Biological and Non-biological Methods for Silver Nanoparticles Synthesis

H. Reza Ghorbani,[a,*] A. Akbar Safekordi,[a] H. Attar,[a] and S. M. Rezayat Sorkhabadi[b]
[a]Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b]Department of Biotechnology, Pharmaceutical Branch, Islamic Azad University, Tehran, Iran

Original scientific paper
Received: April 14, 2011
Accepted: August 2, 2011

The synthesis of metallic nanoparticles is an active area of academic and, more significantly, applied research in nanotechnology. Several methods (chemical, physical or biological) have been introduced for the synthesis of these materials. In chemical reduction methods, for example, the reducing agent is a chemical solution, whereas in biological ones, the collection of enzymes especially nitrate reductase plays this role. This study is an attempt to present an overview of silver nanoparticles (Ag NPs) preparation by various methods including biological and non-biological. Focusing on the advantages and disadvantages of each method, the paper aims to discuss some fundamental issues about biological and non-biological methods for silver nanoparticles synthesis.

Key words:
Synthesis, silver nanoparticles, biological, chemical, physical

Introduction

Nanotechnology plays an increasingly crucial role in many key technologies of the new millennium.[1] The application of nanoscale materials and structures, usually ranging from 1 to 100 nm, is an emerging area of nanoscience and nanotechnology. Nanomaterials may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatment.[2]

Nanomaterials often show unique and considerably changed physical, chemical and biological properties compared to their macroscaled counterparts.[2] The noble metals, especially silver and gold, have attracted great attention due to their innumerable applications in various branches of science, namely catalysis, photonics, photography, chemical sensing, Surface Enhanced Raman Scattering (SERS), and most importantly, in the medicinal field as anti-microbial agents.[3] Colloidal silver is of particular interest because of its distinctive properties, such as good conductivity, chemical stability, catalytic and antibacterial activity.[2]

Silver nanoparticles have many important applications that include spectrally selective coating for solar energy absorption and intercalation material for electrical batteries, as optical receptors, polarizing filters, catalysts in chemical reaction, biolabelling, and as antimicrobial agents.[5]

There has been an extraordinary growth in nanoscience and technology in recent years, mainly due to both the development of new techniques to synthesize nanomaterials and the accessibility of tools for the classification and manipulation of nanoparticles.[4] Production of nanoparticles requires understanding the fundamentals of nanoscale chemistry and physics, as well as the know-how to commercialize them. Broadly speaking, there are two approaches to nanoparticle production: top-down and bottom-up. The former makes a material decrease its size from large to nanoscale, whereas the latter produces nanomaterials by starting from the atomic level.[6]

Generally, metal nanoparticles can be prepared and stabilized by chemical, physical and biological methods; the chemical approach, such as chemical reduction, electrochemical techniques, photochemical reduction[2] and pyrolysis and physical methods, such as Arc-discharge and physical vapor condensation (pvc)[7] is used. Living organisms have huge potential for the production of nanoparticles/nanodevices of wide applications. However, the elucidation of the exact mechanism of nanoparticles production using living organisms needs much more experimentation.[8]

Studies have shown that the size, morphology, stability and properties (chemical and physical) of the metal nanoparticles are influenced strongly by the experimental conditions, the kinetics of interaction of metal ions with reducing agents, and adsorption processes of stabilizing agent with metal nanoparticles. Hence, the design of a synthesis method in which the size, morphology, stability and properties are controlled has become a major field of interest.[2] In this paper the fundamentals, advantages, and disadvantages of each synthesis method are discussed.

*Corresponding author: E.mail: hamidghorbani6@gmail.com

Silver nanoparticles synthesis

Chemical methods

Chemical methods are usually used to synthesize silver nanoparticles and among them chemical reduction is the most frequently applied method for the preparation of stable, colloidal dispersions in water or organic solvents.[2] However, there is no special boundary between the different chemical methods to synthesize Ag NPs which can be classified into the following methods.

Chemical reduction

Typical reducing agents include polyols, $NaBH_4$, N_2H_4, sodium citrate and N,N-dimethyformamide.[9] Doubtless, in order to prevent aggregation of Ag NPs, it needs to stabilize with capping agents such as Sodium dodecyl sulphate (SDS), polyvinyl pyrrolidone (pvp), tri-sodium citrate.

Some of the chemical reducing reactions can be carried out at room temperature. However, most of them need elevated temperatures for a higher reaction rate.[9]

Thermal methods such as reduction of Ag^+ by dextrose[10] and/or hydrazine[11] as a reduction agent and the well-known Tollen's reduction with reducing agent of m-hydroxy banzaldehide[3] are from chemical reduction methods. Nanoparticle morphologies strongly depend on the temperature adopted during the synthesis. For example, Sarkar *et al.* have been able to synthesize both 2D and 3D Ag nanostructures having disk and globular morphology, by carrying out the simple silver-mirror reaction in the presence of an anionic surfactant.[3] Successful experiments with tri-sodium citrate as initial surfactant-cum-reducing agent followed by a secondary reducing agent i.e. sodium formaldehyde sulphoxylate (SFS) to silver nitrate were performed, which established a clear large-scale method for the preparation of silver nanopowder of particle size less than 50 nm.[12]

To develop a flower-like silver nanoarchitecture at room temperature with size 20 nm, ascorbic acid was used as the reducing agent while citric acid was found to play a key role in the nanostructure formation.[13,14]

In 2009, Janardhanan *et al*. synthesized silver nanoparticles by an aqueous chemical method with an organic base and with no external capping agents. Silver nanoparticles of 40–80 nm size are formed in the process of oxidation of glucose to gluconic acid by amine in the presence of silver nitrate, and the gluconic acid caps the nanosilver particle.[15] Silver nanoparticles have been synthesized by the polyol process with the assistance of supercritical carbon dioxide ($SCCO_2$), with silver nitrate used as the base material, polyvinyl pyrrolidone (PVP) as the stabilizer for the silver clusters, and ethylene glycol as the reducing agent and solvent. Polyvinyl pyrrolidone not only protected the nanosize silver particles from aggregation, but it also promoted nucleation. The silver nanoparticles synthesized by $SCCO_2$ were smaller and had a more even dispersion than those made under the same conditions by the conventional heating process.[16]

