes were obtained	Chellapandian et al. (2019)
8	Vitamin B8 (inositol)	Inositol which is a strong reducing agent oxidizes itself to produce inosose form to reduce gold nanoparticles.	1.95 nm	Spherical	Halawa et al. (2018)
9	Mannan polysaccharide	Mannan polysaccharide acted as reducing, capping, as well as stabilizing agent for prepared AuNP.	9.18 ± 0.71 nm	Spherical	Uthaman et al. (2018)
10	<i>Ziziphus zizyphus</i>	Aqueous leaf extract of <i>Ziziphus zizyphus</i> and its phytoconstituents acted as reducing agent to form gold nanoparticles.	51.8 ± 0.8 nm	Majorly spherical shapes. Triangular and hexagonal platelet shaped also observed	Aljabali et al. (2018)

(continued)

Table 18.1 (continued)

Sr. no	Source	Description	Size of AuNP	Shape of AuNP	References
11	<i>Artemisia dracunculus</i> (tarragon)	The aqueous leaf extracts of <i>Artemisia dracunculus</i> which contained phenolic and flavonoid compounds were responsible for reducing the precursor gold solution.	Different shapes had different sizes and range was 30–100 nm	Spherical, hexagonal, triangular, nanobox shaped	Waclawek et al. (2018)
12	<i>Annona squamosa</i> L (AS)	The peel of fruit extracts of <i>Annona squamosa</i> L (AS) containing hydroxyl and carbonyl functional groups in its constituents acted as reducing as well as stabilizing agent for formation of gold nanoparticles in the presence of microwave irradiation.	5–10 nm	Spherical	Gangapuram et al. (2018)
13	<i>Eucalyptus globulus</i> and <i>Rosmarinus officinalis</i>	Aqueous extracts and natural essential oils of both <i>Eucalyptus globulus</i> and <i>Rosmarinus officinalis</i>	i. <i>E. globulus</i> – aqueous extract, 12.8 nm Natural oil, 42 nm ii. <i>R. officinalis</i> Aqueous extract, 8.66 nm Natural essential oil, 60.7 nm	i. Majorly spherical shaped for aqueous extracts ii. Essential oil extract showed majorly spherical but also triangular, rods, etc.	Dzimitrowicz et al. (2019)
14	<i>Chaenomeles sinensis</i>	Aqueous fruit extracts of <i>Chaenomeles sinensis</i> containing flavonoids and triterpenes were responsible for reducing gold solution and capping of AuNPs.	Core size 40 nm	Spherical, icosahedral	Oh et al. (2018)
15	<i>Platycodon grandiflorum</i>	The triterpenoid platycodon saponins from Platycodi Radix through aqueous extract were obtained and used in reducing precursor gold solution.	14.94 ± 2.14 nm	Spherical	Choi et al. (2018)

4 Manufacturing Techniques for Silver Nanoparticles

4.1 Wet Chemistry

4.1.1 Monosaccharide Reduction

There are many methods of AgNP manufacturing; one of those methods is monosaccharide reduction method. In this method, glucose, fructose, maltose, and maltodextrins are used as reducing agents, but sucrose is not used as a reducing agent. It is generally a simple technique which involves the single-step process to reduce

silver ion to AgNPs (Iravani et al. 2014). The use of reducing sugar along with alkali and AgNO₃ also yields AgNPs at high pH levels. The free aldehyde and ketone in reducing sugar facilitate monosaccharides to get oxidized into gluconate (El-Rafie et al. 2014).

Reducing agents must have a free ketone group which enables them to go through tautomerization (Darroudi et al. 2011). Whereas, if the aldehydes are present in the reducing agents, they will be trapped in cyclic form and do not qualify as reducing agents. For example, glucose has an aldehyde functional group that is able to reduce

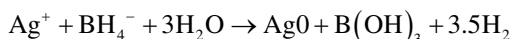
silver cations to silver atoms and is then oxidized to gluconic acid. The oxidation reaction for the sugars occurs in aqueous solutions. The capping agent is also not present when heated.

