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Stability of Colloidal Silver Nanoparticles Synthesized with Variance Silver Ions as Antimicrobial in Cosmetic Formulation

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Silver nanoparticles have been synthesized at variance silver ions and present glycerin as matrix in aqua solution in presence of buffer sodium. The silver ions concentrations are 5, 10, 15, 20, 25 and 30 ppm. This synthesis process using thermal oxidation-reduction treatment with 10 min. time control and temperature control at 100 °C. The concentration of glycerin was controlled to 1 mL and total 100 mL of solution. The silver cluster encapsulated by glycerin in the surface and glycerin form the ring above the clusters. These concentrate of silver ions are dependent with clusters form and clusters diameter, than used independent variable in this research. Characterization of colloidal silver nanoparticles used UV-visible spectrophotometer and TEM analysis. The λ maximum absorption of silver nanoparticles is in the range 420-450 nm. The change of λ maximum at variation of concentration give information that clusters move be bigger or smaller. Absorbance and λ maximum absorption of UV-visible accordance with clusters diameter are discussed. The form and factual diameter of cluster nanoparticle observed by TEM. Future prospects of silver nanoparticle as potential antimicrobial in pharmaceutical formulation include formulation of cosmetics. That is important to study the stability of this colloidal. The stability of colloidal gate by measure λ maximum absorption and absorbance are discussed. The characteristic and stability of colloidal are discussed. The colloidal with high stability is very good to prepare cosmetics formulation.

Keywords: Colloidal, Silver, Clusters, Nanoparticles, Stability, Antimicrobial.

INTRODUCTION

Influenza is a viral infectious disease with frequent seasonal epidemics causing world-wide economic and social effects. Due to antigenic shifts and drifts of influenza virus, long-lasting vaccine has not been developed so far. The current annual vaccines and effective antiviral drugs are not available sufficiently. Small particles of silver have a long history as general antiseptic and disinfectant. Silver does not induce resistance in microorganisms and this ability in nanoparticle size is stronger. It was found that silver nanoparticle has destructive effect on the virus membrane glycoprotein knobs as well as the cells[1]. The interaction of nanoparticles with biomolecules and microorganisms is an expanding field of largely unexplored. Interaction of metal nanoparticles with viruses showed that silver nanoparticles undergo a size-dependent interaction with HIV-1, with nanoparticles exclusively in the range of 1-10 nm attached to the virus. The regular spatial arrangement of the attached nanoparticles, the center-to-center distance between nanoparticles. The fact that the exposed sulfur-bearing residues of the glycoprotein knobs would be attractive sites for nanoparticle interaction suggest that silver nanoparticles interact with the HIV-1 virus *via* preferential binding to the gp120 glycoprotein knobs[2].

Antimicrobial effect of silver nanoparticle was showed in Fig. 1. The spot with black colour is silver nanoparticle in the bacteria zone. White area or transparent area formed by activity of silver nanoparticle. It was death of microbial zone. Diameter of white area or transparent area will be bigger and bigger at the long time. The small cluster of silver nanoparticle has strong antimicrobial activity, it is can see from diameter of white area. That a bigger white area a stronger antimicrobial activity. The big cluster of silver nanoparticle has not strong antimicrobial activity. There for synthesis process must be result silver nanoparticle with small diameter and uniform cluster. The antibacterial activity of different sizes of silver nanoparticle was investigated against Gram-positive (*Staphylococcus aureus*) and Gram-negative bacteria (*Salmonella typhimurium* SL1344) by the disk diffusion method using Müeller-Hinton Agar[3].

Fig. 1. Antimicrobial effect of silver nanoparticles

Silver nanoparticles (Ag-NPs) have been inhibitory and bactericidal effects in the past decades[4]. Antibacterial activity of silver containing materials for reduction of infection[5] on the burn treatment[6], prevention of bacteria colonization[7] on catheters[8] and antimicrobial on textile[9] and textile fabric[10] as well as disinfection in water treatment[4]. Silver nanoparticles were also being reported to exhibit a strong protective activity towards human immunodeficiency virus (HIV) infections[11] and also have biocompatibility with biomaterials[12]. The future prospect of silver nanoparticles as antimicrobial in cosmetics products, that it is necessary to study properties of silver nanoparticles.

The UV-visible spectra for all the silver nanoparticle preparations were correlated with size and form of cluster synthesized. All samples presented a minimum at 320 nm that corresponds to the wavelength at which the real and imaginary parts of the dielectric function of silver[13]. The optical signature of this sample can be better understood in terms of the distribution of sizes and shapes as observed by TEM. As mentioned, the distribution of shapes in the sample is broad and a significant amount of nanoparticles are not spherical such as multitwinned with five-fold symmetries. The presence of nanoparticles with pentagonal and triangular cross-sections could be responsible for the absorption at longer wavelengths. Thus, it is clear that the characteristic absorption of these nanoparticles arises from the contribution of different shapes and sizes, which agrees with the TEM observations[2].

