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The study on the stability of silver nanoparticles by using simple spectrophotometric method

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ABSTRACT

Silver nanoparticles using different concentrations of $AgNO_3$ precursor were successfully synthesized using sodium borohydride as the reducing and capping agent. This study investigated the stability of silver nanoparticles at two different silver nitrate concentrations using a simple UV-Vis Spectroscopic technique. The UV-Vis spectroscopy confirmed the formation of silver nanoparticles by exhibiting the typical surface plasmon absorption maxima ranging from 390-408 nm for higher (10^{-3}M) $AgNO_3$ concentration, whereas for lower (10^{-4}M) $AgNO_3$ concentrations, we observed variation in the SPR band which can be attributed to aggregation of Ag NPs. During this study, we concluded that nanoparticles at lower $AgNO_3$ concentration were much more stable than nanoparticles at higher $AgNO_3$ concentration. The synthesized Ag NPs may have many potential applications such as antibacterial, antifungal, catalyst and sensor etc.

KEYWORDS

Silver nanoparticles;
Spectrophotometric method;
Stability;
Nanoparticles;
Aggregation.

INTRODUCTION

During past few decades, noble metal nanoparticles have been the subjects of focused research due to their unique electronic, optical, mechanical, magnetic and chemical properties which differ significantly from their bulk counter parts[1,2]. These special and unique properties of the metal nanoparticles could be attributed to their small sizes and large specific surface area. Metallic nanoparticles find applications in many fields such as catalysis, electronics, photonics, etc. Wide range of synthesis techniques have been reported for the preparation of metallic nanoparticles[3,4]: Reverse micelles process[5], Salt reduction[6], Ultrasonic irradiation[7], Radiolysis[8], Solvothermal synthesis[9], Electrochemical synthesis[10], Microwave dielectric heating reduction[1,11], etc.

Silver nanoparticles (Ag NPs) possess unique properties, such as high thermal conductivity, high resistance of oxidation hence is being used in chemical industry and medicine[12,13]. Recently, Ag NPs exhibiting antimicrobial activity have been synthesized[14]. Silver containing materials can be employed to eliminate microorganisms on textile fabrics[10,15] or they can be used for water treatment[16]. Many synthesis techniques have been used in the past to synthesize Ag NPs such as, chemical reduction of silver ions in aqueous solutions with or without stabilizing agents[17,18], thermal decomposition in organic solvents[19], chemical and photo reduction in reverse micelles[20], radiation chemical reduction[21,22], spray pyrolysis[23]. Out of which the chemical reduction method has been widely studied, due to its advantages over other techniques such as, yielding nanoparticles without aggregation, high yield and low preparation cost[24]. The formation of Ag NPs by chemical reduction method involves the reduction of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer which protects the growth of silver particles through aggregation. The particle size and the aggregation state of the Ag NPs during the synthesis technique depends on many parameters which includes initial $AgNO_3$ concentration, stabilizer concentrations and reducing agent/$AgNO_3$ molar ratio[12].

Since the Ag NPs strongly absorb in the visible region due to surface plasmon resonance, it has been found that in the case of Ag NPs, the UV-Vis absorption spectra are very sensitive to the particle size and their aggregation state[25,26]. In this study we have focused on the preparation of Ag NPs from aqueous solution of silver nitrate, we employed sodium borohydride as the reducing agent. The aggregation period of Ag NPs were investigated by UV-Vis absorption spectra, prepared by varying the experimental parameters of initial $AgNO_3$ concentrations and reducing agent/$AgNO_3$ molar ratios. The aggregation state of Ag NPs was observed with a UV-Vis Spectrophotometer (UV-1800, Shimadzu, Japan).

EXPERIMENTAL

Silver nitrate ($AgNO_3$, 99%) purchased from MERCK specialities Pvt. Ltd. Mumbai was used as the precursor to prepare silver nanoparticles. Sodium borohydride ($NaBH_4$, 98% assay) purchased from RANKEM was used as reducing and a stabilizing agent. Milli-Q water was used to prepare all the solutions. All the glass wares were cleaned by aqua regia followed by washing with Milli-Q water.

