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Der Chemica Sinica, 2011, 2 (2):88-97

ISSN: 0976-8505
CODEN (USA) CSHIA5

A bird's eye view on Biogenic Silver nanoparticles and their applications

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ABSTRACT

Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology. The development of reliable experimental protocols for the synthesis of nanomaterials over a range of chemical compositions, sizes, and high monodispersity is one of the challenging issues in current nanotechnology. In the context of the current drive to develop green technologies in material synthesis, this aspect of nanotechnology is of considerable importance. Recent studies on the use of biological material in the synthesis of nanoparticles are a relatively new and exciting area of research with considerable potential for development. This review describes a brief overview of the current research worldwide on the use of microorganisms and plants in the biosynthesis of metal silver nanoparticles and their applications with reference to antimicrobial activity studies.

Keywords: nonomaterial, biosynthesis, microorganisms, antimicrobial activity.

INTRODUCTION

Nanotechnology refers broadly to a field of applied science and technology whose unifying theme is the control of matter on the molecular level in scales smaller than 1µm, normally 1-100 nm, and its fabrication of devices within the range. It is a highly multidisciplinary drawing from fields such as pharmaceutical sciences, applied physics, material sciences, colloidal science, device physics, supramolecular chemistry, and even mechanical and electrical engineering. Nanotechnology can be seen as an extension of existing sciences into the nano scale, or as a recasting of existing sciences using a newer, more modern term. The term "nanotechnology" was first defined by Norio Taniguchi, Tokyo Science University in 1974[1], as follows:

'Nanotechnology' mainly consists of the processing, separation, consolidation, and deformation of materials by one atom or one molecule.

Nanoparticles [2] of noble metals such as gold, silver, and platinum, are widely applied in products that directly come in contact with the human body such as shampoos, soaps, detergent, shoes, cosmetic products, and toothpaste, besides medical and pharmaceutical applications. Nanoparticle exhibit completely new or improved properties as compared to the larger particles of the bulk material that they are composed of based on specific characteristics such as size, distribution, and morphology [3]. Nanoparticles present a higher surface to volume ratio with their decreasing size. The specific surface area of nanoparticles is directly proportional to their biological effectiveness due to the increase in surface energy [3].

Silver is a white and brilliant metal, positioned at 47 in the periodic chart with Ag, meaning "argentum", as its chemical symbol. Pure silver is ductile, malleable and has the highest electrical and thermal conductivity as well as the lowest contact resistance [4]. Silver has been widely utilized for thousands of years in human history; its applications include jewels, utensils, currency, dental alloy, photography and explosives. Among silver's many applications, its disinfectant property is being exploited for hygienic and medicinal purposes, such as treatment of mental illness, nicotine addiction and infectious disease like syphilis and gonorrhea [5].

Silver vessels were used in ancient times to preserve water and wine and silver powder was believed by Hippocrates, the father of modern medicine, to have beneficial healing and anti disease properties and listed as a treatment for ulcers. But it is mainly silver compounds that actually entered medical practice. Silver compounds were major weapon against infection of wounds in World War I until the advent of antibiotics. In 1884 German obstetrician C.S.F. Crede introduced l% silver nitrate as an eye solution for prevention of Gonococcal ophthalmia neonatorum, which is perhaps the first scientifically documented medical use of silver [6]. Further, topically used silver sulfadiazine cream was standard antibacterial treatment for serious burn wounds and is still widely used in burn units.

Synthesis of silver nanoparticles

A number of approaches are available for the synthesis of silver nanoparticles for example, reduction in solutions [7], chemical and photochemical reactions in reverse micelles [8], thermal decomposition of silver compounds [9], radiation assisted [10], electrochemical [11], sonochemical [12], microwave assisted process [13] and recently via green chemistry route [14,15]. The use of environmentally benign materials like plant leaf extract [16], bacteria [17], and fungi [18] for the synthesis of silver nanoparticles offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemicals for the synthesis protocol. Chemical synthesis methods lead to presence of some toxic chemical absorbed on the surface that may have adverse effect in the medical applications. Biological synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large scale synthesis and in this method there is no need to use high pressure, energy, temperature and toxic chemicals.