In 2006, colloidal silver nanoparticles had been synthesized using silver nitrate solubilized in the water core of one microemulsion as source of silver ions, hydrazine hydrate solubilized in the water core of another microemulsion as reducing agent, dodecane as the oil phase and sodium bis (2-ethylhexyl) sulfosuccinate (AOT) as the surfactant. The resultant nanosilver colloid had low toxicity and high stabilization, and the particles were all spherical with mean diameters in the range of 2–5 nm.[17,18] Akaighe *et al*. studied the formation of silver nanoparticles via reduction of silver ions (Ag^+) in the presence of humic acids (HAs) under various environmentally relevant conditions.[19]

Photochemical method (irradiation)

Ag NPs can be successfully synthesized by using a variety of irradiation methods. For example, laser irradiation of an aqueous solution of Ag salt and surfactant can fabricate Ag NPs of well defined shape and size distribution. No reducing agent is required in this method.[2] In 2007, silver nanoparticles having narrow size distribution were synthesized in ethylene glycol–water mixtures without the use of a stabilizer. They used pulse radiolysis method to produce nanoparticles by silver perchlorate.[20] Remita *et al*. show that X-ray irradiation of metal salt aqueous solutions in the absence of any stabilizer leads to the synthesis of metal nanoparticles, similarly to γ-ray irradiation. The synthesized nanoobjects appear spherical with a radius of about 14 nm.[21]

In 2007, reduction of silver ions was achieved using UV light instead of chemical materials. Silver nanoparticles were formed in a natural rubber matrix via photo reduction of film cast from natural rubber latex (NRL) containing silver salt; their size ranged 4 to 10 nm.[22]

Synthesis procedures using microwave irradiation have also been employed, and this method is known to have a faster heating rate than conventional heating through conduction and convection.[2] Yanagida, Komarneni and Liu have reported the use of a fixed frequency microwave (2.45 GHz) to synthesize platinum and silver nanoparticles. In 2005, Variable Frequency Microwave (VFM) synthesis of silver nanoparticles was discussed. It had shown that using fixed frequency microwave radiation

compared to the fixed frequency microwave, VFM provides more uniform heating, which can lead to more homogeneous nucleation. A 3 mL silver nitrate solution and a 3 mL PVP solution were together put into a 20 mL vial and stirred at room temperature for one minute. The stirring bar was then removed and the solution was placed into the variable frequency microwave oven chamber (VFM, MicroCure 2100, Lamda Technologies Co.) to react for 1 min at 160 °C. The center frequency of the microwave, the bandwidth and the sweeping time were 6.425 GHz, 1.15 GHz and 0.1 sec, respectively.[9]

Electrochemical method (electrolysis)

The electrolysis process has long been used for the reduction of metal ions. However, there are a few reports about using this method in the synthesis of metal nanoparticles, especially silver, however this could be classified in the synthesis of Ag NPs.

In 2006, silver nanospheres of average size in the range of ~11 nm were grown in large scale at room temperature by reducing silver nitrate in polyol solution using the electrochemical method in the presence of PVP and KNO_3. A rotating disk Ti electrode (6 mm diameter) was used as the cathode, and a 2 cm diameter Pt plate was used as the anode, which resulted in the formation of electro-deposited Ag° nanoparticles.[23]

Pyrolysis

Another method of synthesizing Ag nanoparticles is spray pyrolysis. In 2009, nanosilver powder with about 100 nm average grain size had been fabricated by spray pyrolysis, using $AgNO_3$ solution, 336 mL h^{-1} flux of $AgNO_3$ solution, 0.32 MPa flux of carrier gas and at 720 °C furnace set temperature.[24] In another work, nanosilver powder was synthesized from Ag/MgO composite powder fabricated by spray pyrolysis. The effects of furnace set temperature, concentration and molar ratio of the mixed solution, flux of the carrier gas on the morphology and particle size distribution of silver powder were investigated. An appropriate amount of commercial reagent $AgNO_3$ and $Mg(NO_3)_2$ was dissolved into deionized water to form an aqueous solution with a mass percentage of 40.0 %, and molar ratio of $AgNO_3$ and $Mg(NO_3)_2$ of 2:8. The solution was churned up and fed into nozzle with a solution feed rate of 500 mL h^{-1}, carrier gas flux of 0.30 MPa, and spray pyrolyzed in hot air of 790 °C. This was how the Ag/MgO composite powder was prepared. In order to remove MgO template from Ag/MgO composite powder, ammonium chloride (NH_4Cl) solution was used. The MgO obtained from $Mg(NO_3)_2$ by spray pyrolysis was used as template to inhibit nano-Ag growth by separating nano-Ag grains from each other.[25]

In another work by Sawai *et al*., metal silver nanoparticles were deposited on the surface and in the pores of activated carbon by supercritical water impregnation (SCWI). The aqueous feed solution was prepared by dissolving silver acetate $Ag(CH_3COO)$ in distilled water. All experiments were performed using batch type reactor. The reactor was loaded with silver acetate aqueous solution and activated carbon. The synthesis reactions were conducted under the condition of 673 K and 30 MPa. Reaction time varied from 1 to 10 min. Products were then washed out from the reactor several times with distilled water. No additional treatments such as thermal drying or filtration were carried out to avoid unexpected aggregation of the particles during post-processing.[26]

Physical methods

Chemical methods for metal nanoparticle fabrication usually involve toxic chemicals, which can be harmful to our environment. Although these methods may successfully produce pure silver nanoparticles, they require the use of stabilizers to protect the Ag nanoparticles against agglomeration. Additionally, these methods are usually expensive and potentially harmful to the environment.[27] In contrast, physical methods do not involve toxic chemicals and they are usually fast. Physical methods include physical vapor condensation (pvc) and Arc-discharge.

