Synthesis of Silver Nano Particles (Ag-NPs) and their uses for Quantitative Analysis of Vitamin C Tablets

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ABSTRACT: In the present study silver nanoparticles (Ag-NPs) were prepared by using chemical synthesis. Silver nanocolloid solution has been prepared chemically by the reduction of silver salt using sodium borohydride ($NaBH_4$) and trisodium citrate ($C_6H_5Na_3O_7.2H_2O$). Triangular silver nanoplates were also prepared by reducing silver salt using ascorbic acid which is a mild reducing agent. The nanoparticles were characterized by UV-VIS spectrophotometry and Scanning Electron Microscopy (SEM). The reducing character of ascorbic acid was used to determine the amount of ascorbic acid in real sample like vitamin C tablets that are available in the market of Bangladesh.

Key words: Silver nano particles (Ag-NPs), ascorbic acid, reducins agent, SEM, vitamin C

INTRODUCTION

Over the last decades silver nanoparticles have found applications in catalysis, optics, electronics and other areas due to their unique size-dependent optical, electrical and magnetic properties.[1-3] Currently most of the applications of silver nanoparticles are in antibacterial/antifungal agents in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products.[4-7] Samsung has created and marketed a material called Silver nano that includes silver nanoparticles on the surfaces of household appliances.[8] Silver nanoparticles have been used as the cathode in a silver-oxide battery.

Understanding the reasons of change of the size, shape, surface, and aggregation state of the silver nanoparticles after integration into a target application is critical for optimizing performance. Precisely manufactured monodispersable silver nanoparticles that are free from agglomeration, making them ideal for research, development and use in a variety of innovative applications.

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Aldrich Materials Science offers several silver nanoparticles suspended in a dilute aqueous citrate buffer, which weakly associates with the nanoparticle surface. Silver nanoparticles are being used in numerous technologies and incorporated into a wide array of consumer products that take advantage of their desirable optical, conductive, and antibacterial properties. Silver nanoparticles are used in biosensors and numerous assays where the silver nanoparticle materials can be used as biological tags for quantitative detection. Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS). Cosmetics and pharmaceutical usages of Silver/Clay nanocomposites were studied by scientists at University Putra, Malaysia.[10] In the present study, silver nano particles have been synthesized by chemical methods and they were quantitatively used to analyze ascorbic acid in vitamin C tablets.

MATERIALS AND METHODS

Chemicals: The following chemicals were used without further purification. Potassium chloride (KCl

BDH. UK), zinc nitrate ($Zn(NO_3)_2.6H_2O$ MERCK, India), silver nitrate ($AgNO_3$, National chemicals, India), copper sulfate ($CuSO_4.5H_2O$, MERCK, Germany), absolute ethyl alcohol (CH_3CH_2OH, BDH, UK), ethylene glycol (AR, BDH, UK), sodium hydroxide (NaOH, BDH, UK), sodium borohydride ($NaBH_4$, MERCK, Germany), ascorbic acid ($C_6H_8O_6$ Lobachemie, India), trisodium citrate ($C_6H_5Na_3O_7.2H_2O$, MERCK, Germany), ammonia (NH_3, Active Fine Chemical, Bangladesh), poly vinyl alcohol (PVA, MERCK, Germany).

Synthesis of Ag nanoparticles using tri sodium citrate (TSC) as a reducing agent. Silver nitrate and trisodium citrate were used as starting materials for the preparation of silver nanoparticles. The silver colloid was prepared by using chemical reduction method.[4] All solutions of reacting materials were prepared in distilled water. In typical experiment 50 ml of 0.001 M $AgNO_3$ was heated to boil. To this solution 5 mL of 1 % trisodium citrate was added drop by drop. During the process, solutions were mixed vigorously and heated until change of color was evident (pale yellow). Then it was removed from the heating device and stirred until cooled to room temperature.

The mechanism of reaction could be expressed as follows[11,12]:

$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^o + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2\uparrow$

0.002 M silver nitrate and 0.02 M trisodium citrate were also used in another method.[6] The colloidal solution of silver nanoparticles were characterize by using UV-Visible spectroscopy and SEM.