4.1.2 Citrate Reduction

AgNPs are prepared by sodium citrate reduction of AgNO_3 . One of the most common methods of manufacturing AgNPs is citrate reduction. M. C. Lea, in 1889, for the first time successfully developed a citrate-stabilized silver colloid (Graf et al. 2003). Using trisodium citrate, reduction of silver nitrate or silver perchlorate to colloidal silver can be done. The synthesis is normally done at higher temperature ($\sim 100^\circ\text{C}$) to increase the monodispersity of the particle considering the size and shape of the particles (Wojtysiak and Kudelski 2012). The citrate ion acts as a reducing agent as well as a capping agent, making it a valuable agent in the production of AgNPs owing to its very brief reaction period (Nowack et al. 2011). However, the silver particles have wide size distribution with different geometrical shapes. To obtain uniform size and shape particles, addition of stronger reducing agents to the reaction is often used (Wojtysiak and Kudelski 2012; Jin and Dong 2003).

4.1.3 Reduction by Sodium Borohydride

The following reaction takes place in the synthesis of AgNPs using NaBH_4 as a reducing agent:



Metal atom forms the nanoparticle nuclei, and this reduction mechanism is similar to that of the reduction using citrate. The advantage of using sodium borohydride over citrate is that it provides improved monodispersity of the nanoparticles. The rationale behind the improved monodispersity is the strong behavior of NaBH_4 than citrate as a reducing agent (Bahrig et al. 2014). The effect of reducing agent strength can be observed by studying a LaMer diagram which illustrates the nucleation and growth of nanoparticles. The development of nucleation and growth

through the LaMer mechanism is split into three steps:

- (I) Rapid growth in the concentration of free monomer in the solution.
- (II) The monomer undergoes burst nucleation which drastically decreases the concentration of free monomers in solution. The rate of this nucleation is described as “effectively infinite,” and after this point, there is almost no nucleation occurring due to the low concentration of monomers after this point.
- (III) Following nucleation, growth occurs under the control of the diffusion of the monomers through the solution (Thanh et al. 2014).

When weak reducing agent like citrate is used, there is simultaneous new nuclei formation and growth of earlier nuclei (Liu et al. 2009; Bastús et al. 2011). This is the main reason behind the decreased monodispersity of nuclei with citrates. A strong reducing agent like NaBH_4 provides nuclei formation in shorter duration of time and a good yield potential of monodispersed AgNPs (Song et al. 2009). Particles produced by using reducing agents must have surface stabilization in order to avoid unwanted particle cluster or bonding with each other, growth, or coarsening (Jana et al. 2001; Mallick et al. 2001). Since the nanoparticles have greater surface area to volume ratio, they may allow rapid agglomeration, and this can be prevented by diminishing the surface energy (Bahrig et al. 2014). This decrease in surface energy can be responded by adding an agent which will be adsorb to the surface of the nanoparticles and decreases the activity of the particle surface, thus inhibiting particle agglomeration according to the DLVO theory (Jana et al. 2001; Kim et al. 2005). Chemicals which adsorb to the nanoparticle surface are referred as ligands. For example, NaBH_4 in large quantities, polyvinylpyrrolidone (PVP) (Pierrat et al. 2007), SDS (Song et al. 2009; Pierrat et al. 2007), and dodecane thiol. There are number of general methods to eliminate nanoparticles from solution; this can be done by evaporating the solvent or by adding a chemical entity in the solution that decreases the

solubility of the nanoparticles. These methods lead to precipitation of the nanoparticles.

4.1.4 Polyol Process

This method of manufacturing is important where the size and the shape of the nanoparticles are the most important aspects and a narrow size distribution is desired. Generally, this synthesis begins with the heating of a polyol such as ethylene glycol, 1,5-pentanediol, or 1,2-propylene glycol, Ag^+ source, and a capping agent. The Ag^+ source is reduced by the polyol to form a colloidal nanoparticle (Wiley et al. 2004). This method is extremely susceptible to reaction parameters like change in temperature, chemical nature, and concentration of reactants (Leonard et al. 2005). Therefore, the size and shape of the nanoparticles can be controlled, and varied shapes of particles like quasi-spheres, pyramids, spheres, and wires can be produced by changing these variables (Leonard et al. 2005; Coskun et al. 2011; Smetana et al. 2005).

