



SYNTHESIS OF NANOSILVER USING CHEMICAL REDUCTION METHODS

Landage S.M.*

Wasif A. I.*

Dhuppe P.*

Abstract: *The use of nanotechnology in textiles aims to improve the materials functionalities and/or give it new characteristics. This review presents an overview about antimicrobial activity of silver nanoparticles and then various synthesis approaches such as physical, biological and chemical methods. Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles as stable, colloidal dispersions in water or organic solvents. Different reducing agents can produce different size of silver nanoparticles having different antimicrobial action. Metallic silver in the form of silver nanoparticles has made a remarkable comeback as a potential antimicrobial agent. The use of silver nanoparticles is also important; the several pathogenic bacteria have developed resistance against various antibiotics. Hence, silver nanoparticles have emerged up with diverse medical application.*

Keywords: *Antibacterial Agent, Nanosilver, Nanotechnology, Textiles.*

*D.K.T.E. Society's, Textile & Engineering Institute, Ichalkaranji, India



I. INTRODUCTION

Nanotechnology

In recent years nanotechnology has become one of the most important and exciting forefront fields in physics, chemistry, engineering and biology. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of technological advances in wide range of applications. [1]

The transition from micro particles to nanoparticles can lead to a number of changes in physical properties. Two of the major factors in this are the increase in the ratio of surface area to volume, and the size of the particle moving into the realm quantum effects predominate. The increase in the surface-area-to-volume ratio, which is a gradual progression as the particle gets smaller, leads to an increasing dominance of the behaviour of atoms on the surface of the particle over that of those in the interior of the particle. This affects both the properties of the particle in isolation and its interaction with other material. [2]

Nanotechnology research in the textiles is rather intense and has three main objectives:

1. Up gradation of both functionality and performance of textile materials, characterised by, for example, enhanced strength and tear/wear resistance, hydrophilic or hydrophobic, or insulating properties, and flame resistance.
2. Introduction of innovative functionalities, not yet present in textiles. Among these are, features like antibacterial, self-cleaning, UV-blocking, conductivity, controlled release for active agents, etc.
3. Development of smart/intelligent textiles that is textiles with new functions through the integration of electronics into fabrics, which make them responsive to inputs, to show/modify specific properties, or with sensing and actuating capabilities.[3]

Nanotechnology has the potential to have a positive effect on the environment. For instance; airborne nano-robots could be programmed to rebuild the thinning ozone layer. Contaminants could be automatically removed from water sources, and oil spills could be cleaned up instantly. [4]

For imparting antibacterial properties, nano-sized silver, titanium dioxide and zinc oxide are used. Metallic ions and metallic compounds display a certain degree of sterilizing effect. Silver nanoparticles are of interest because of the unique properties (e.g., size and shape



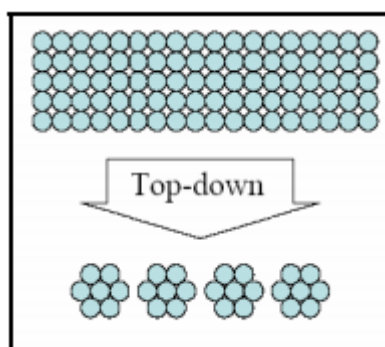
depending optical, electrical, and magnetic properties) which can be incorporated into antimicrobial applications, biosensor materials, composite fibres, cryogenic superconducting materials, cosmetic products, and electronic components and the current investigation supports that use of silver ion or metallic silver as well as silver nanoparticles can be exploited in medicine for burn treatment, dental materials, coating stainless steel materials, textile fabrics, water treatment and possess low toxicity to human cells, high thermal stability and low volatility.[5]

II. SYNTHESIS OF NANOPARTICLES

There are two methods for the production of nanoparticles which is summarized below:

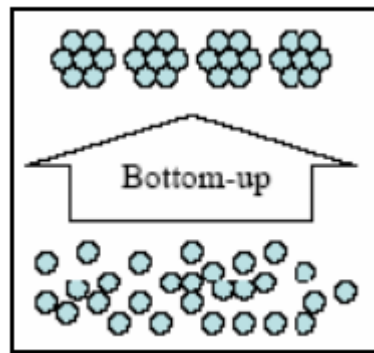
A) *Top-down approach*

The principle behind the top-down approach is to take a bulk piece of the material and then modify it into the wanted nanostructure and subsequent stabilization of the resulting nanosized metal nanoparticles by the addition of colloidal protecting agents. Cutting, grinding and etching are typical fabrication techniques, which have been developed to work on the nano scale. The sizes of the nanostructures which can be produced with top-down techniques are between 10 to 100 nm. [1]



