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Synthesis of Silver Nanoparticles by using Sodium Borohydride as a Reducing Agent

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Abstract

Silver nanoparticles easily interact with other particles and increase their antibacterial efficiency moreover have received considerable attention due to their attractive physical, chemical and optical properties. The optical properties of silver nanoparticles are highly dependent on the nanoparticle diameter and refractive index near the nanoparticle surface. Silver nanoparticles are extraordinarily efficient at absorbing and scattering of light due to its optical properties. These particles were synthesized by the chemical reduction method of $AgNO_3$ using $NaBH_4$. The borohydride anions were adsorbed onto silver nanoparticles and addition of PVP prevented the aggregation of particles. A yellow colour was given by the silver nanoparticle solution using a spectrophotometer that had Surface Plasmon Resonance (SPR) at 386 nm. The silver nanoparticles were estimated to be 10 to 20 nm in diameter.

1. INTRODUCTION

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nanoscale, size-dependent properties are often observed. Thus, the properties of the materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometre the percentage of atoms at the surface is insignificant as compared to the number of atoms in the bulk of the material.
Silver is currently used to control bacterial growth in a variety of applications, including dental work and burn wounds [1,2].

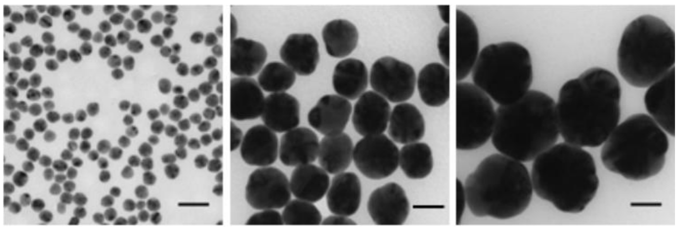

Figure 1 shows images of silver nanoparticles with diameters of 20 nm [3]

Also Ag ions and Ag-based compounds are highly toxic to environment, health, and aquatic life. Reducing the particle size of materials is an efficient and reliable tool for improving their biocompatibility. The extremely small size of nanoparticles exhibit different properties when compared with the bulk material. As a result nanoparticles with very large surface area relative to their volume have become possible.These particles easily interact with other particles and increase their antibacterial efficiency.

Due to vast application of nanotechnology in the area of bioscience, synthesis of silver nanoparticles was possible. Reagents such as formaldehyde, glycol ethylene, sodium borohydride are used as a reducing agent. The formation of silver nanoparticles can be observed by a change in colour since they form yellow colour on synthesis.

2. SYNTHESIS OF SILVER NANOPARTICLES

Nanosized metal colloids are synthesized by in-situ reduction method, such as chemical reduction, photo reduction, electrochemical reduction, or thermal decomposition.

Chemical reduction of silver nanoparticles involves the reduction of a silver salt such as silver nitrate with a reducing agent like sodium borohydride in the presence of colloidal stabilizer. Sodium borohydride has been used with PolyVinylAlcohol (PVA), PolyVinylPyrrolidone (PVP), Bovine Serum

Albumin (BSA), citrate and cellulose which are used as stabilizing agents.

Ag nanoparticles were synthesised by sodium borohydride as per the literature [4,5]

One of the most popular methods to synthesize silver nanoparticles is by the use of ice-cold sodium borohydride to reduce silver nitrate. A large excess of sodium borohydride is needed both to reduce the ionic silver and to stabilize the formed nanoparticles.

Add 30 mL of 0.002M sodium borohydride ($NaBH_4$) to anErlenmeyer flask. Add a magnetic stir bar and place the flask in an ice bath on a stir plate. Ice bath is used to slow down the reaction and give better control over final particle size/shape. Stir and cool the liquid for about 20 minutes.Drip 2 mL of 0.001M silver nitrate ($AgNO_3$) into the stirring $NaBH_4$ solution at approximately 1 drop per second. Stop stirring as soon as all of the $AgNO_3$ is added.By mixing both solutions (i.e. $NaBH_4$ and $AgNO_3$), Ag ions were reduced and clustered to form monodispersedNano particles as a transparent sol in the aqueous medium. Transfer a small portion of the solution to a test tube. The addition of a few drops of 1.5 M sodium chloride (NaCl) solution causes the suspension to turn darker yellow, then grey as the nanoparticles aggregate. The Ag solution became yellow because of absorption at 386nm. Transfer a small portion of the solution to a test tube. Add a drop of 0.3% Polyvinylpyrrolidone (PVP). PVP prevents aggregation. Addition of NaCl solution then has no effect on the colour of the suspension. Add enough solid polyvinyl alcohol (PVA) to give a 4% solution. To get the PVA to dissolve,slowly add it to the stirred, hot, silver colloid solution. Thenpour the mixture into a mould leaving air bubbles and undissolved PVA in the beaker. Evaporate in a toaster oven for about 30 minutes. The silver nitrate reduction reaction can be written as [6]

$$AgNO_3 + NaBH_4 \rightarrow Ag + \frac{1}{2} H_2 + \frac{1}{2} B_2H_6 + NaNO_3$$