4.1.5 Seed-Mediated Process

This is a synthetic method which produces the small, stable nuclei in a separate chemical environment to a desired size and shape. It consists of two steps, namely, nucleation and growth. This synthetic process of manufacturing is more popular in controlling the morphology of nanoparticles; this can be easily achieved by varying the following factors in the process like ligand, nucleation reaction time, and concentration of reducing agent (Wu et al. 2016). The nucleation step of seed growth comprises the reduction of metal ions to metal atoms. Period of nucleation needs to be kept short in order to control the size distribution of the seeds and to get monodispersity of particles. This can be studied using the LaMer model (Thanh et al. 2014; LaMer and Dinegar 1950). Smaller nanoparticles referred to as seeds are typically stabilized by the ligands, which are usually small organic molecules attached to the surface of the nanoparticles that prevent the seed growth. Ligands prevent particle agglomeration by increasing the energy barrier of coagulation. Ligand binding attraction and selectivity can be utilized to monitor geometry and

growth of nanoparticles. The balance among attractive and repulsive forces in colloidal solutions is demonstrated by the DLVO theory (Kim et al. 2005). The ligand to be used in seed synthesis should have medium to low binding affinity to allow for exchange during the growth phase. Nano-seeds can be produced by positioning the seeds in a growth solution comprising a low concentration of a metal source and ligands. The ligands will readily exchange with active seed ligands and a low concentration of weak reducing agent. Growth is the outcome of the competition among surface energy and bulk energy. The balance between the energy of growth and dissolution is the rationale for uniform growth only on active seeds (Navrotsky 2004). Growth occurs by the accumulation of metal atoms from the growth solution to the seeds and ligand exchange between the growth ligands and the seed ligands (Liu et al. 2009). Ultimately, to control the size and geometry of the nanoparticles, parameters to be controlled include the concentration of metal precursor and ligand and reaction conditions. Anisotropic particles, i.e., nonspherical particles, can be the result of dissimilar growth in the particles (Bastús et al. 2011).

4.1.6 Light-Mediated Process

Generation of AgNPs from Ag^+ is mainly dependent upon the redox potential of the reducing agents (Wu et al. 2008). Agents with greater negative redox potential than Ag^+ will rapidly produce AgNPs by reducing the Ag^+ . It is proven that light has enormous capability to obtain, energize, and bring electrons from water to reduce various ions. This ability of light can be exploited to reduce Ag^+ . This light-mediated method supports the reduction of Ag^+ to Ag^0 and also helps prompt oxidation of Ag^0 to Ag_2O by release of oxygen through photolysis of water to produce biphasic AgNPs (Manikprabhu et al. 2016).

4.1.7 Silver Mirror Reaction

This manufacturing technique involves conversion of AgNO_3 to $\text{Ag}(\text{NH}_3)\text{OH}$ which is further reduced to colloidal silver in the presence of sugar containing aldehyde group (Qu and Dai 2005). The size and geometry of the produced

nanoparticles is a challenge to control, and frequently, the particles have wide distribution range. However, this manufacturing method is frequently used for thin coatings of silver nanoparticles onto surfaces (Li et al. 2012).

4.1.8 Ion Implant

This method is widely used to create AgNPs implanted in different surfaces like glass, polyurethane, silicone, polyethylene, and poly(methyl methacrylate). Particles are implanted onto the surface using high accelerating voltage with constant current density of ion beam which produces the monodisperse AgNPs. An additional increase in the ion beam dosage can reduce the nanoparticle size and density onto the target material, whereas an ion beam working at a high accelerating voltage with a slowly rising current density is found to yield an increase in the nanoparticle size (Popok et al. 2005). There are a few proposed mechanisms that can result in the lower nanoparticle size. These are destruction of AgNPs on collision to the material, splitting of the sample surface, particle fusion upon heating, and dissociation. It involves processes of diffusion and clustering which can be divided into separate subprocesses like implantation, diffusion, and growth. High temperature in implantation process will increase the impurity (Stepanov 2010). Implant temperature and ion beam current density are critical in order to achieve a monodisperse nanoparticle size. After implantation on the surface, the beam currents can be increased as the with increase in surface conductivity. This is followed by diffusion of nanoparticles in the material surface. This diffused particle now acts as a seed for the growth of the uniform monodispersed nanoparticles.

4.2 Biological Route

The major requirement for the production of silver nanoparticle through the biological source is resistance of the organism to silver ions (Rai and Duran 2011; Gahlawat and Choudhury 2019). The usual fabrication method of nanoparticles involves either “top-down” or “bottom-up strat-

egy” (Ahmed et al. 2016a). Biological method for synthesizing nanoparticles has become a promising substitute for established techniques (Singh et al. 2016). The microbial route provides an inexpensive and reliable way for producing nanoparticles with various sizes, shapes, compositions, and physicochemical compositions (Pattanayak et al. 2013). Biosynthesizing of nanoparticles does not require capping or stabilizing agent as the biomolecules perform the function themselves (Sintubin et al. 2012; Mukherjee et al. 2012; Zsembik 2005).