Synthesis of Ag nanoparticles using sodium borohydride as a reducing agent. A large excess of $NaBH_4$ was needed to reduce the ionic silver and to stabilize the silver nanoparticles that were formed. Different volumes of 0.001M silver nitrate were added drop wise (about 1 drop per second) to 30 mL of 0.002 M sodium borohydride solution that had been chilled in an ice bath. The reaction mixture was stirred vigorously on a magnetic stirrer. The solution turned to light yellow after the addition of 2 mL of silver nitrate and to brighter yellow when all of the silver nitrate had been added.

$AgNO_3 + NaBH_4 \rightarrow Ag + H_2 + B_2H_6 + NaNO_3$

The entire addition process took about 3 minutes, after which the stirring was stopped and the stir bar was removed. Reaction conditions including stirring time and relative quantities of reagents (both the absolute number of moles of each reactant as well as their relative molarities) must be carefully controlled to obtain stable yellow colloidal silver. If stirring was continued once all of the silver nitrate was added, aggregation began as the yellow solution first turned to darker yellow then violet and eventually grayish after which the colloid broke down and particle settled out.

Real samples analysis by using AgNPs. A tablet 'Ceevit' (vitamin C from Square Pharmaceuticals) was weighed, ground to a fine powder. A sample equivalent to approximately 150 mg of ascorbic acid was weighed accurately, transferred into a 100 mL volumetric flask and diluted upto the mark with water. The mixture was sonicated for 10 min to aid dissolution and filtered. Then the filtrate was diluted 100 times. From the dilute solution 10 mL aliquot was transferred into 25 mL volumetric flask and 100 µL of silver seeds, 150 µL of TSC (2.5×10^{-2} M) was added to the solution. To this solution, $AgNO_3$ (0.01 M) was added slowly for 5 times, each time 50 µL with vigorous stirring. Then, a portion of that solution was transferred within 2 min into a 1 cm spectrophotometric cell to record the absorbance. The same procedure was followed for the Nutrivit-C (vitamin C tablet from ACI pharmaceuticals Ltd).

RUSLTS AND DISCUSSION

Characterization of Ag NPs colloid solution. UV-Visible spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. It is quite sensitive to the presence of silver colloids because these nanoparticles exhibit an intense absorption peak due to the surface plasmon excitation. The absorption band in the 350 nm to 450 nm region is typical for

the silver nanoparticles.[13] With increasing particles size, the plasmon absorption shifts toward red.

The absorbance of colloid solution of Ag nanoparticles using 10 mL and 5 mL of $AgNO_3$ (0.001M) were observed by the UV-VIS spectrophotometer and the absorbance of the resultant solution were recorded which is shown in the Figure 1.

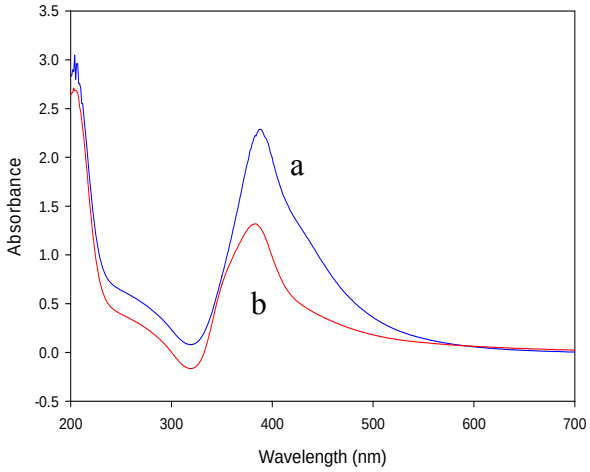

Figure 1. The absorption spectra of Ag NPs using (a) 10 mL of $AgNO_3$ and (b) 5 mL $AgNO_3$

The absorption spectra of the colloidal solution of silver are shown in Figure 1 (a) and 1(b). Both the spectra exhibit a plasmon absorption band at ~ 400 nm which is the characteristic of silver nanoparticles. Such plasmon bands are unique physical properties of the nanoparticles themselves. When an external electro-magnetic field such as light is applied to a metal, the conduction electrons move collectively so as to screen the perturbed charge distribution that is known as plasma localized near the metal surface. Using 10 mL $AgNO_3$ solution to 30 mL $NaBH_4$ (0.002 M) the absorbance was 2.2860 at the wavelength 390 nm and using 5 mL $AgNO_3$ solution to 30 mL $NaBH_4$ (0.002 M) the absorbance was 1.3180 at the wavelength 388 nm .