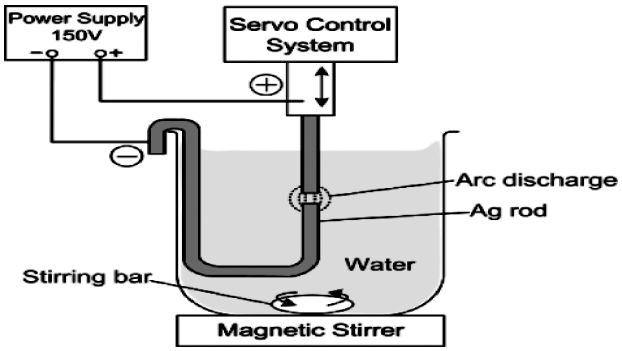
Physical vapor condensation (PVC)

In order to fabricate nanoparticles, the vaporization method has been frequently used, in which the target materials are vaporized by heat source and then rapidly condensed. The vaporization process can be subdivided into physical and chemical methods depending on whether the reaction is present. If the resultant nanoparticles have the same composition with the target materials, they are prepared by physical vapor condensation (PVC). However, nanoparticles having a different composition with the target are usually obtained by chemical vapor condensation (CVC), because the chemical reaction occurs between the vapor and other system components during the vaporization and condensation.[7]

Arc-discharge method

In 2008, a novel technique for preparing a nanosilver water suspension without surfactants and stabilizers was studied using the arc-discharge method. Silver wires (99.99 %) 1 mm in diameter submerged in deionized water (pH = 5.8, conduc-

tivity = 0.8–0.9 μS) were used as electrodes. The DC arc-discharge system (Fig. 1) consists of five main parts: i) two silver electrodes 1 mm in diameter, ii) a servo control system that maintains a constant distance between the electrodes, iii) a power supply system that controls the DC arc-discharge parameters, iv) a glass container with an electrode holder and deionized water to collect the silver colloids, v) a stirring system with magnetic stirrer and stirring bar.[27]



F i g . 1 – *DC arc-discharge system (reprinted from Ref. [27])*

In order to ionize the aqua medium between the electrodes, the DC arc-discharge system provides a pulse voltage of 70–100 V for 2–3 ms and then maintains a pulse of 20–40 V for around 10 μs. During the arc-discharge, the surface layer of the Ag wires evaporates and condenses in the water. The transparent solution converts to a characteristic pale yellow color and then a silver suspension is created.[27]

Table (1) summarizes the characteristics and operating conditions of Ag nanoparticles produced via physical and chemical (non-biological) methods.

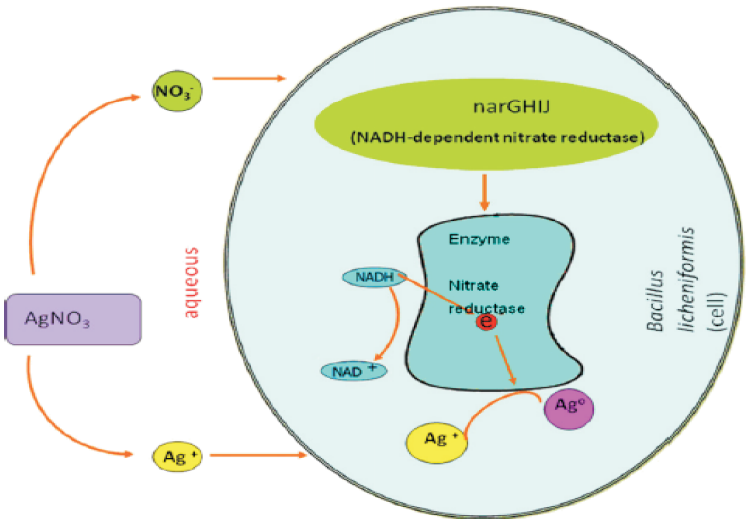
Biological methods

As mentioned above, living organisms such as bacteria, fungi and plants have huge potential for the production of metal nanoparticles. Microorganisms have recently been explored as potential biofactories for the synthesis of metallic nanoparticles such as CdS,[28] Ti/Ni,[29] titanate,[30] zirconia,[31] gold[32,33] and silver.[34,36] The use of microorganisms in the synthesis of nanoparticles emerges as an eco-friendly and exciting approach.[37,38] On the other hand, researchers have turned to biological synthesis because of the good control over size distribution of nanoparticles.[39,40]

Here, we summarize some of the organisms used in the biosynthesis of Ag nanomaterials and describe the properties that should be inherent for the production of Ag nanoparticles of desired characteristics (Table 2).

Use of bacteria

The first synthesis of Ag nanoparticles by bacteria was reported in 2000. Joerger *et al*. used *P. stutzeri* AG259 to synthesize Ag nanoparticles with size less than 200 nm. Bacteria were grown on Lennox L (LB) agar substrate, containing 50 mmol L^{-1} $AgNO_3$, at 30 °C for 48 h in the dark.[64] In 2008, biosynthesis of silver nanocrystals by *Bacillus licheniformis* was studied. Aqueous silver ions were reduced to silver nanoparticles when added to the biomass of *B. licheniformis*. This was indicated by the change in color from whitish-yellow to brown. The probable mechanism for the formation of silver nanoparticles involves the enzyme nitrate reductase.[42] (See Fig. 2)



F i g . 2 – *Possible mechanism for silver nanoparticles synthesis in B. licheniformis for the biosynthesis of nanoparticle involving NADH-dependent nitrate reductase enzyme that may convert Ag^+ to Ag^0 through electron shuttle enzymatic metal reduction process (reprinted from Ref. [42])*