4.2.1 Synthesis of AgNPs Through Bacteria and Fungi

Microbial synthesis of AgNPs can occur intracellularly or extracellularly (Roy et al. 2019). Intracellular production of AgNPs occurs after the accumulation of silver inside the cell. Accumulation of silver leads to nucleation of AgNPs inside the live microbial cells. The cells are harvested for an optimum time before they are given special treatment to release synthesized nanoparticles (Roy et al. 2019). The extracellular secretion plays an important role in the synthesis of AgNPs. Although the exact mechanism is unknown, proposed mechanism involves reduction of the Ag^+ ions in the presence of several biomolecules such as enzymes, proteins, amino acids, polysaccharides, and vitamins. The most accepted mechanism is based on the presence of enzyme nitrate reductase (Jin and Dong 2003; Kumar et al. 2007; Pandian et al. 2010; Kalimuthu et al. 2008; Rai et al. 2008). Nitrate reductase, an enzyme of the nitrogen cycle, is responsible for the conversion of nitrate (NO_3^-) to nitrite (NO_2^-) (Durán et al. 2005). During this conversion, the generated electron gets transferred to free silver ion (Ag^+) reducing it to (Ag^0) (Iijima and Ichihashi 1993; Hutchison et al. 2001; Roy et al. 2019). The use of specific enzyme α -NADPH (nicotinamide adenine dinucleotide phosphate)-dependent nitrate reductase as a homogenous catalase in the synthesis of nanoparticles plays an important role by down-streaming the process (Zomorodian et al. 2016; Baymiller et al. 2017). The most preferred method for the biosynthesis is extracellular route as it does not require

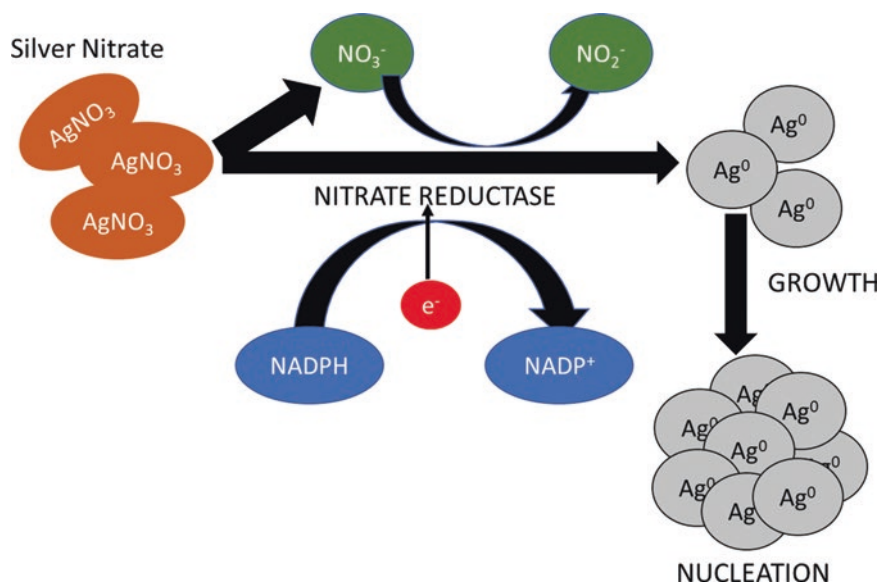


Fig. 18.1 Mechanism of nitrate reductase

extraction of prepared AgNPs from the cells (Guilger-Casagrande and de Lima 2019). Once the method for manufacturing gets established, high yield can be obtained by performing optimization of temperature, pH, biological load, etc. Figure 18.1 depicts the nitrate reductase mechanism helpful in the synthesis of AgNPs.