Ag/PVP nanocomposites was synthesised as per the literature [7]

Silver n-propylcarbamate(Ag-PCB) complex is dissolved in the NVP (N-Vinylpyrolidone) monomer and decomposed by heat treatment in the range of 110°C to 130°C to form silver metal. Silver nanoparticles with a narrow size distribution (5-40 nm) were obtained, which were dispersed in the PVP matrix. Polyvinylpyrrolidone (PVP) is a polymer that binds strongly to the silver nanoparticle surface. It provides greater stability than citrate or tannic acid, but is more difficult to displace. PVP is used to protect the silver nanoparticles from growing and agglomerating.
Advantages of the in situ synthesis of Ag/PVP composites include that no additives(e.g., solvent, surface-active agent, or reductant of metallic ions) are used, and the stable silver nanocolloid solution can be directly prepared in high concentration sample by dissolving the Ag/PVP nanocomposites in water or organic solvent.

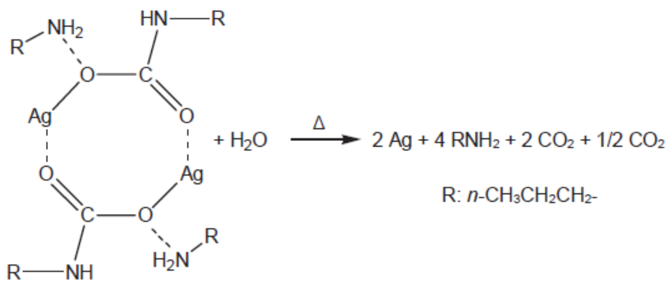

Figure 2 shows the synthesis of PVP from Silver n-propylcarbamate.

Protection of PVP on the silver nanoparticles as per the literature[8]

The reaction between silver ions and glucose was given by formula (1), OH^- was needed in the reaction, and H^+wasdissociated from the by-product $CH_2OH–(CHOH)_4–COOH$ with the consumption of $OH^-$and the generation of H^+. Then from reactions (3) to (5), PVP would coordinate with Ag^+ and H^+, and other complex compounds, so that $Ag(PVP)^+$ and $H(PVP)^+$ were generated and Ag^+ and H^+ will be stabilized. The stabilization of Ag^+ restrained the reaction, but the stabilization of H^+ facilitated it.

$CH_2OH–(CHOH)_4–CHO + 2Ag^+ + 2OH^- \rightarrow CH_2OH–(CHOH)_4–COOH + 2Ag\downarrow + H_2O$ (1)

$CH_2OH–(CHOH)_4–COOH \leftrightarrow CH_2OH–(CHOH)_4=COO^- + H^+$ (2)

$Ag^+ + PVP \leftrightarrow Ag\,(PVP)^+$ (3)

$H^+ + PVP \leftrightarrow H\,(PVP)^+$ (4)

$CH_2OH–(CHOH)_4–CHO + 2[Ag\,(PVP)]^+ + 2OH^- \rightarrow CH_2OH–(CHOH)\ 4–COOH + 2Ag\,(PVP)\downarrow + H_2O$ (5)

3. PROPERTIES

Due to the unique optical properties of silver nanoparticles, information about the physical state of the nanoparticles can be obtained by analysing the spectral properties of silver nanoparticles in solution. Silver nanoparticles are extraordinarily efficient at absorbing and scattering of light due to its optical properties. Their strong interaction with light occurs because the conduction electrons on the metal surface undergo a collective oscillation when they are excited by light at specific wavelengths. This oscillation is known as a Surface Plasmon Resonance (SPR), and it causes the absorption and scattering intensities of silver nanoparticles to be much higher than identically sized non-plasmonic

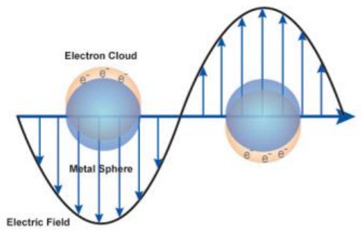

Figure 3 represents Surface plasmon resonance (SPR) where the free electrons in the metal nanoparticle are driven into oscillation due to a strong coupling with a specific wavelength of incident light.

When this occurs, the Surface Plasmon Resonance (SPR) shifts to lower energies, causing the absorption and scattering peaks to shift to longer wavelengths. Silver nanoparticles acquire colour depending upon the size and the shape of the particle. The optical properties of silver nanoparticles change when particles aggregate and the conduction electrons near each particle surface become delocalized and are shared amongst neighbouring particles. The disinfecting properties of silver and silver-based compounds have been known from ancient times. The bactericide properties of the silver nanoparticles are size-dependent and the particles that are in direct contact with the bacteria, with a preferential diameter of 1-10 nm, are the most efficient.