Table 1 – *Synthesis of Ag nanoparticles by chemical and physical methods*

Method	Reducing agent	Stabilizer (surfactant)	Reaction time	Size range (nm)	Silver precursor	Operating condition	Reff/ year
Chemical reduction (thermal)	Dextrose	Polyvinyl pyrrolidone (pvp)	<1 h	22 ± 4.7	$AgNO_3$	t = 70 °C p = 1 atm	(10)/ 2008
Chemical reduction (Tollen)	m-Hydroxy benzaldehyde	Sodium dodecyl sulphate (SDS)	5–15 min	15–260	$AgNO_3$	t = 80–86°C p = 1 atm	(3)/ 2007
Chemical reduction	Sodium borohydrate ($NaHB_4$)	Surfactin (a lipopeptide biosurfactant)	5 min	3–28	$AgNO_3$	Room temp. p = 1 atm + mixing	(13)/ 2009
Chemical reduction	Tri-sodium citrate (initial) + sodium formaldehyde sulphoxylate (SFS) (secondary)	Tri-sodium citrate	<30 min	<50	$AgNO_3$	Room temp. p = 1 atm	(12)/ 2007
Chemical reduction	Ascorbic acid	–	<1.5 h	petal (diameter = 200–650 nm thickness = 20)	$AgNO_3$	Room temp. p = 1 atm	(14)/ 2009
Chemical reduction	Sodium borohydrate ($NaHB_4$)	Dodecanoic acid	1 h	Nanocrystal 7 nm	$AgNO_3$	Room temp. p = 1 atm	(69)/ 2006
Chemical reduction (thermal)	Hydrazine	–	3 day	2–10	$AgNO_3$	t = 60 °C p = 1 atm + mixing	(11)/ 2009
Chemical reduction (oxidation of glucose)	Glucose	Gluconic acid	–	40–80	$AgNO_3$	Room temp. p = 1 atm	(15)/ 2009
Chemical reduction (polyol process)	Ethylene glycol	Polyvinyl pyrrolidone (PVP)	–	Central cubic 5–25	$AgNO_3$	t = 100 °C p = 8.3 Mpa ($SCCO_2$)	(16)/ 2007
Chemical reduction (in situ)	N,N'-dimethylformamide (DMF)	–	24 h	<25	$AgNO_3$	Room temp. Under vacuum/N_2	(55)/ 2007
Chemical reduction (water/oil micro emulsion)	Hydrazine hydrate	Bis(2-ethylhexyl) sulfosuccinate (AOT)	2 h	Spherical 2–5	$AgNO_3$	Room temp. p = 1 atm + mixing	(17)/ 2006
Chemical reduction (water/oil micro emulsion)	Hydrazine hydrate	Bis(2-ethylhexyl) sulfosuccinate (AOT)	2 h	<1.6	$AgNO_3$	Room temp. p = 1 atm + mixing	
Photochemical reduction (pulse radiolysis)	Ethylene glycol	–	–	17–70	$AgClO_4$	irradiation	(20)/ 2007
Photochemical reduction (microwave radiation)	Ethylene glycol	Polyvinyl pyrrolidone (pvp)	–	5–10	$AgNO_3$	t = 160 °C frequency of the microwave = 6.425 GHz	(9)/ 2005
Photochemical reduction (photo reduction)	UV light instead of chemicals	–	20 min	4–10	$AgNO_3$	p = 1 atm	(22)/ 2007
Photo chemical reduction (X-ray radiolysis)	X-Ray	–	–	Spherical 28	Ag_2SO_4	p = 1 atm	(21)/ 2007
Spray pyrolysis	–	–	–	37.5–61.3 (average = 48)	$AgNO_3$	t = 790 °C p = 0.3 Mpa	(25)/ 2008
Spray pyrolysis	–	–	–	20–150 (average = 100)	$AgNO_3$	t = 620–820 °C p = 0.28–0.32 Mpa	(24)/ 2009
Chemical reaction (using supercritical water)	–	–	1–10 min	<20	$Ag(CH_3COO)$ Silver acetate aqueous	t = 673 °C p = 30 Mpa	(26)/ 2008
Electrochemical (polyol process)	Electrolysis cathode: titanium anode: Pt	Polyvinyl pyrrolidone (PVP)	–	Spherical 11	$AgNO_3$	Room temp. p = 1 atm	(23)/ 2006
Arc-discharge (physical method)	DC voltage between the electrodes	–	–	20–30	Silver wires (99.99 %) as electrodes	Room temp. p = 1 atm	(27)/ 2008

Table 2 – *Synthesis of Ag nanoparticles by different organisms*

Organism	Intracellular/Extracellular	Size range	Reaction time	Reff./year
A) Bacteria				
Bacillus licheniformis	Extracellular	50 nm	24 h	(42)/2008
Bacillus licheniformis	Extracellular	40–50 nm	24 h	(43)/2008
Klebsiella pneumonia		28.2–122 nm (52.5 nm)	5 min	(44)/2007
Escherichia coli		28.2–122 nm (52.5 nm)	5 min	(44)/2007
Enterobacter cloacae		28.2–122 nm (52.5 nm)	5 min	(44)/2007
P. stutzeri AG259		<200 nm	48 h	(64)/2000
Klebsiella pneumonia		1–6 nm (3 nm)	20 min	(45)/2009
Staphylococcus aureus	Extracellular	120–180 nm	5 min	(46)/2009
B) Fungi				
Fusarium oxysporum	Extracellular	20–50 nm	28 h	(51)/2005
Fusarium oxysporum	Extracellular	2–5 nm	28 h	(41)/2007
Fusarium oxysporum	Extracellular	5–15 nm	28 h	(4)/2003
Aspergillus fumigatus	Extracellular	5–25 nm	10 min	(5)/2006
Verticillium	Intracellular	25±12 nm	72 h	(49)/2001
Aspergillus flavus		8.92 ± 1.61 nm	72 h	(62)/2007
Nitrate Reductases (purified from Fusarium oxysporum)		10–25 nm	5 h	(60)/2007
Cladosporium cladosporioides	Extracellular	10–100 nm	78 h	(57)/2009
Penicillium fellutanus		5–25 nm	24 h	(58)/2009
C) Yeast				
MKY3	Extracellular	2–5 nm		(67)/2009
D) Plant				
Alfalfa Sprouts		2–20 nm	24 h	(4)/2002
Pelargonium graveolens	Extracellular	16–40 nm	24 h	(68)/2003
Azadirachta indica (Neem)	Extracellular	5–35 nm	4 h	(52)/2004
Jatropha curcas (latex)		20–40 nm	4 h	(54)/2009
Aloe vera	Extracellular	15.2 ± 4.2 nm		(65)/2006
Cinnamomum camphora	Extracellular	55–80 nm		(73)/2007
Emblica officinalis		10–25 nm		(71)/2005
Apiin (from henna leaves)		21–39 nm	~1 min	(59)/2009
Ocimum		3–20 nm		(72)/2011
Cassia auriculata	Extracellular	20–40 nm	48 h	(74)/2011