B) *Bottom-up approach*

Bottom-up self assembly refers to construction of a structure atom by atom, molecule-by-molecule or cluster-by-cluster. Colloidal dispersion used in the synthesis of nanoparticles is a good example of a bottom-up approach. An advantage of the bottom-up approach is the better possibilities to obtain nanostructures with less defects and more homogeneous chemical compositions.[1]



These two techniques contain three sub methods to synthesis silver nanoparticles:

a) Physical synthesis method

In physical processes, metal nanoparticles are generally synthesized by evaporation–condensation, which could be carried out using a tube furnace at atmospheric pressure. The source material within a boat centered at the furnace is vaporized into a carrier gas. Nanoparticles of various materials, such as Ag, Au, PbS and fullerene, have previously been produced using the evaporation/condensation technique. However, the generation of silver nanoparticles (AgNPs) using a tube furnace has several drawbacks, because a tube furnace occupies a large space, consumes a great deal of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability.[6]

b) Biological synthesis method

Extracts from bio-organisms may act both as reducing and capping agents in silver nanoparticles synthesis. The reduction of Ag⁺ ions by combinations of biomolecules found in these extracts such as enzymes/proteins, amino acids, polysaccharides, and vitamins is environment friendly, yet chemically complex. For example, the extract of unicellular green algae *Chlorella vulgaris* was used to synthesize single-crystalline silver nanoplates at room temperature. Proteins in the extract provide dual function of Ag⁺ reduction and shape-control in the nanosilver synthesis. The carboxyl groups in aspartic and/or glutamine residues and the hydroxyl groups in tyrosine residues of the proteins were suggested to be responsible for the Ag⁺ ion reduction. The reduction process was carried out by a simple bifunctional tripeptide Asp-Asp-Tyr-OMe further identified the involvement of these residues. This method of synthesis gave small Silver nanoplates with low polydispersity and good yield (>55%). Plant extracts from live Alfalfa, the broths of Lemongrass, Geranium



Leaves and others have served as green reactants in Silver Nanoparticles synthesis. The reaction of aqueous AgNO_3 with an aqueous extract of leaves of a common ornamental geranium plant, *Pelargonium grave lens*, gave Silver Nanoparticles after 24 hrs. The reaction time was reduced to 2 hrs by heating the reaction mixture just below the boiling point. Secreted proteins in spent mushroom substrate reduced Silver+ to give uniformly distributed Silver-protein (core-shell) Nanoparticles with an average size of 30.5 nm. A vegetable, *Capsicum annum L.*, was used to synthesize Silver Nanoparticles.

Studying the synthesis of Silver Nanoparticles with isolated/purified bioorganics may give better insight into the system mechanism. Glutathione (γ -Glu-Cys-Gly-) as a reducing/capping agent can produce water-soluble and size tunable Silver Nanoparticles that easily bind to model protein (bovine serum albumin) — attractive for medical applications. Tryptophan residues of synthetic oligopeptides at the C-terminus were identified as reducing agents giving Silver Nanoparticles.

Recently, it was found that aqueous silver ions may be reduced extracellularly using the fungus *F. Oxysporum* to generate silver nanoparticles in water. The mechanistic aspects were very recently described and this process occurs probably by conjugation of reductase action and by electron shuttle quinones. Different strains of *F. Oxysporum* have been used by different scientists to produce nanosilver particles. [7, 8]

c) Chemical reduction method:-

Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles as stable, colloidal dispersions in water or organic solvents. Commonly used reducing agents are borohydride, citrate, and elemental hydrogen. The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers. Initially, the reduction of various complexes with Ag^+ ions leads to the formation of silver atoms, which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of colloidal silver particles. When the colloidal particles are much smaller than the wavelength of visible light, the solutions have a yellow color with an intense band in the 380–400 nm range and other less intense or smaller bands at longer wavelength in the absorption spectrum. This band is attributed to collective excitation of the electron gas in the particles, with a periodic change in electron density at the surface (surface plasmon absorption). Controlled synthesis of silver



nanoparticles is based on a two-step reduction process⁴⁸. In this technique a strong reducing agent is used to produce small Silver particles, which are enlarged in a secondary step by further reduction with a weaker reducing agent. Chemical reduction of metal salts using various reducing agents in the presence of stabilizer is currently of interest for preparation of metal nanoparticles. Reducing agents such as sodium Borohydride (NaBH_4), hydrazine (N_2H_4), formaldehyde, etc. can be used to reduce a silver containing salt to produce nanosilver particles. [7]