Bacteria

For the production of AgNPs from bacterial colonies, an Erlenmeyer flask containing Luria Bertani medium (LB) or Luria-Bertani medium plus nitrate (LBN) or Luria-Bertani medium plus lactose (LBE) or nutrient broth or Mueller-Hinton broth is used for sufficient time at 37 °C at 100 rpm. The obtained bacterial suspension is centrifuged between 5000 and 15,000 rpm for 10 min to obtain cell-free supernatant. Different concentration of silver nitrate solution with a maximum concentration of 1 mM is added to the supernatant solution in a different Erlenmeyer flask, and cell-free suspension is added to the flask. These flasks and their positive, negative controls are subjected to incubation at 37 °C at 100 rpm for sufficient time. Light or dark conditions are maintained depending upon the type of bacteria. Production of AgNPs can be confirmed

with visual color change from light brown to dark brown and through ultraviolet-visible spectroscopic method of analysis (Zomorodian et al. 2016; Baymiller et al. 2017; Guilger-Casagrande and de Lima 2019; Deljou and Goudarzi 2016; Eswari et al. 2018; Hamouda et al. 2019; Kumar et al. 2016; Sani et al. 2017; Das et al. 2014; Siddiqi et al. 2018; Abostate and Partila 2015; Baltazar-Encarnación et al. 2019; Khaleghi et al. 2017). AgNPs of varying shapes were developed by researchers working on different bacterial colonies. Most of the findings report that the AgNPs were spherical having a particle size between 1 and 50 nm (Gahlawat and Choudhury 2019). Some researchers reported that triangular and hexagonal AgNPs could also be obtained using *Pseudomonas stutzeri*, a special type of bacteria found in the silver mines (Klaus et al. 1999). The bacterial colonies which were explored for the synthesis of AgNPs include *Pseudomonas aeruginosa*, *Brevibacterium casei*, *Bacillus cereus*, *Gluconacetobacter xylinus*, *Streptomyces coelicolor*, *Bacillus subtilis*, *Salmonella typhimurium*, *Bacillus atrophaeus*, *Lactobacillus rhamnosus*, *Gordonia amicalis*, *Actinobacteria* sp., *Sinomonas mesophila*, *Nocardiopsis flavescens*, *Streptomyces griseo-*

planus, *Phanerochaete chrysosporium*, *Weissella oryzae*, *Serratia nematodiphila*, *Ochrobactrum* sp., *Shewanella loihica*, *Escherichia coli*, *Klebsiella pneumoniae*, and *Deinococcus radiodurans* (Gahlawat and Choudhury 2019; Zsembik 2005; Singh 2019).

Fungi

Fungi are an attractive and efficient source for the synthesis of AgNPs. They have a higher resistance to metals, and their extracellular protein and enzyme secretion is comparatively higher than bacterial colonies (Balaji et al. 2009; Netala et al. 2016; Du et al. 2015). Fungi produce a larger volume of biomass which is easy to filter and possess resistance to agitation and pressure in comparison to bacterial biomass (Gade et al. 2008; Velusamy et al. 2016). Fungi can be cultivated at large scale and lead to production of nanoparticles with controlled size and morphology (Velusamy et al. 2016; Ahluwalia et al. 2014; Satish et al. 2015). Similar to the process discussed for intracellular synthesis using bacterial colonies, metal precursor is added to the mycelial culture. Consequently, the internalization of precursor promotes formation of AgNPs. Nanoparticles are extracted by using chemical treatment, centrifugation, and filtration (Molnár et al. 2018; Castro-Longoria et al. 2011; Rajput et al. 2016).

Briefly, extracellular synthesis of AgNPs from fungi involves the growth of mycelium in Erlenmeyer flask over suitable media such as Vogel's Minimal Medium, Malt Extract Broth, Potato Dextrose Broth, seed medium, malt extract glucose yeast peptone media. The media are supplemented with glucose and peptone to enhance mycelium production. Fungi are allowed to grow for 48–96 h at 32 °C, and later growth media are separated by centrifugation at 5000 x g (rcf) to 10,000 x g for 10 min. The biomass is filtered through Whatman filter paper no. 1 or 3, resuspended in distilled water for 24–48 h, and filtered again. To the filtrate, silver nitrate at a maximum concentration of 1 mM is added and allowed to convert into AgNPs. The conversion is checked visually or by UV-Vis spectroscopic analysis between 400 and 450 nm (Gade et al. 2008;

Castro-Longoria et al. 2011; Singhal et al. 2011; Sintubin et al. 2009; Gudikandula et al. 2017; Vahabi et al. 2011; Gudikandula and Charya Maringanti 2016; Ottoni et al. 2017; Elamawi et al. 2018; Shaligram et al. 2009; Rose et al. 2019).