In 2008, silver nanoparticles in the range of 50 nm were synthesized by the supernatant of *B. licheniformis* when silver nitrate was added to it. The synthesized silver nanoparticles were highly stable. Also, the time required for reaction completion was 24 hour.[43] Biosynthesis of silver nanoparticles using microorganisms is rather slow. However, finding microorganisms to synthesize Ag nanoparticles is an important aspect. Shahverdi *et al*. reported on the rapid synthesis of metallic nanoparticles of silver using the reduction of aqueous Ag^+ ion using the culture supernatants of *Klebsiella pneumonia*, *Escherichia coli,*[61,63] and *Enterobacter cloacae* (Enterobacteriacae). The synthetic process was quite fast and silver nanoparticles were formed within 5 min of the silver ion coming into contact with the cell filtrate.[44] However, the culture supernatants of different bacteria from Enterobacteriacae are potential candidates for the rapid synthesis of silver nanoparticles. In 2009, investigated was the effect of different visible-light irradiation on the formation of silver nanoparticles from silver nitrate using the culture supernatant of *Klebsiella pneumonia*. In addition, the study experimentally investigated the liquid mixing process effect on silver nanoparticle synthesis by visible light irradiation. That study successfully synthesized evenly dispersed silver nanoparticles of uniform size and shape in the range of 1–6 nm and average size of 3 nm.[45] Another report focused on the synthesis of metallic bio-nanoparticles of silver using a reduction of aqueous Ag^+ ion with the culture supernatants of *Staphylococcus aureus*. The observation indicated that the reduction of the Ag^+ ions took place extracellularly. Also, the reaction between this supernatant and Ag^+ ions was carried out in bright conditions for 5 minutes.[46]

Use of fungi

The use of fungi in the synthesis of nanoparticles is a relatively recent addition to the list of microorganisms. The use of fungi is potentially exciting since they secrete large amounts of enzymes and are simpler to deal with in the laboratory.[47,48] In 2001, a novel biological method for the synthesis of silver nanoparticles using the fungus *Verticillium* was reported. Exposure of the fungal biomass to aqueous Ag^+ ions resulted in the intracellular reduction of the metal ions and formation of silver nanoparticles of dimensions 25 ± 12 nm.[49] In another investigation, Ahmad *et al*. observed that aqueous silver ions when exposed to the fungus *Fusarium oxysporum* are reduced in solution, thereby leading to the formation of an extremely stable silver hydrosol. The silver nanoparticles were in the range of 5–15 nm in dimension and were stabilized in solution by proteins secreted by the fungus. It is believed that the reduction of the metal ions occurs by an enzymatic process.[50] Extracellular production of metal nanoparticles by several strains of the fungus *Fusarium oxysporum* was carried out by Duran *et al*. The *F. oxysporum* strains used were the following: O6 SD, 07 SD, 534, 9114 and 91248 out of which the 07SD strain appeared as the most efficient one in the silver nanoparticles production. Apparently, the different efficiencies are related to the reductase and/or to the quinine generation.[51,52]

In 2007, investigated was the antibacterial effect of silver nanoparticles produced by fungal process on Textile Fabrics. In that work, the extracellular production of silver nanoparticles by *F. oxysporum* and its antimicrobial effect when incorporated into cotton fabrics against S. aureus were studied.[41] Vigneshwaran *et al*. reported biological synthesis of silver nanoparticles using the fungus *Aspergillus flavus*. The transmission electron micrographs of dislodged nanoparticles in aqueous solution showed the production of reasonably monodisperse silver nanoparticles (average particle size: 8.92 ± 1.61 nm) by the fungus.[62]

Another investigation for the first time detailed the use of enzyme nitrate reductase purified from *Fusarium oxysporum* and phytochelatin for the synthesis of silver nanoparticles in vitro in the presence of a co-factor, a-NADPH. For the synthesis of silver nanoparticles, freshly prepared $AgNO_3$, phytochelatin, 4-hydroxyquinoline and a-NADPH were incubated with nitrate reductase at 25 °C for 5 h under anaerobic conditions. The biggest advantage of this protocol based on purified enzyme can be the development of a new approach for the synthesis of nanomaterials over a range of chemical compositions, shapes as well as their separation.[56,60]

Balaji *et al*. (2009) reported the extracellular biosynthesis of silver nanoparticles (AgNP) employing the fungus *Cladosporium cladosporioides*. The AgNP were 10–100 nm in dimensions as measured by TEM images.[57] In 2009, in vitro biosynthesis of silver nanoparticles was achieved using $AgNO_3$ as a substrate by Penicillium fellutanum isolated from coastal mangrove sediment. The biosynthesis of nanoparticles was the maximum when the culture filtrate was treated with 1.0 mmol L^{-1} $AgNO_3$, maintained at 0.3 % NaCl and pH of 6.0, incubated at 5°C for 24 h.[58] Filamentous fungi are a very good candidate for the synthesis of metal nanoparticles. Hence, Bhainsa *et al*. investigated extracellular biosynthesis of silver nanoparticles using the filamentous fungus, *Aspergillus fumigatus*. The synthesis process was quite fast and silver nanoparticles were formed within minutes of the silver ion coming into contact with the cell filtrate.[5]

Then the mechanistic aspects are still an open question, however, this process occurs in the fungal case probably either by reductase action or by electron shuttle quinones, or both.[51,53]

Use of yeast

Few, if any, reports exist about yeast-mediated synthesis of metallic nanoparticles. In an individual report, silver nanoparticles in the size range of 2–5 nm were synthesized extracellularly by a silver-tolerant yeast strain MKY3, when challenged with 1 mmol L^{-1} soluble silver in the log phase of growth. This work was demonstrated by Kowshik *et al*. in 2002.[67]

Use of plants

Whereas microorganisms such as bacteria, actinomycetes, yeasts, and fungi continue to be researched and investigated in the synthesis of metallic nanoparticles, the use of parts or whole plants for similar nanoparticle biosynthesis methodologies is an exciting possibility that is relatively unexplored and underexploited.