Sodium borohydride solution was taken in a beaker and was cooled using an ice-bath. Then silver nitrate was added to the pre-cooled $NaBH_4$ solution (at the rate of 1 drop/sec). The reaction mixture was stirred vigorously and color changes were observed till the complete addition of $AgNO_3$ solution. Different sets of reaction were carried out to check the stability of Ag NPs at different $AgNO_3$ concentration whose details are given in TABLE 1.

TABLE 1 : Details of $AgNO_3$ concentration

Sr. No.	$AgNO_3$ (ml)	2.2mM $NaBH_4$ (ml)	Conc. of $AgNO_3$ (mM)
1.	10	20	3.30
2.	10	30	2.50
3.	10	40	2.00
4.	1	20	0.33
5.	1	30	0.25
6.	1	40	0.20

UV-Vis absorption spectra of Ag NPs were measured in optical quartz cuvetts using a Shimadzu 1800 UV-Vis Spectrophotometer. The measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Silver nanoparticles were synthesized according to the method described in the previous section. The distinct colors of Ag NPs are observed due to a phenomenon known as plasmon absorbance. The conduction electrons on the surface of nanoparticle undergo oscillations on interaction with the incident light which results into the absorption of electromagnetic radiation[27]. During the synthesis of Ag NPs at different $AgNO_3$ concentrations the colloidal solution turned from colorless to pale yellow to brown. Figure 1 shows the photographs of samples obtained at different $AgNO_3$ concentrations.

To prepare stable Ag NPs the selection of appropriate reducing agent is very essential. In the present work sodium borohydride is used as the reducing and stabilizing agent. It has been observed that the adsorption of borohydride on the silver ions surface plays a key role in stabilizing growing silver nanoparticles by providing a particle surface charge. The reduction of the silver nitrate by sodium borohydride can be represented according the equation as shown in Figure 2[27].

UV-Vis absorption results confirmed the formation of Ag NPs prepared in liquid by chemical reduction method ($AgNO_3$ reduced by $NaBH_4$). We have measured UV-Visible absorption characteristics of all the synthesized samples which are shown in figures of UV-Vis spectra.

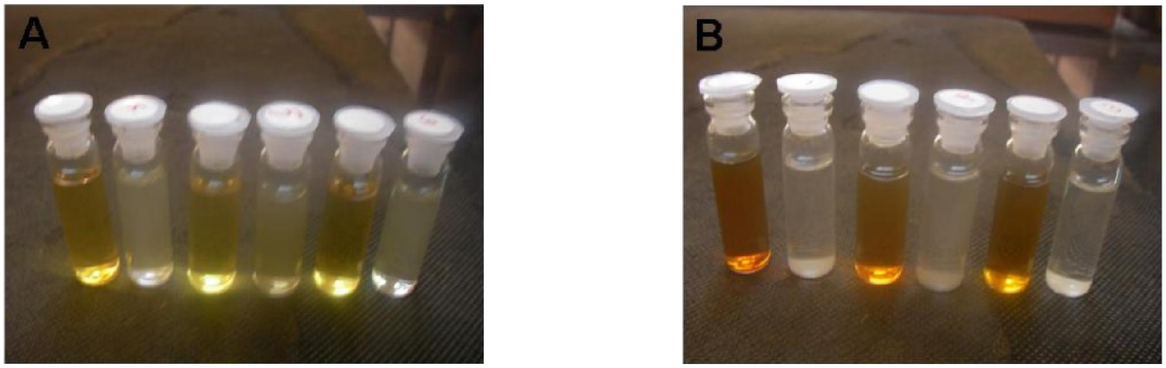

Figure 1 : Silver nanoparticles (light yellow (A)) obtained before aggregation from lower $AgNO_3$ concentrations (X=0.0001M) and (dark brown (B)) obtained from higher $AgNO_3$ concentrations (10X=0.001M) and after aggregation (colorless (A) to light grey (B)) with aggregated particles settled at the bottom of the glass vials (B).