Some reducing agents to synthesis silver nanoparticles:-

1) Glucose as a reducing agent:-

Silver nanoparticles by glucose which are spherical in shape and have smooth surface morphology. It also apparent that resulting nanoparticles are more and less uniform in size and shape. Smaller particles 8nm were produced in glucose. The silver nanoparticles produced by using glucose showed better uniformity and superior antibacterial action. Glucose nanosilver colloids are biologically compatible and have the potential to be used in medical and pharmaceutical applications due to their homologous size distribution and superior antimicrobial actions. Glucose nanosilver colloids showed a shorter killing time against most of the gram positive and gram negative bacteria which could be due to their nanostructures and uniform size distribution pattern. [9]

2) Ethylene glycol as a reducing agent:-

SEM shows uncontrolled growth of metallic particles in ethylene glycol silver nanoparticles. Ethylene glycol silver nanoparticles had higher antibacterial activity than glucose silver nanoparticles. [9]

3) Sodium borohydried as a reducing agent:-

A 10ml volume of 10mM silver nitrate was added drop wise to 30ml of 2.0mM solution that had been chilled in an ice-bath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of 2ml of silver nitrate and a brighter yellow when all of the silver nitrate had been added. The stirring is continued once all of the silver nitrate has been added aggregation begins as the yellow sol first turns; darker yellow, then violet and eventually grayish, after which the colloid breaks down and particles settle out. The Ag solution becomes yellowish in colour because of absorption of wavelength at 386nm. There must be enough borohydried to stabilize the particles as the



reaction proceeds. However, later in the reaction too much sodium borohydride increases the overall ionic strength and aggregation will occur. [10]

4) *Aniline in the presence of Cetyltrimethylammonium bromide as a reducing agent:-*

Silver nanoparticles were prepared by the reduction of silver nitrate solution with aniline in presence of CTAB. A series of experiments were performed, varying the concentration of oxidant, reductant and stabilizer to obtain a perfectly transparent silver sol. Aniline is one of the relatively milder reductant used for the reduction of silver ions. CTAB used as a stabilizer. Plasmon absorption band with a λ_{max} at 400nm is commonly presented as the characteristics of successful spherical or roughly spherical faceted Ag-nanoparticles prepared. It can be seen that the size of roughly spherical nanoparticles ranges between 10 and 30 nm and their size distribution is relatively wide. [11]

5) *Ethanol as a reducing agent:-*

Uniform silver nanoparticles can be obtained through the reduction of silver ions by ethanol at a temperature of 90°C under atmospheric conditions in presence of linoleic acid and sodium linoleate. Ethanol in the solution phases reduced silver ions into silver nanoparticles. The linoleic acid caps the silver nanoparticles along with the reduction process thereby stabilizes the nanoparticles. Silver nanoparticles having average diameter (size) of 12nm with the size range 7 – 15nm. [12]

6) *Citrate of sodium as reducing agents:-*

Silver nanoparticles can be obtained by reducing aqueous $AgNO_3$ with sodium citrate at boiling temperature. In typical procedure $AgNO_3$ is heated to boiling. To this solution, 1% trisodium citrate is added drop by drop. The solution is then heated at boiling point under continuous stirring. The reaction allowed taking place until colour changed to greenish yellow solution. The particles are in broad size distribution from 15 to 60nm with an average size of 40nm. These particles are separated and are not uniform. The silver nanoparticles possessed a negative charge due to the adsorbed citrate ions; a repulsive force worked along the particles and prevented aggregation. Therefore, the particles in the solution remain in a stable state without using other stabilizing agents. [13]

7) *Hydrazine hydrate as a reducing agent:-*

The absorption spectrum of the pale yellow-brown silver colloid prepared by hydrazine reduction showed a surface Plasmon absorption band with a maximum of 418 nm indicating



the presence of spherical or roughly spherical Ag nanoparticles. The particles range in size from 8 to 50nm with mean diameter 24nm. The presence of nanoparticles at a certain level inhibited bacterial growth by more than 90%. [14]

III. CONCLUSION

A variety of chemical synthesis methods have been available for the preparation of different silver nanoparticle solutions. In each case, particular attention was paid to modification of the nanoparticle average size as well as the shape distribution.

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