Biological synthesis of silver nanoparticles

Synthesis of silver nanoparticles using microorganisms

The microorganisms have received the most attention in the area of biosynthesis of nanoparticles. Silver is highly toxic to most of the microbial cells. Nonetheless, several bacterial strains are reported as silver resistant [19] and may even accumulate silver at the cell wall to as much as 25% of the dry weight biomass, thus suggesting their use for the industrial recovery of silver from ore material. The silver resistant bacterial strain *Pseudomonas stutzeri* AG259 accumulates silver nanoparticles, along with some silver sulfide, in the cell where particle size ranges from 35 to 46 nm [20]. Larger particles are formed when *P. stutzeri* AG259, isolated from a silver mine, is placed in a concentrated aqueous solution of silver nitrate (50mM) [21]. Nanoparticles of well-defined size, ranging from a few to 200 nm or more and distinct morphology are deposited within the periplasmic space of the bacteria. Cell growth and metal incubation conditions may be the reasons for the formation of different particle sizes. The exact reaction mechanisms leading to the formation of silver nanoparticles by this species of silver resistant bacteria is yet to be elucidated. The ability of microorganisms to grow in the presence of high metal concentrations might result from specific mechanisms of resistance. Such mechanisms include the following: efflux systems, alteration of solubility and toxicity by changes in the redox state of the metal ions, extracellular complexation or precipitation of metals, and the lack of specific metal transport systems [22]. Bacteria not normally exposed to large concentrations of metal ions may also be used to synthesize nanoparticles. The exposure of *Lactobacillus* strains [23], which are present in buttermilk, to silver and gold ions resulted to the large-scale production of metal nanoparticles within the bacterial cells. Moreover, the exposure of lactic acid bacteria present in the whey of buttermilk to mixtures of gold and silver ions can be used to grow alloy nanoparticles of gold and silver.

Fungi are known to secrete much higher amounts of proteins, thus might have significantly higher productivity of nanoparticles in biosynthetic approach. Mukherjee *et al* [24] has first time opened up a novel fungal/enzyme-based in vitro approach for nanomaterials synthesis. Based on properties of *F. oxysporum* was used in the formation of extremely stable silver hydrosol [25]. The acidophilic fungus *Verticillium* sp. has capability of producing gold as well as silver nanoparticles upon their incubation with Ag^{+} and AuCl4 ions [26]. However, a novel biological method for the intra- and extra-cellular synthesis of silver nanoparticles using the fungi, *Verticillium* and *F. oxysporum* respectively has been documented. This has opened up an exciting possibility wherein the nanoparticles may be entrapped in the biomass in the form of a film or produced in solution, both having interesting commercial potential [27]. The fungus, *A. flavus* also resulted in the accumulation of silver nanoparticles on the surface of its cell wall when incubated with silver nitrate solution [28]. Yeast has been used to synthesize intracellular nanoparticles for several years, Very recently, silver nanoparticles have been synthesized extracellularly by a silver tolerant yeast strain, MKY3 [29]. Biosynthesis of silver nanoparticle using microorganisms have some disadvantages, which are follow as very difficult to maintenance the culture, synthesizing time are very high, Some pathogenic microorganisms are used for synthesis of nanoparticle synthesis and special media used for culture maintenance etc. The synthesis of silver nanoparticles using plant material offers numerous advantages as follows: eco-friendliness, compatibility for pharmaceutical and other biomedical applications, cost effective, environment friendly, economic viability, non toxic easily scaled up for large scale synthesis and in this method there is no need to use high pressure, energy, temperature and toxic chemicals.

Synthesis of silver nanoparticle using plant material

Synthesis of nanoparticles using plants can potentially eliminate this problem by make the nanoparticles more bio-compatible. Use of plant extract for the synthesis of nanoparticles could be advantageous over other environmentally benign biological processes by eliminating the elaborate process of maintaining cell cultures. Jose-Yacaman and co-workers first reported the formation of gold and silver nanoparticles by living plants [30, 31]. Very recently green silver nanoparticles have been synthesized using various natural products like green tea, *Camellia sinensis* [32], natural rubber [33], starch [34], *Aloe vera* plant extract [35],Papaya fruit extract [36], lemongrass leaves extract [37,38] leguminous shrub (*Sesbania drummondii*) [39], latex of *Jatropha curcas* [40] etc.

Using Geranium (*Pelargonium graueolens*) leaf extract silver ions were reduced to silver nanoparticles. These nanoparticles were highly stable and crystalline in solution. In addition to individual pure metallic Ag and Au, bimetallic Ag/Au nanopaticles (50–100 nm) using *Azadirachta indica* leaf broth has also been synthesized extracellularly [37]. Synthesis of bimetallic Au core - Ag shell nanoparticles in solution was accomplished due to competitive reduction of Au^{3+} and Ag^{+} ions present simultaneously in the solution during the exposure to Neem leaf extract. The rate of reduction of metal ions by Neem leaf extract has been found to be much faster compared to that of microorganisms use. While, treatment of aqueous solutions of silver nitrate and chloroauric acid with Neem leaf extract has been observed for rapid formation of stable Ag and Au nanoparticles at higher concentration. It was believed that flavanone and terpenoid constituents of leaf broth were the surface active molecules stabilizing the formation of nanoparticles.