$$AgNO_3 + NaBH_4 \longrightarrow Ag + ½ H_2 + ½ B_2H_6 + NaNO_3$$

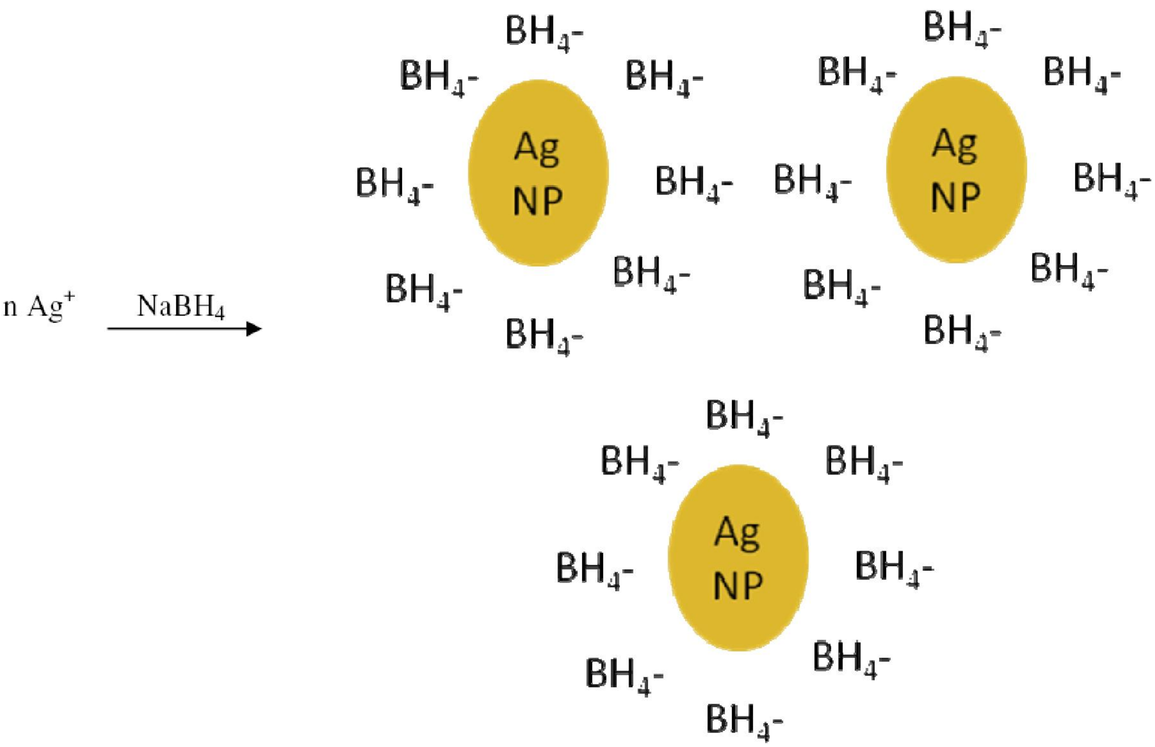

Figure 2 : Electrostatic repulsive forces between negatively charged adsorbed borohydride layers separate Ag nanoparticles[27].

For structural characterization of Ag NPs, UV-Vis Spectroscopy is one of the most widely used techniques. Figures 3A, 4A and 5A show variation in the absorbance with respect to time for 3.3mM, 2.5mM and 2.0mM $AgNO_3$ solutions respectively, whereas Figures 3B, 4B and 5B shows the variation in the absorbance with time for 0.33mM, 0.25mM and 0.20mM $AgNO_3$ solutions respectively.

The absorption spectrum for brownish silver colloid synthesized by reduction of $AgNO_3$ using $NaBH_4$ as reductor showed a surface plasmon absorption bands with a maximum of 390 nm, 384 nm and 408 nm (Figures 3A, 4A and 5A respectively). Whereas the absorption maxima observed for 0.33mM, 0.25mM and 0.20mM $AgNO_3$ concentrations are listed in the TABLE 2.

It can be observed that for 0.33mM $AgNO_3$ as the aggregation period varied from 45 min to 312 hrs the absorption maxima was fluctuating from 369-391 nm (Figure 3B), for 0.25mM for aggregation period from 1 hr to 263 hrs the absorption maxima was 386-391 nm (Figure 4B) and for 0.20mM the absorption maxima was fluctuating from 384-390nm for aggregation period ranging from 4 hrs 35 min to 143 hrs (Figure 5B). These values for absorption maxima indicate the presence of spherical or roughly spherical Ag NPs however the variations observed in the values of absorption band can be attributed to the occurrence of aggregation of Ag NPs with increase in the time.

TABLE 2 : Showing details of SPR bands at different $AgNO_3$ concentrations.