4. SILVER NANOPARTICLE APPLICATIONS

As Silver nanoparticles have unique optical, electrical and thermal properties, they are been incorporated into products that range from photovoltaics to biological and chemical sensors. An increasingly common applicationis the use of silver nanoparticles for antimicrobial coatings, and many textiles, keyboards, wound dressings, biomedical devices, ink-jets, inks, safety labels, pigments, conducting strips. Silver nanoparticles in fabric are used to kill bacteria, making clothing odour-resistant.

Applications of Silver Nano particles in Various Technologies[9, 10]

i. **Diagnostic Applications**: Silver nanoparticles are used in biosensors where they can be used as biological tags for quantitative detection.
ii. **Antibacterial Applications**: Silver nanoparticles are incorporated in footwear, paints, wound dressings, appliances, cosmetics, and plastics for their antibacterial properties. Silver nanoparticles are now replacing silver sulfadiazine as an effective agent in the treatment of wounds.
iii. **Conductive Applications**: Silver nanoparticles are used in conductive inks and integrated into composites to enhance thermal and electrical conductivity.
iv. **Optical Applications**: Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS).

Application of Silver nanoparticles in home appliances

i. Washing Machine

Silver Wash Technology, with superb bacteria killing capabilities where 400 billion silver ions are released and penetrate deep into fabric for effective sanitization are used in washing machines. Silver Wash Nano technology, combining the disinfectant and antibiotic properties of electrolytic silver Nano-particles (Ag^{+}), removes 99.9% of harmful germs without having to wash clothes in hot water, thus saving electricity and disinfectant detergents like bleach, which leads to fabric's colour loss.

ii. Refrigerator

When Silver Nano particles in refrigerator come into contact with bacteria, they suppress the respiration of bacteria. This, in turn, adversely affects bacteria's cellular metabolism and inhibits cell growth. As a result the Silver Nano particles coat the inner surfaces of refrigerator with Silver Nano ions for an overall anti-bacterial and anti-fungal effect. As air circulates, the coated surfaces allow the silver ions to control the airborne bacteria. The spread of fungi and bacteria inside refrigerators is prevented leading to healthiest and purest food.

iii. Aqua Guards

Silver nanoparticles of diameter 60 to 80 nm had the tendency to adsorb pesticides in aqua guards. These particles changed colour while interacting with water that had residual pesticides.

5. EFFECTS OF SILVER NANOPARTICLES

i. Environment

Silver nanoparticles used in many consumer products can have an adverse effect on plants and microorganisms. Silver nanoparticles are used in consumer products because they can kill bacteria, inhibiting unwanted odours. The main route by which these particles enter the environment is sewage treatment plants. The nanoparticles are too small to be filtered out, so they and other materials end up in the resulting wastewater treatment "sludge," which is then spread on the land surface as a fertilizer. As a result, mesocosms are created, which are small, human-made structures containing different plants and microorganisms meant to represent the environment [11].

ii. Soil communities

Silver has toxic effects on bacteria in soil, which plays a major role in nitrogen fixation and the breakdown of organic matter. Silver, with its bactericidal activity, inhibits soil microbial growth at levels below the concentrations of other heavy metals. It shows toxic effects on human-friendly microbes like heterotrophic (nitrogen-fixing and ammonifying bacteria) and chemolithotrophic bacteria in soil communities. These organisms destroy many crucial nutrients which are most essential in soil formation.

iii. Aquatic systems

In freshwater, toxicity of Ag appears to be caused solely by ionic Ag^+ interacting at the gills of fish. Silver causes lethal damage to hepatocytes in rats and finally it leads to cell death.

iv. Health

The chronic exposure to silver causes adverse effects such as permanent bluish-grey discoloration of the skin (argyria) and eyes (argyrosis). Besides argyria and argyrosis, exposure to soluble silver compounds may produce other toxic effects like liver and kidney damage, irritation of the eyes, skin, respiratory and intestinal tract and changes to blood cells and also to brain.

Ag^+ causes early changes in the permeability of the cell membrane to K^+ and then to Na^+ at concentrations that do not limit Na^+, K^+. Silver nanoparticles also show intensive toxic effects on the proliferation and cytokine expression by peripheral blood mononuclear cells (PMBCs).

6. CONCLUSION

Nanotechnology has helped in overcoming the limitations of size and can change the outlook of the world regarding science.

Synthesis of silver nanoparticles has become possible using $NaBH_4$ as a reducing agent and using $AgNO_3$as a reductant.These gave dark yellowish colour when synthesised by a protective layer of borohydride ions. The Ag solution became yellowish in colour because of absorption of wavelength at 386nm.As Silver nanoparticles are very delicate to the absorption of light, they interact with light due to very high dielectric constant that makes the light response occur in the visible region.Thus Silver nanoparticles absorption and scattering properties can be tuned by controlling the particle size, shape, and the local refractive index near the particle surface. Silver nanoparticles are harmful to the environment, due to which mesocosms are created to protect it.

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