The UV-visible absorption spectrum of the product solution was measured by a Shimadzu UV-2500PC. Evaluation of the s-value which is defined as follows: $s = \partial \log Abs / \partial \log \lambda$. Abs is the absorbance of colloidal dispersion and λ is the wavelength, respectively. It has been suggested that the s-value characterizes the size and shape of the silver nanoparticles. When the s-value is large, nanoparticles are small and spherical. When the s-value is small, particles are non-spherical and relatively large. We evaluated the s-value from the absorption spectrum between 400 and 800 nm. In present case the s-value gave a rough estimate of the extent of aggregation of nanoparticles. The diameter of each particle was determined from enlarged photographs. The histogram of the particle size distribution and the average diameter were obtained by measuring about 400 particles in arbitrarily chosen areas[14].

EXPERIMENTAL

Silver ions, silver, glycerin and sodium citrate were obtained from Sigma (www.sigmaaldrich.com,USA). All the chemicals and solvents used were of analytical grade and were used as received. All solutions were made up with double-distilled water. Silver colloids or silver nanoparticles were prepared according to the literature by adding 1g sodium citrate to100 mL boiling solution of $AgNO_3$ 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL of silver ion 1000 ppm, than result silver colloids 5, 10, 15, 20, 25 and 30 ppm. The size of the prepared silver colloids or silver nanoparticles was about 20-80 nm, which was estimated from transmission electron microscopy (TEM) JEOL/E0 version 1.0 JEM-1400.

Glycerin (3 mL) dissolved in 95 mL of water was prepared in double distilled water. The solution boiled at 100 °C. 1 g of sodium citrate is added in boiling solution and then exposed to a solution of $AgNO_3$ about 0.5, 1.0, 1.5, 2,0, 2.5 and 3.0 mL 1000 ppm. The synthesis was carried out for 10 min. Characterization synthesis result with UV-visible Spectrophotometer and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

The range of λ maximum absorption silver nanoparticle is 420-450 nm. Generally the λ maximum absorption and absorbance increase by increase of silver nanoparticle concentrate (Figs. 2 and 3), except in 10 ppm concentration the λ maximum was decrease. The λ maximum correlation with dominant cluster size of silver nanoparticle, that λ maximum longer than the size of cluster is bigger. The absorbance correlated with cluster concentrate in the colloidal system. The higher absorbance showed that presented cluster in the colloidal system was high too (Table-1).

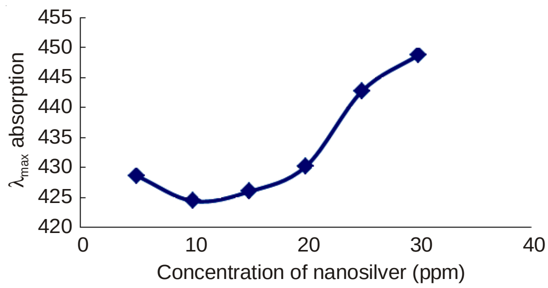

Fig. 2. Correlation of λ maximum absorption by concentration of silver nanoparticle

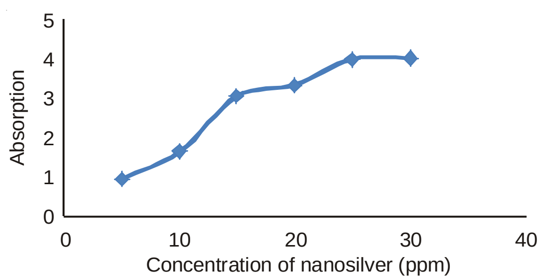

Fig. 3. Correlation of absorbance by concentration of silver nanoparticle

s-Value which is defined as follows: $s = \partial \log Abs / \partial \log \lambda$. s-value of the silver nanoparticle at variation concentrate were following calculation:

TABLE-1
λ MAXIMUM ABSORPTION AND ABSORBANCE OF SILVER NANOPARTICLE

Concentration of silver nanoparticles (ppm)	λ_{max} (nm)	Absorbance
5	428.60	0.962
10	424.40	1.618
15	426.00	3.045
20	430.20	3.334
25	442.80	3.977
30	448.80	4.000