Sr. No.	$AgNO_3$ Conc. (0.33mM)		$AgNO_3$ Conc. (0.25mM)		$AgNO_3$ Conc. (0.20mM)	
	Time	Absorbance Maxima (SPR) (nm)	Time	Absorbance Maxima (SPR) (nm)	Time	Absorbance Maxima (SPR) (nm)
1.	45 min	369	1 h	371	1 hr	378
2.	1 hr	371	5 hrs	386	4 hrs 35 min	384
3.	1.5 hrs	376	6 hrs	385	47 hrs 35 min	387
4.	4 hrs	381	23 hrs	391	93 hrs	389
5.	6 hrs	384	29 hrs	386	143 hrs	390
6.	7 hrs	383	48 hrs	391	-	-
7.	20.5 hrs	384	110 hrs	389	-	-
8.	73 hrs	390	111 hrs	388	-	-
9.	291 hrs	389	189 hrs	389	-	-
10.	312 hrs	391	263 hrs	389	-	-

From UV-Vis spectra it can be clearly observed that with increase in the time the absorbance maxima decreases and then reaches to a minimum value indicating the aggregation of Ag NPs. At lower $AgNO_3$ concentrations (0.33-0.20mM), narrow surface plasmon peaks were observed, confirming the well dispersed state of silver nanoparticles (Figures 3B, 4B and 5B). However at higher $AgNO_3$ concentrations (3.3-2.0mM), the absorption peaks become broad, indicating the aggregation of Ag NPs (Figure 3A, 4A and 5A). The aggregation period observed for higher $AgNO_3$ concentration was much less than the aggregation period observed for lower $AgNO_3$ concentration which supports the fact that the Ag NPs at lower $AgNO_3$ concentrations are highly stable compared to the Ag NPs at higher $AgNO_3$ concentrations. Indeed, analogous effects were previously reported by Sobczak-Kupiec et al.[28] where they have prepared nanosilver suspension using PVP as stabilizer and $NaBH_4$ as a reducing agent. They have synthesized Ag NPs which were stabilized by the polymer, whereas in our work we have utilized $NaBH_4$ as reducing as well as the stabilizing agent and studied their stability using different precursor concentrations.

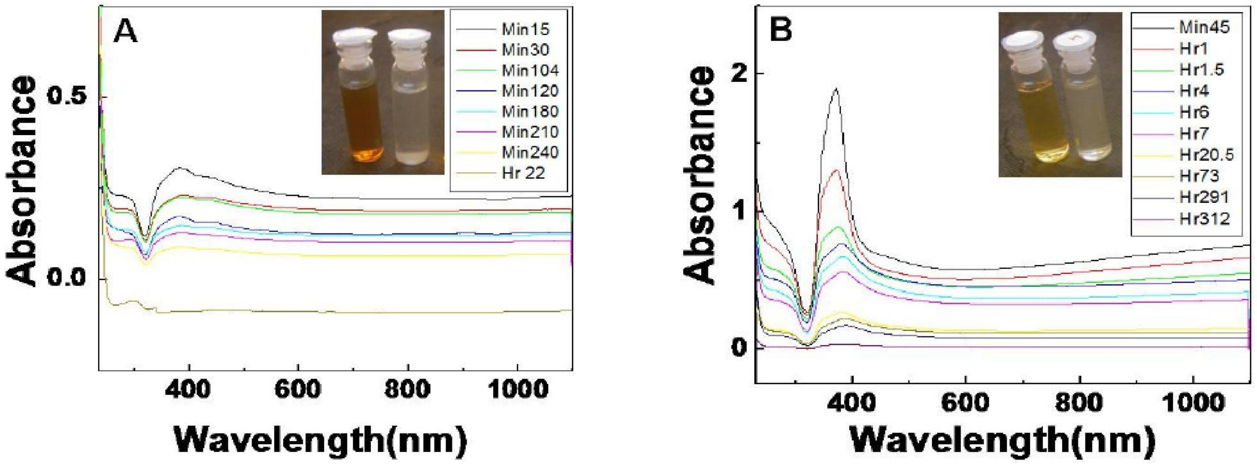

Figure 3 : The kinetic study and the comparison on the stability of silver nanoparticles at higher concentration of $AgNO_3$ 3.3mM (A) and at lower concentration of $AgNO_3$ 0.33mM (B) using UV-Vis Spectrophotometer.