Effect of size on the antimicrobial activity of nanoparticles

The surface plasmon resonance plays a major role in the determination of optical absorption spectra of metal nanoparticles, which shifts to a longer wavelength with increase in particle size. The size of the nanoparticle implies that it has a large surface area to come in contact with the bacterial cells and hence, it will have a higher percentage of interaction than bigger particles [41-43]. The nanoparticles smaller than 10 nm interact with bacteria and produce electronic effects, which enhance the reactivity of nanoparticles. Thus, it is corroborated that the bactericidal effect of silver nanoparticles is size dependent [44, 42]. We have tabulated these various plants exploited for the synthesis silver nanoparticles based on size (Table 1).

Effect of shape on the antimicrobial activity of nanoparticles

The antimicrobial efficacy of the nanoparticle depend on the shapes of the nanoparticles also, this can be confirmed by studying the inhibition of bacterial growth by differentially shaped nanoparticles [42]. According to Pal et al [43] truncated triangular nanoparticles show bacterial inhibition with silver content of 1 μg. While, in case of spherical nanoparticles total silver content of 12.5 μg is needed. The rod shaped particles need a total of 50 to 100 μg of silver content. Thus, the silver nanoparticles with different shapes have different effects on bacterial cell. We have tabulated these various plants exploited for the synthesis silver nanoparticles based on shape (Table 2).

Application of silver nanoparticles

Silver has been known to possess strong active properties both in its metallic and nanoparticle forms hence; it has found variety of application in different fields. Silver nanoparticles are emerging as one of the fastest growing product categories in the nanotechnology industry. Still, the remarkably strong anti-microbial activity is a major direction for development of nanosilver products. A wide category of products in this respect has already been available on the market. In medical arena, there are wound dressings, contraceptive devices, surgical instruments and bone prostheses are coated or embedded with nanosilver [45,46]. In daily life, consumers may have nano silver containing room spays laundry detergents, water purificants and wall paint [47].

Table 1. Use of various biological entities in the production of silver nanoparticles based on the size

Biological entity	Size (nm)	Extracellular/ intracellular	References
Plant			
Azadirachta indica	50-100 nm	Extracellular	Shankar *et al*. [37]
Aloe vera	15-20 nm	-	Chandran *et al*. [35]
Emblica Officinalis	10–20 nm	Extracellular	Ankamwar *et al*. [62]
Pelargonium graveolens	16–40 nm	Extracellular	Shankar *et al*. [56]
Cinnamomum camphora	55–80 nm	Extracellular	Huang *et al*. [63]
Tamarind Leaf Extract	20–40 nm	Extracellular	Ankamwar *et al*.[64]
Carica papaya	25-50 nm	Extra cellular	Devendra *et al*. [36]
Parthenium hysterophorus L	40 -50 nm	Extracellular	Vyom *et al*.[65]
Diopyros kaki)	15-19 nm	Extracellular	Jae and Beom [66]
Camellia sinensis	30-40 nm	-	Alfredo *et al* [67]
Eucalyptus hybrida	50-150 nm	-	Manish *et al* [68]
Microoganisms			
Pseudomonas stutzeri	200 nm		Joerger *et al*. [69]
Aspergillus fumigates	5-25 nm	Extracellular	Bhainsa and Souza.[18]
Fusarium oxysporium	5- 15 nm	Extracellular	Ahmad *et al*. [25]
MKY3 (Yeast)	2–5 nm	Extracellular	Kowshik *et al*.[29]
Verticillium	25-30 nm	Intracellular	Mukherjee *et al*.[70]
Nitrate reductases (*Fusarium oxysporum*)	10–25 nm	Extracellular	Kumar *et al*. [71]
Staphylococcus aureus	160-180 nm	Extra cellular	Anima, [72]
Penicillium sp. K1	10-100 nm	-	Maliszewska[73]
Penicillium sp. K10	18-100 nm	-	Maliszewska [73]
Pseudomonas stutzeri	200 nm	Intracellular	Klaus *et al*.[21]
Morganella sp.	20-30 nm	Extracellular	Parikh *et al* .[74]
Plectonema boryanum	1-10 nm	Intracellular	Lengke *et al* [75]
Klebsiella pneumoniae	5-32 nm	Extracellular	Shahverdi *et al*[76]
Phoma sp. 3.2883	71-74 nm	Extracellular	Chen. *et al* [77].
Aspergillus fumigates	5-25 nm	Extracellular	Bhainsa and souza [18]
Trichoderma asperellum	13-18 nm	Extracellular	Mukherjee *et al*.[78]
P. chrysosporium	50-200 nm	Extracellular	Vigneshwaran *et al* [34]

Silver nanoparticles are also incorporated into textiles for manufacture of clothing, underwear and socks [48]. There are washing machines, which employs nanosilver [49]. It is estimated that of all the nanomaterials in medical and healthcare sector, nanosilver application has the highest degree of commercialization. Therefore, exposure to nanosilver in the body is becoming increasingly widespread and intimate. Consequently, silver in the form of nanoparticles has gained an increasing access to tissues, cells and biological molecules within the human body.