Stability of colloidal solution. The absorbtion spectra of freshly prepared Ag nanocolloids solution and after 1 week of the synthesis of the solution were also recorded and shown in Figure 2.

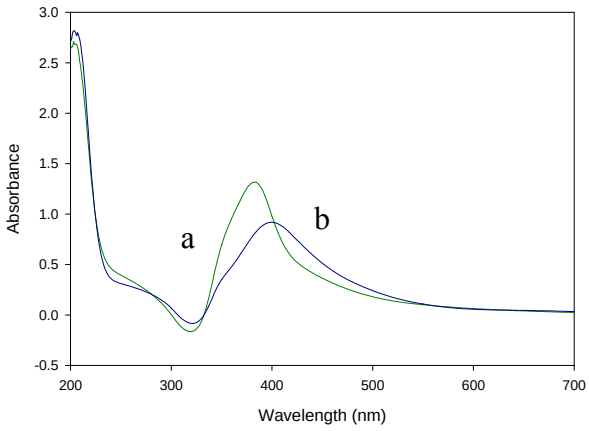

Figure 2. Ag NPs (a) freshly prepared and (b) after 1 week of the synthesis.

The absorbance of freshly prepared Ag nanocolloid solution using 5 mL $AgNO_3$ gave an absorbance of 1.3180 at a wavelength of 388 nm. However, after 1 week of the synthesis of the Ag nano colloids, the absorbance spectrum showed a red shift (at around 400 nm) with the decrease in the absorbance value. The absorbance was found to be 0.9190. The absorption peak became broader when the spectrum was recorded after 1 week of preparation. This indicated that the Ag nanocolloids aggregated with time.

Synthesis of AgNPs by ascorbic acid. Silver nanoparticles can be prepared by milder reducing agent like ascorbic acid. This is the slower growth process. Reduction of Ag^+ occurs on silver seeds. The formation of Ag-NPs was confirmed by taking the absorbance of the resultant colloidal solution. So, the absorbance of the silver nanoparticles colloid solution was measured and it is given in Figure 3.

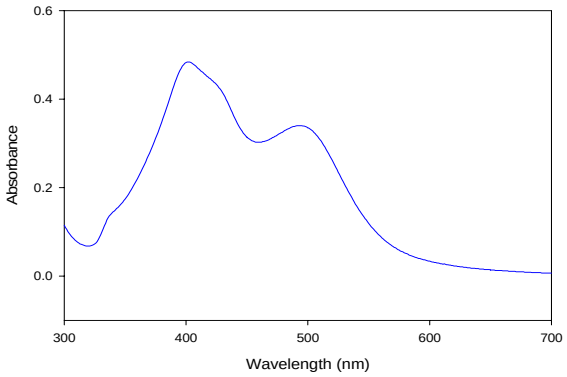

Figure 3. The absorbance spectrum of AgNPs formed by ascorbic acid.

Figure 3 shows the absorption spectrum of Ag nanocolloid prepared by ascorbic acid from $AgNO_3$ solution. The spectrum displayed a peak at a wavelength of 402 nm with an absorbance value 0.4840. A broad peak was observed at 495 nm with an absorbance of 0.3400. The UV-VIS spectrum illustrated three peaks located at approximately 495 nm, 402 nm and 330 nm. These values may correspond to the in-plane dipole resonance, the out-of plane dipole resonance and the out-of-plane quadruple for triangular nanoplates respectively. [14-17]

Determination of ascorbic acid. In 25 mL volumetric flask 100 µl of silver seeds, 150 µl of TSC (2.5×10^{-2} M) and different concentrations of ascorbic acid were added. To this solution, $AgNO_3$ (0.01 M) was added slowly for 5 times (50 µl each time) with vigorous stirring. Then, a portion of that solution was transferred within 2 min into a 1 cm spectrophotometric cell to record the absorbance. The absorbance of each solution was recorded and compiled in table 1.