AgNPs synthesized from fungi have spherical, quasispheroidal, hexagonal, pseudospherical, cubical, cuboctahedral, icosahedral, rod-shaped, irregular, roughly spherical, oval, and ellipsoidal shapes. The typical particle size of nanoparticles can be as low as 5 nm and goes up to 200 nm (Rai and Duran 2011; Gahlawat and Choudhury 2019; Roy et al. 2019; Singh 2019; Ovais et al. 2018). The size of nanoparticles depends upon the species, temperature, pH, dispersion medium, and presence or absence of a capping agent (Khandel and Shahi 2018; Lee and Jun 2019). The fungal species explored till date for the synthesis are *Penicillium* sp., *Curvularia lunata*, *Raphanus sativus*, *Pleurotus ostreatus*, *Cryptococcus laurentii*, *Candida* sp., *Rhodotorula* sp., *Saccharomyces cerevisiae*, *Trichoderma harzianum*, *Aspergillus foetidus*, *Cladosporium* sp., and *Rhizopus stolonifer* (Rai and Duran 2011; Gahlawat and Choudhury 2019; Roy et al. 2019; Singh 2019; Ovais et al. 2018).

The production yield can be optimized by the culture conditions such as rate of agitation, time, temperature, pH, the quantity of biomass, and the concentration of silver nitrate (Zielonka and Klimek-Ochab 2017). Temperature plays a vital role in affecting the biomass and rate of conversion of Ag⁺ to Ag⁰. Certain microbes showed linear relation between temperature and amount of biomass. The time required for synthesis considerably decreases, and rate considerably increases with increase in temperature, indicating faster and scalable process (Elamawi et al. 2018; Almasaudi 2018; Birla et al. 2013). During the synthesis, adjustment of pH helps in modifying various characters of nanoparticles (Nayak et al. 2011). Higher pH allows higher stabilization of metal ion, resulting in increase in production at alkaline pH (Sintubin et al. 2009). Ideal concentration of silver nitrate as a precursor in extracellular scheme is 1 mM (Saxena et al. 2016). Some researchers have confirmed that smaller nanopar-

ticles are synthesized with lower levels of metal precursor; however, contrasting results were obtained with some species (Phanjom and Ahmed 2017). The amount of biomass may or may not affect the synthesis and characters of AgNPs. Some cases reported that lower biomass content yielded higher number of nanoparticles, while other reports showed the opposite (Elamawi et al. 2018; Birla et al. 2013; Balakumaran et al. 2015). Therefore, it is important to optimize the amount of biomass responsible for desired physicochemical characteristics of the AgNPs.

4.2.2 Biological Synthesis of AgNPs: Through Plants

Synthesis of AgNPs through plant source is eco-friendly, nonpathogenic, rapid, and economical. Plants have several primary and secondary metabolites such as proteins, amino acids, enzymes, carbohydrates, polysaccharides, alkaloids, tannins, phenolics, saponins, terpenoids, and vitamins (Kulkarni and Muddapur 2014; Sun et al. 2014). These agents act as reducing agents and stabilizers during the synthesis of AgNPs.

For the synthesis of AgNPs, the plant part is collected and washed multiple times such as twice or thrice with water which removes epiphyte, necrotic plants, and debris. The clean plant parts are dried in sunshade for sufficient time, specifically 10–15 days. The dried crushed plant parts with increased surface area are boiled with water to liberate plant components. The resulting solution is filtered to collect infusion media. The infusion media are then mixed with different concentrations of silver nitrate with a maximum level up to 1 mM. The conversion of Ag^+ ions to Ag^0 is monitored visually with time and quantified through UV-visible spectroscopic analysis between 400 and 450 nm (Hebbalalu et al. 2013; Eisa et al. 2019; Dhand et al. 2016; de Barros et al. 2018; Chung et al. 2016; Allafchian et al. 2016; Christopher et al. 2015; Ahmed et al. 2016b).