The coalescence of the silver nanoparticles could represent a self-protective mechanism against possible toxic effects of excess silver inside the living plant.[66] The results of an investigation showed that alfalfa roots are capable of absorbing silver as Ag^0 from the agar medium and then transferring it to the shoot of the plant in the same oxidation state. Gardea *et al*. used a natural source (Alfalfa Sprouts) for the synthesis of silver nanoparticles. The particles are usually found in specific areas in the plants. These areas are possibly related to the internal anatomy of alfalfa stems. The plants absorb Ag atoms through specific channels, and consequently, the Ag nucleates or coalesces as particles inside these channels. However, nanoparticles also were found outside the channels. This observation was either due to a collapse in the plant structure, allowing the silver nanoparticles to move out of these original areas, or possibly due to silver diffusing and nucleating nanoparticles in different places.[4]

Shankar *et al*. reported on the use of Geranium (Pelargonium graveolens) leaf extract in the extracellular synthesis of silver nanoparticles. On treating aqueous silver nitrate solution with geranium leaf extract, rapid reduction of the silver ions was observed leading to the formation of highly stable, crystalline silver nanoparticles in solution. The AgNP were 16–40 nm in dimensions and the time required for reaction completion was 24 hour.[68] In year 2004, they again investigated the use of Neem (Azadirachta indica) leaf broth in the extracellular synthesis of pure metallic silver. The reduction of the metal ions occurred fairly rapidly; more than 90 % of reduction of Ag^+ ions was completed within 4 h after addition of the Neem leaf broth to the metal ion solutions.[52,70]

In 2009, silver nanoparticles were successfully synthesized from $AgNO_3$ through a simple green route using the latex of Jatropha curcas as reducing and capping agent. Crude latex was obtained by cutting the green stems of Jatropha curcas plants. The mixture was heated at 85 °C with constant stirring for 4 hours in oil bath and silver nanoparticles were obtained gradually.[54] Kasthuri *et al*. reported a novel strategy for the biological synthesis of quasi-spherical silver nanoparticles by using Apiin as reducing and stabilizing agent. The size and shape of the nanoparticles were controlled by varying the ratio of metal salts to Apiin compound in the reaction medium. TEM photograph confirming the average size of the silver nanoparticles was found to be at 21 and 39 nm. Under continuous stirring conditions, after 1 min, the light yellow colour of $AgNO_3$ solution turned to pink indicating the formation of silver nanoparticles.[59] In 2011, Silver nanoparticles were synthesized using Ocimum leaf extract. The size of the silver nanoparticles was estimated as 3–20 nm.[72] In another study, the bio-reduction of aqueous silver ions with the leaf extract of Cassia auriculata was demonstrated. The complete reduction of silver ions was observed after 48 h of reaction at 300 °C under shaking condition.[74]

Conclusions

Ag NPs are the most important NPs because of their applications. These nanoparticles have many important applications that include spectrally selective coating for solar energy absorption and intercalation material for electrical batteries, as optical receptors, polarizing filters, catalysts in chemical reaction, biolabelling and as antimicrobial agents. Application of silver nanoparticles in these fields is dependent on the ability to synthesize particles with different chemical composition, shape, size, and monodispersity.

Generally, there are various methods to synthesize Ag NPs. Many methods are based on the reduction of Ag^+ ions in a water solution. These methods use a reducing agent for the reduction of Ag^+ ions in solution (especially). In chemical reduction methods, the reducing agent is a chemical solution such as polyols, $NaBH_4$, N_2H_4, sodium citrate, and N, N-dimethyformamide, whereas in biological methods, collection of enzymes especially nitrate reductase play such role. Spray pyrolysis methods are carried out in operating conditions of high temperature and pressure; electrochemical

methods are based on electrolysis of solution. In the physical method of Arc-discharge, the Ag metal evaporates in the pure water by electric voltage, then it condenses and produces Ag NPs.

From among the mentioned methods, chemical methods have mostly been applied to synthesize Ag NPs. However, nowadays, this method is used to synthesize Ag NPs in large scales. In some chemical methods, a stabilizer (surfactant) is added to the first solution to prevent agglomeration of Ag NPs, whereas in biological methods there is no need to add a stabilizing agent. Toxicity is a disadvantage of the chemical methods. In addition, many of these methods are energy-intensive, although Ag NPs are synthesized fast. In contrast, biological methods, as an alternative, are carried out in environmental conditions and consume no energy. Of course, the time required to synthesize Ag NPs is longer compared to chemical methods, although the synthesis time has recently decreased with finding suitable microorganisms or organisms.

In addition, the current interest in nanomaterials is focused on the controllable properties of size and shape because the optical, electronic, magnetic, and catalytic properties of metal nanoparticles strongly depend on their sizes and shapes. Controllability in biological methods is far easier to achieve than with other methods. Therefore, the use of microorganisms in the synthesis of nanoparticles emerges as an eco-friendly and exciting approach. In addition, the use of bacteria as a novel biotechnology to facilitate the production of nanoparticles is in its infancy.