Silver nanoparticles showed good antimicrobial activity and therefore can be used for purification in water-filtering apparatus [50]. Nanoparticles ranging in size from 1 to 10 nm readily interact with the HIV-1 virus via preferential binding to gp120 glycoprotein knobs. This specific interaction of silver nanoparticles inhibits the virus from binding to host cells, demonstrated by *in vitro* study. Hence, silver nanoparticles could find application in preventing as well as controlling HIV infection [51]. Silver nanoparticles have also found application in Surfaced-Enhanced Raman Spectroscopy (SERS). Use of SERS surfaces prepared by self-assembly of gold and silver nanoparticles on glass and other substrates has shown a high degree of reproducibility [52]. A novel, direct, rapid, and label-free electrochemical immunoassay based on a core/shell Ag–Au nanoparticle monolayer as sensing interface has been developed for probing IgG [53].

Table 2. Use of various biological entities in the production of silver nanoparticles based on the shape.

Biological entity	Shape	Extracellular/ intracellular	References
Plant			
Carica papaya	Cubic	Extracellular	Devendra *et al.*[36]
Parthenium hysterophorus L	Irregular	Extracellular	Vymon *et al.* [65].
Diopyros kaki)	Spherical	Extra cellular	Jae and Beom.[66]
Azadirachta indica	Spherical	Extracellular	Shankar *et al.* [37]
Camellia sinensis	Triangle	-	Alfredo *et al*.[67]
Eucalyptus hybrida	Cubical	-	Manish *et al.* [68].
Hibiscus rosa sinensis	Triangle	-	Daizy Philip.[79]
Jatropha curcas	Polycrystalline		Harekrishna *et al.*[80]
Capsicum annuum	Polycrystalline	-	Shikuo *et al* .[81]
Aloe vera	Triangular, spherical	-	Chandra *et al*.[82]
Microorganisms			
Staphylococcus aureus	Rod	Extra cellular	Anima [72]
Penicillium sp. K1	Poly dispersive		Maliszewska.[73]
Penicillium sp. K10	Spherical	-	Maliszewska.[73]
Pleurotus sajor caju	poly dispersaive	Extracellular	Nithya.[82]
Fusarium oxysporum	poly dispersaive	-	Marcato *et al.* [83]

Nanotechnology could be useful to make nanoscale confining environments channels or post arrays for long polymers such as DNA [54]. Silver nanoparticles also find application in topical ointments and creams used to prevent infection of burns and open wounds [55]. Silver-containing consumer products such as colloidal silver gel and silver-embedded fabrics are now used in sporting equipment [56]. The sensitivity and performance of biosensors have been improved by using nanomaterials. Many new signal transduction technologies have been introduced in biosensors, bioprobes and other biosystems using nanomaterials produced through living organisms [57]. Nanoparticles have found applications in antibacterial effects. It has been shown that extracellularly produced silver or gold nanoparticles using *F.oxysporum*, can be incorporated in several kinds of materials such as cloths. These cloths with silver nanoparticles are sterile and can be useful in hospitals to prevent or to minimize infection with pathogenic bacteria such as *S. aureus* [58].

Biominerals have been formulated by using several bacteria such as *Pseudomonas aeruginosa* [59], *E. coli* [60] and *Citrobacter sp.* Metal sulphide microcrystallites were formulated by using *S. pombe,* which can function as quantum semiconductor crystallite. These crystallites also have properties like optical absorption, photosynthetic and electron transfer. Small interfering RNA (siRNA) delivery can be monitored by a novel method based on nano device that combines unmodified siRNA with semiconductor quantum dots (QDs) as multicolor biological probes. Co-transfection of siRNA with QDs using standard transfection techniques has led to the formation of photo stable fluorescent nanoparticles that helps in tracking the delivery of nucleic acid, the degree of transfection in cells and also in purifying homogeneously silenced subpopulations [61].

CONCLUSION AND FUTURE PROSPECTS

Living organisms have huge potential for the production of nanoparticles of wide applications. By using the organisms from simple bacteria to highly complex eukaryotes in the reaction mixture, the production of nanoparticles with desired shape and size can be obtained. Though nano-biotechnology is at its infancy but various examples through which this technology and their use have been explained in this article would attract the attention of peoples towards its applications. Among these studies, a few have shown that different kind of reeducates of these organisms might be involving in the mechanism of nanoparticles production and attribute them various shape and size. However, the elucidation of exact mechanism of nanoparticles production using living organisms needs much more experimentations.

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