TABLE-2
S-VALUE AND DIAMETER CLUSTER OF SILVER NANOPARTICLE

Concentrate of silver nanoparticles (ppm)	s-Value	Diameter
5	-0.0064	17.15
10	0.0795	16.99
15	0.1839	17.05
20	0.1986	17.19
25	0.2266	17.65
30	0.2270	17.87

$$5\text{ ppm, s-value} = \log 0.962 / \log 428.60 = -0.0168 / 2.6321 = -0.0064$$

Diameter of cluster calculation by following equation:

$$\frac{hc}{\lambda} = E_{g(bulk)} + \left(\frac{h^2}{8R^2}\right)\left(\frac{1}{m_g} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi \in R \in_0}$$

$$\frac{4.13546 \text{ eV s } 3\times10^8 \text{ m/s}}{428\times10^{-9}\text{ m}} = 1.3 + \left(\frac{(4.13546 \text{ eV s})^2}{8R^2}\right)$$

$$\left(\frac{1}{0.25} + \frac{1}{0.25}\right) g - \frac{1.8\times1.6\ c^2}{4\pi\ 6.5R\ \frac{10^7}{4\pi c^2}}$$

$$\frac{1240.6}{428} = 1.3 + \frac{14.84}{R^2}\left(\frac{1}{0.25} + \frac{1}{0.25}\right) - \frac{2.6}{6.5R}$$

$$2.89\text{-}1.3 = \frac{14.84}{R^2}\left(\frac{2}{(0.25)^2}\right) - \frac{2.6}{6.5R}$$

$$1.59 = \frac{29.68}{0.0625R^2} - \frac{2.6}{6.5R},\ 1.59 = \frac{29.68}{0.0625R^2} - \frac{0.025R}{0.0625R^2}$$

$$1.59 = \frac{29.68 - 0.025R}{0.0625R^2},\ 1.59\times0.0625\ R^2 = 29.68\text{–}0.025R$$

$$0 = 0.0994\ R^2 + 0.025\ R\text{-}29.68,\ \ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$R = \frac{-0.025 \pm \sqrt{(0.025)^2 - 4\times0.0994\times(-29.68)}}{2\times0.0994}$$

$$= \frac{-0.025 \pm \sqrt{0.000625 + 11.800}}{0.01988},\ R = \frac{-0.025 \pm 0.3659}{0.01988}$$

$$R = \frac{0.3409}{0.01988} \qquad R = 17.15 \text{ nm}$$

s-Value and diameter cluster for all concentration of silver nanoparticles are in the Table-2.

s-Value is parameter of easy the cluster nanoparticle to be aggregation. The big s-value showed that the cluster nanoparticle easy form big aggregate. Fig. 4 showed that concentrate decrease following with s-value, It is means that in the high concentration, aggregation process have big possibility. It is clear by show Fig. 5 at the following. Fig. 5 give information that the dominant diameter cluster of silver nanoparticle decrease in high concentration, that is means the aggregation was occur.

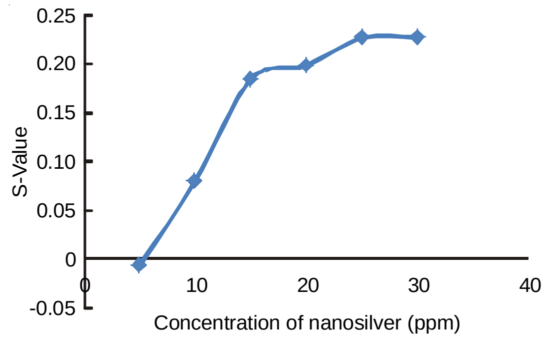

Fig. 4. s-Value of silver nanoparticles at different concentration

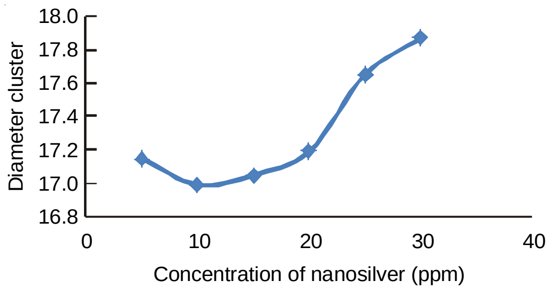

Fig. 5. Diameter cluster of silver nanoparticles at different concentration

Diameter of cluster and size of the cluster can see at the TEM picture in Fig. 6. The diameter of cluster in the range 10-70 nm and sizes of the clusters are octahedral, cubic, tube and cubic-octahedral. Variation of form and size of the cluster were correlated with concentration of silver nanoparticle. At the high concentration the cluster form aggregation and form a big cluster. The dominant cluster size of silver nanoparticle synthesized with glycerin as matrix in the range 17-18 nm was suitable using in cosmetic formulation. That was fit with size of skin pore that in the range 20-50 nm. If this application worked soon as possible, the using of antimicrobial methyl paraben, ethyl paraben and propyl paraben can limitation in cosmetics formulation. The uniformity of the cluster will be get to increase activity of the catalytic effect.