References

1. *Mandal, D., Bolander, M. E., Mukhopadhyay, D., Sarkar, G., Mukherjee, P.,* Appl. Microbiol. Biotechnol. **69** (2006) 485.
2. *Sharma, V. K., Yngard, R. A., Lin, Y.*, Adv. Colloid Interfac. **145** (2009) 83.
3. *Sarkar, S., Jana, A. D., Samanta, S. K., Mostafa, G.*, Polyhedron **26** (2007) 4419.
4. *Gardea-Torresdey, J. L., Gomez, E., Peralta-Videa, J. R., Parsons, G. J., Troiani, H., Jose-Yacama, M.*, Langmuir **19** (2003) 1357.
5. *Bhainsa, K. C., D'Souza, S. F.*, Colloid Surface B **47** (2006) 160.
6. *Charinpanitkul, T., Faungnawakij, K., Tanthapanichakoon, W.*, Adv. Powder Technol. **19** (2008) 443.
7. *Tavakoli, A., Sohrabi, M., Kargari, A.*, Chem. Pap. **61** (2007) 151.
8. *Mohanpuria, P., Rana, N. K., Yadav, S. K.*, J. Nanopart. Res. **10** (2008) 507.
9. *Jiang, H., Moon, K. S., Zhang, Z., Pothukuchi, S., Wong, C. P.*, J. Nanopart. Res. **8** (2006) 117.
10. *Lu, Y., Chou, K.*, J. Chin Inst. Chem. Eng. **39** (2008) 673.
11. *Torres-Cisneros, M., Velásquez-Ordónez, C., Sánchez-Mondragón, J., Campero, A., Ibarra-Manzano, O. G., May-Arrioja, D. A., Plascencia-Mora, H., Espinoza-Calderón, A., Sukhoivanov, I.*, Microelectr. J. **40** (2009) 618.
12. *Khanna, P. K., Singh, N., Kulkarni, D., Deshmukh, S., Charan, S., Adhyapak, P. V.*, Mater. Lett. **61** (2007) 3366.
13. *Reddy, A. S., Chen, C. Y., Baker, S. C., Chen, C. C., Jean, J. S., Fan, C. W., Chen, H. R., Wang, J. C.,* Mater. Lett. **63** (2009) 1227.
14. *Schabes-Retchkiman, P. S., Canizal, G., Herrera-Becerra, R., Zorrilla, C., Liu, H. B.,* J. A. Opt. Mater. **29** (2006) 95.
15. *Janardhanan, R., Karuppaiah, M., Hebalkar, N., Rao, T. N.,* Polyhedron **28** (2009) 2522.
16. *Chih, Y. W., Cheng, W. T.*, Mater. Sci. Eng. B **145** (2007) 67.
17. *Zhang, W., Qiao, X., Chen, J.*, Colloid Surface A **299** (2007) 22.
18. *Zhang, W., Qiao, X., Chen, J.*, Chem. Phys. **330** (2006) 495.
19. Akaig*he, N., Maccuspie, R. I., Navarro, D. A., Aga, D. S., Banerjee, S., Sohn, M., Sharma, V. K.,* Environ. Sci. Technol. **45** (2011) 3895.
20. *Jacob, J. A., Kapoor, S., Biswas, N., Mukherjee, T.*, Colloid Surface A **301** (2007) 329.
21. *Remita, S., Fontaine, P., Lacaze, E., Borensztein, Y., Sellame, H., Farha, R., Rochas, C., Goldmann, M.,* Nucl. Instrum. Meth. B **263** (2007) 436.
22. *Abu Bakar, N. H. H., Ismail, J., Abu Bakar, M.,* Mater. Chem. Phys. **104** (2007) 276.
23. *Lim, P. Y., Liu, R. S., She, P. L., Hung, C. F., Shih, H. C.,* Chem. Phys. Lett. **420** (2006) 304.
24. *Qiaoxin, Z., Hao, L., Xiaohui, W., Xiaoliang, S., Xinglong, D.,* J. Wuhan Univ. Technol. **24** (2009) 871.
25. *Shia, X., Wang, S., Duan, X., Zhang, Q.*, Mater. Chem. Phys. **112** (2008) 1110.
26. *Sawai, O., Oshima, Y.*, J. Supercrit. Fluid **47** (2008) 240.
27. *Tien, D. C., Liao, C. Y., Huang, J. C., Tseng, K. H., Lung, J. K., Tsung, T. T., Kao, W. S., Tsai, T. H., Cheng, T. W., Yu, B. S., Lin, H. M., Stobinski, L.,* Rev. Adv. Mater. Sci. **18** (2008) 750.
28. *Kowshik, M., Deshmukh, N., Vogel, W., Urban, J., Kulkarni, S. K., Paknikar, M. K.*, Biotechnol. Bioeng. **28** (2002) 583.
29. *Mukherjee, P., Ahmad, A., Mandal, D., Senapati, S., Sainkar, S. R., Khan, M. L., Ramani, R., Parischa, R., Ajayakumar, P. V., Alam, M., Sastry, M., Kumar, R.,* Angew. Chem. Int. Ed. **40** (2001) 3585.
30. *Bansal, V., Poddar, P., Ahmad, A., Sastry, M.,* J. Am. Chem. Soc. **128** (2006) 11958.
31. *Bansal, V., Rautaray, D., Ahmad, A., Sastry, M.*, J. Mater. Chem. **14** (2004) 3303.
32. *Ankamwar, B., Chaudhary, M., Sastry, M.*, Syn. React. Inorg. Met. Nano **35** (2005) 26.
33. *Armendariz, V., Herrera, I., Peralta-Videa, J. R., Jose-Yacaman, M., Troiani, H., Santiago, P., Gardea-Torresdey, J. R.,* J. Nanopart. Res. **6** (2004) 377.
34. *Gericke, M., Pinches, A.*, Hydrometallurgy **83** (2006) 132.
35. *Roh, Y., Lauf, R. L., McMillan, A. D., Zhang, C., Rawn, C. J., Bai, J., Phelps, J. L.,* Solid State Commun. **8** (2001) 529.
36. *Sastry, M., Ahmad, A., Islam Khan, M., Kumar, R.,* Curr. Sci. India **85** (2003) 162.
37. *Salata, O.,* J. Nanobiotechnol. **2** (2004) 3.
38. *He, S., Guo, Z., Zhang, Y., Zhang, S., Wang, J., Gu, N.,* Mater. Lett. **61** (2007) 3984.
39. *Ahmad, A., Senapati, S., Islam Khan, M., Kumar, R., Sastry, M.,* Langmuir **19** (2003) 3550.