AgNPs have been prepared using various plant parts such as leaves, seeds, peel, fruit, rhizomes, whole plant, and inflorescence. Although most of the researchers obtained spherical AgNPs using plant extract, other shapes of the AgNPs

obtained were quasispheroidal, flower-shaped, triangular, pentagonal, hexagonal, circular, and quasilinear. The size of the AgNPs obtained was as low as 0.5 nm and as high as 350 nm. Some researchers have reported the biological activity of AgNPs from plant origin having a particle size below 50 nm (Sintubin et al. 2012; Allafchian et al. 2016). Some of the plants from which nanoparticles have been prepared are *Acorus calamus*, *Boerhaavia diffusa*, tea extract, *Tribulus terrestris*, *Cocos nucifera*, *Abutilon indicum*, *Cymbopogon citratus*, *Acalypha indica*, *Centella asiatica*, *Argyrea nervosa*, *Brassica rapa*, *Vitex negundo*, *Melia dubia*, *Thevetia peruviana*, *Pogostemon benghalensis*, *Trachyspermum ammi*, *Swietenia mahagoni*, *Moringa oleifera*, *Acalypha indica*, *Allium sativum*, aloe vera, *Eucalyptus* hybrid, *Datura metel*, *Carica papaya*, and *Nelumbo nucifera* (Allafchian et al. 2016).

4.3 Product and Functionalization

Production of AgNPs can be synthetically modified to yield nonspherical and functionalized AgNPs with materials such as silica. Functionalization benefit in producing surface-modified AgNPs includes different types of coatings, sizes, and shapes.

4.3.1 Anisotropic Structure

Anisotropic AgNPs can be prepared because silver exhibits localized surface plasmon resonance (LSPR) because of its smaller size.

Most of the methods used for the synthesis of AgNPs involve seed mediation approach, i.e., synthesizing smaller nanoparticle, usually between 3 and 5 nm. These AgNPs can be grown into larger nanoparticles having a triangular shape. Synthesis of these AgNPs involves physical admixture of AgNO_3 and sodium citrate in aqueous media followed by rapid addition of NaBH_4 . This initiates the production of AgNPs. An additional amount of AgNO_3 is added to the seed solution at low temperature yielding generation of triangular AgNPs with modulation of excess AgNO_3 with ascorbic acid (Dong et al. 2010). Photo mediation can also transform existing AgNPs into a triangular shape

by exposing the reaction mixture to high-intensity light (Xue et al. 2008).

This seed mediation process can be modified by altering the reducing as well as capping agent. Cube-shaped and rod-shaped AgNPs can be produced by using reducing agent such as ethylene glycol and PVP as capping agent (Chang et al. 2011; Zeng et al. 2010). Ageing AgNO₃ solution before being used benefits in the production of wire-shaped AgNPs (Chang et al. 2011).

4.3.2 Coating with Silica

AgNPs can be coated with silica by adsorbing PVP over the surface of AgNPs by mixing them with an aqueous solution of PVP. Separation of PVP-coated AgNPs can be mediated through centrifugation process. The coated AgNPs are stirred in a solution containing ethanol, ammonia, and tris(hydroxymethyl)methyl]-2-aminoethanesulfonic acid (TES) to promote formation of surrounding layer of ether-linked silicon dioxide. Modifications in the amount of TES can produce shells of varying thickness (Graf et al. 2003).

5 Concluding Remarks and Future Perspectives

Tremendous research is ongoing on CNTs, AuNPs, and AgNPs for the treatment of various diseases. However, the challenges like reproducibility, scalability, cost-effectiveness, etc., need to be strengthened for commercialization of these products in the market. AuNPs have been prepared by different methods, and the most facile method to prepare is by chemical reduction technique. Chemical reduction technique faces issues like reproducibility and concentration-dependent toxicity which needs to be monitored. Physical methods like laser ablation and sonochemical-assisted reduction give narrow particle size range as well but are expensive. Green method-based reduction has been amply explored as it does not use chemicals that can pose a risk of toxicity. Recent years have witnessed the use of AuNPs in imaging along with therapy which necessitates that the prepared AuNPs are pure, stable, and

nontoxic. Over the years, AgNPs have been synthesized from AgNO₃ using physical, chemical, and biological methods. These techniques involve the conversion of AgNO₃ to elemental state followed by growth of nanoparticles. Physical and chemical methods of AgNP synthesis are costly and involve usage of hazardous chemicals. In turn, biological method is helpful in synthesizing AgNPs, is cost-effective, stable, quick, and nontoxic, and produces higher yield. Biological methods can be modified to generate AgNPs having size between 0.5 nm and 500 nm and various shapes. However, there could be concerns about industrial scalability with these methods to provide uniform size and shape of nanoparticles. We expect that with the newer technology, polymers, and targeting, it is expected that more products will be available in the market by 2025.

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