Conclusions

- The λ maximum absorption (420-450 nm) correlated with dominant size of silver nanoparticle. The dominant clusters of silver nanoparticle is present in the range 17-18 nm.
- Absorbance correlated with cluster concentrate in the colloidal system.

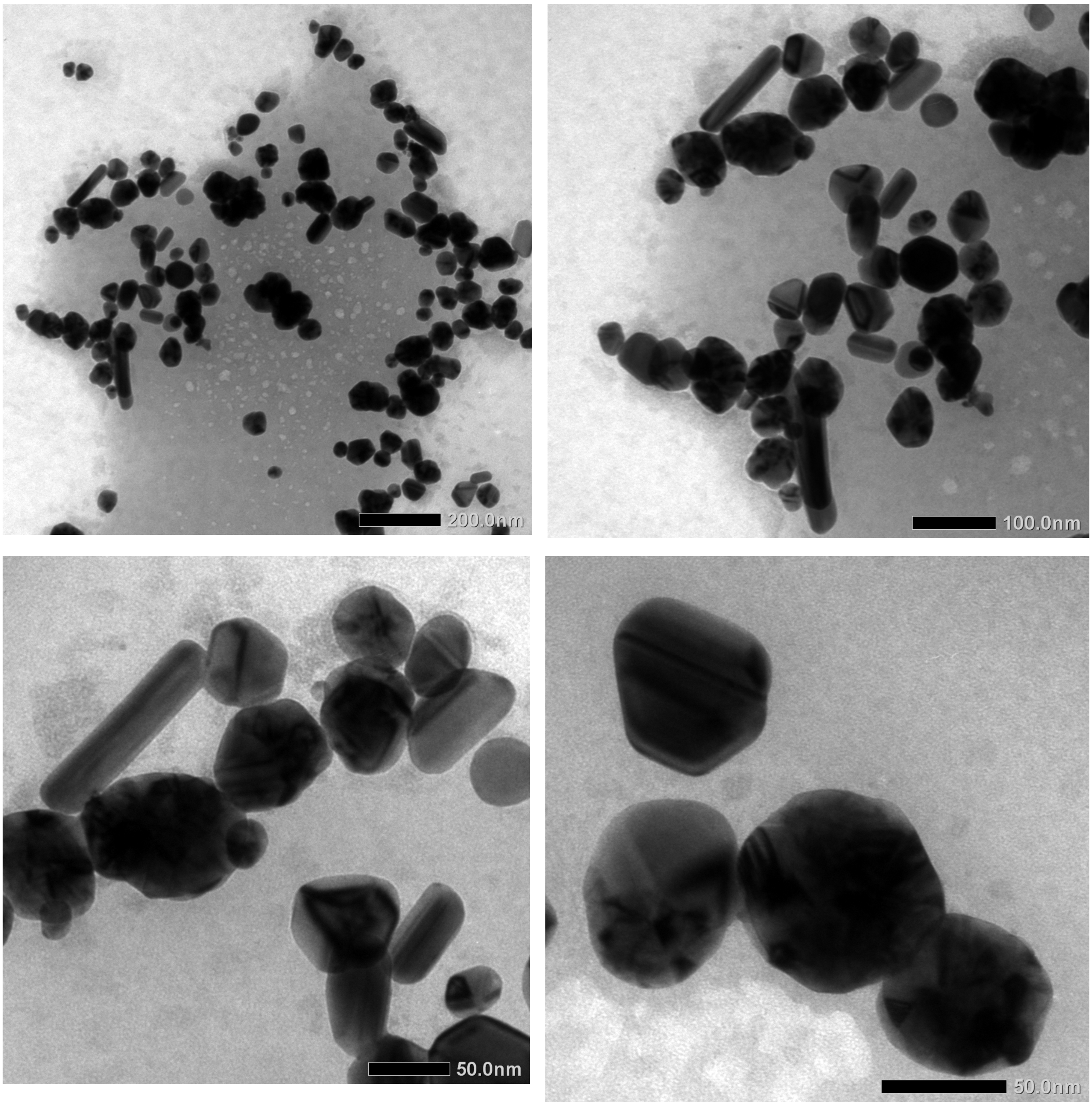

Fig. 6. TEM picture of silver nanoparticles

• s-Value is parameter ease the cluster nanoparticle to be aggregation.

• The diameter cluster of silver nanoparticle increases in high concentration.

• The forms of cluster silver nanoparticle are cubic, octahedral, tube and cubic-octahedral and the size of cluster is in the range of 10-70 nm.

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