40. *Bansal, V., Rautaray, D., Bharde, A., Ahire, K., Sanyal, A., Ahmad, A., Sastry, M.,* J. Mater. Chem. **15** (2005) 2583.
41. *Durán, N., Marcato, P. D., Alves, O. L., DeSouza, G. L. H., Esposito, E.,* J. Biomed. Nanotechnol. **3** (2007) 203.
42. *Kalimuthu, K., Babu, R. S., Venkataraman, D., Bilal, M., Gurunathan, S.,* Colloid Surface B **65** (2008) 150.
43. *Kalishwaralal, K., Deepak, V., Ramkumarpandian, S., Nellaiah, H., Sangiliyandi, G.,* Mater. Lett. **62** (2008) 4411.
44. *Shahverdi, A. R., Minaeian, S., Shahverdi, H. R., Jamalifar, H., Nohi, A.,* Process Biochem. **42** (2007) 919.
45. *Mokhtari, N., Daneshpajouh, S., Seyedbagheri, S., Atashdehghan, R., Abdi, K., Sarkar, S., Minaian, S., Shahverdi, H. R., Shahverdi, A. R.,* Mater Res. Bull. **44** (2009) 1415.
46. *Nanda, A., Saravanan, M.,* Nanomed. **5** (2009) 452.
47. *He, S., Zhang, Y., Guo, Z., Gu, N.,* Biotechnol. Prog. **24** (2008) 476.
48. *Hong, L., Li, Q., Lin, H., Li, Y.,* Mater. Res. Bull. **44** (2009) 1201.
49. *Mukherjee, P., Ahmad, A., Mandal, D., Senapati, S., Sainkar, S. R., Khan, M. L., Parishcha, R., Ajaykumar, P. V., Alam, M., Kumar, R., Sastry M.,* Nano Lett. **1** (2001) 515.
50. *Ahmad, A., Mukherjee, P., Senapati, S., Mandal, D., Islam Khan, M., Kumar, R., Sastr, M.,* Colloid Surface B **28** (2003) 313.
51. *Durán, N., Marcato, P. D., Alves, O. L., DeSouza, G. L. H., Esposito, E.,* J. Nanobiotechnol. **3** (2005) 8.
52. *Ahmad, A., Mukherjee, P., Mandal, D., Senapati, S., Islam Khan, M., Kumar, R., Sastry, M.*, J. Am. Chem. Soc. **124** (2002) 12108.
53. *Sanghi, R., Verma, P.*, Bioresource Technol. **100** (2009) 501.
54. *Bar, H., Bhui, D. K., Sahoo, G. P., Sarkar, P., De, S. P., Misra, A.,* Colloid Surface A **339** (2009) 134.
55. *Singh, N., Khanna, P. K.,* Mater. Chem. Phys. **104** (2007) 367.
56. *Pinsky, M. J., Stok, J. L.*, J. Bacteriol. **64** (1952) 337.
57. *Balaji, D. S., Basavaraja, S., Deshpande, R., Mahesh, D. B., Prabhakar, B. K., Venkataraman, A.,* Colloid Surface B **68** (2009) 88.
58. *Kathiresan, K., Manivannan, S., Nabeel, M. A., Dhivya, B.,* Colloid Surface B **71** (2009) 131.
59. *Kasthuri, J., Veerapandian, S., Rajendiran, N.,* Colloid Surface B **68** (2009) 55.
60. *Kumar, S. A., Kazemian, Abyaneh, M., Gosavi, S. W., Kulkarni, S. K., Pasricha, R., Ahmad, A., Khan, M. L.,* Biotechnol. Lett. **29** (2007) 439.
61. *Lee, S. Y.,* Trends Biotechnol. **14** (1996) 98.
62. *Vigneshwaran, N., Ashtaputre, M. N., Varadarajan, P. V., Nachane, R. P., Paralikar, K. M., Balasubramanya, R. H.*, Mater. Lett. **61** (2007) 1413.
63. *Shehata, T. E., Marr, A. G.,* J. Bacteriol. **107** (1971) 210.
64. *Joerger, R., Klaus, T., Granqvist, C. G.,* Adv. Mater. **12** (2000) 407.
65. *Chandran, S. P., Chaudhary, M., Pasricha, R., Ahmad, A., Sastry, M.*, Biotechnol. Prog. **22** (2006) 577.
66. *Thakkar, T. N., Mhatre, S. S., Parikh, R. Y.*, Nanomed. **6** (2010) 257.
67. *Kowshik, M., Ashtaputre, S., Kharrazi, S., Vogel, W., Urban J., Kulkarni, S. K., Paknikar, K. M.,* Nanotechnol. **14** (2003) 95.
68. *Shankar, S. S., Ahmad, A., Sastry, M.,* Biotechnol. Prog. **19** (2003) 1627.
69. *Lee, K. J., Lee, Y. I., Shim, I. K., Joung, J., Oh, Y. S.,* J. Colloid Interf. Sci. **304** (2006) 92.
70. *Shankar, S. S., Rai, A., Ahmad, A., Sastry, M.,* J. Colloid Interf. Sci. **275** (2004) 496.
71. *Ankamwar, B., Damle, C., Absar, A., Mural, S.,* J. Nanosci. Nanotechnol. **10** (2005) 1665.
72. *Mallikarjuna, K., Narasimha, G., Dillip, G. R., Praveen, B., Shreedhar, B., Sree Lakshami, C., Reddy, B. V. S., Raju, B. D. P.,* Dig. J. Nanomater. Bios. **6** (2011) 181.
73. *Huang, J., Li, Q., Sun, D., Lu, Y., Su, Y., Yang, X., Wang, H., Wang, Y., Shao, W., He, N., Hong, J., Chen, C.,* Nanotechnol. **18** (2007) 105104.
74. *Udayasoorian, C., Vinoth Kumar, K., Jayabalakrishnan, R. M.,* Dig. J. Nanomater. Bios. **6** (2011) 279.