Table 1. Absorbance of ascorbic acid solutions

Concentration (mM)	Absorbance
0.01	0.108
0.02	0.187
0.03	0.297
0.04	0.372
0.05	0.484

Absorbance spectra for ceevit and nutrivit-C. The absorbance spectra of of Ag nanoparticles in the presence of the ascorbic acid in Ceevit and Nutrivit-C are shown below in Figure 4.

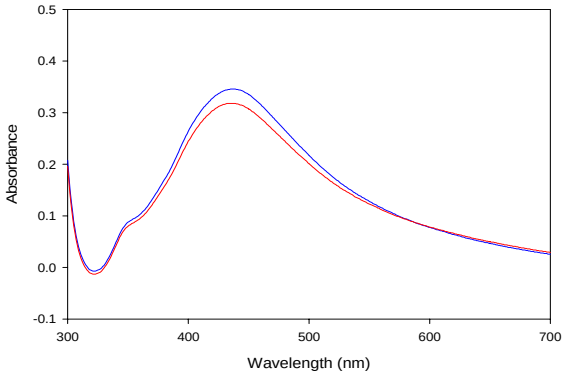

Figure 4. Absorbance spectra of Ag nanoparticles in the presence of Ceevit (upper) and Nutrivit-C (lower).

Figure 4 depicts that the solution containing ascorbic acid from Ceevit shows an absorbance value 0.336 at a wavelength 435 nm and Nutrivit-C shows an absorbance value 0.319 at a wavelength 432 nm.

Determination of ascorbic acid in vitamin C tablet in Ceevit and Nutrivit-C. The absorbance value of Ag nanoparticles in the presence of Ceevit and Nutrivit-C is plotted on the calibration curve of Ag nanoparticles in the presence of different amount ascorbic acid containing solution to determine the concentration of the ascorbic acid present in the solution as shown in Figure 5.

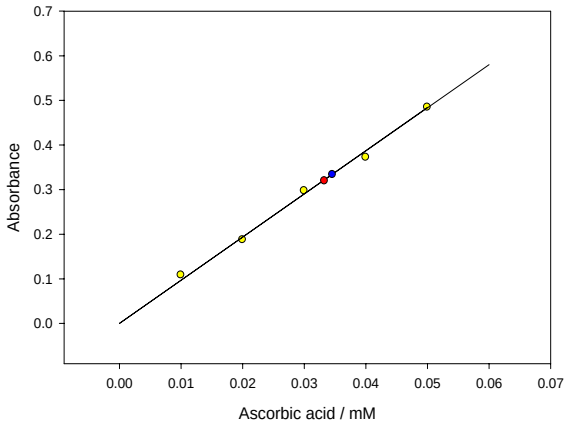

Figure 5. Absorbance of Ag NPs in the presence of ascorbic acid vs concentration of ascorbic acid.

Figure 5 shows the calibration curve, from which the concentration of ascorbic acid present in Ceevit solution was found to be 0.0346 mM and for Nutrivit-C, the concentration was 0.0335 mM. The same procedure was followed for 2 times for both of the samples and the observed values are shown in the following table (Table 2.)

Table 2. Quantitative results of ascorbic acid in tablet samples

Samples	Acsorbic acid found (mg per tablet)	
	Claimed	Proposed Method
Ceevit	250	248.05
	250	253.91
	250	256.85
Nutrivit-C	250	242.90
	250	245.85
	250	248.05

CONCLUSION

In the present study, silver nanoparticles and silver nanocolloid solution were prepared chemically by the reduction of silver salt. The nano species were characterized by UV-VIS spectrophotometry and SEM. The prepared silver nanomaterials were used to determine the amount of ascorbic acid present in real sample like vitamin C tablets (Ceevit and Nutrivit-C) that are available in the market of Bangladesh. The results obtained by the proposed method were in good agreement with that of the claimed values of ascorbic acid by the pharmaceutical companies.

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