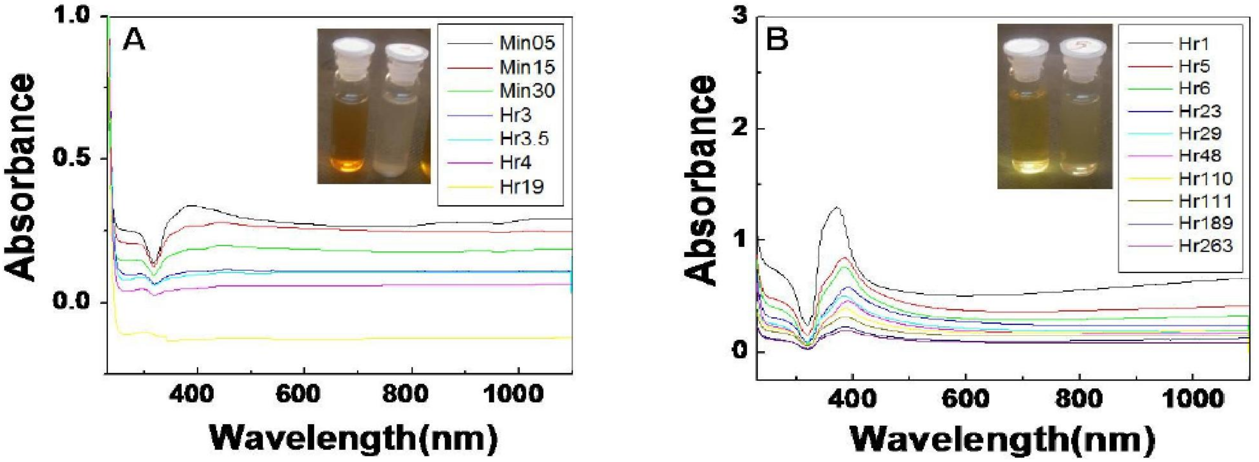

Figure 4 : The kinetic study and the comparison on the stability of silver nanoparticles at higher concentration of $AgNO_3$ 2.5mM (A) and at lower concentration of $AgNO_3$ 0.25mM (B) using UV-Vis Spectrophotometer.

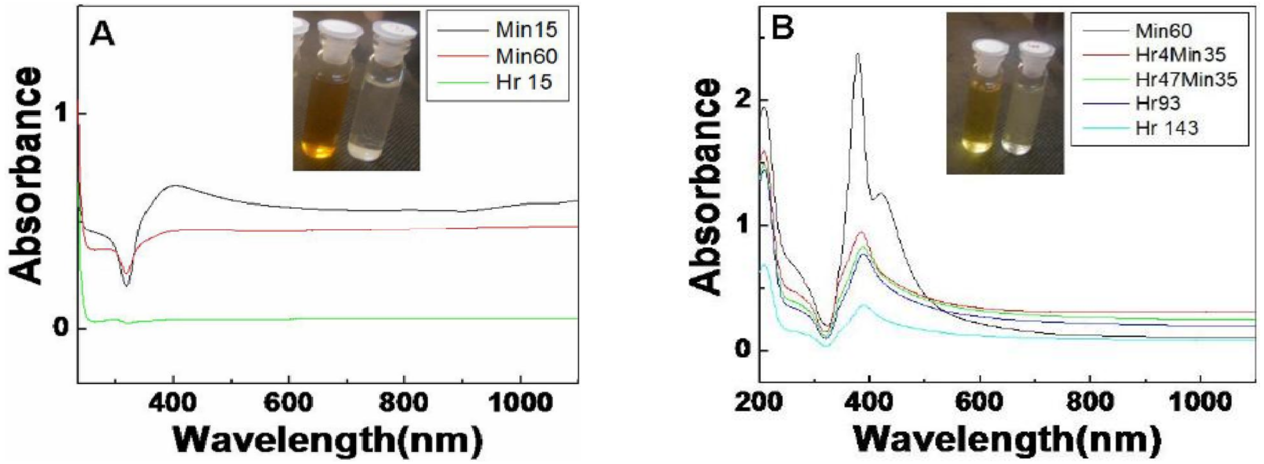

Figure 5 : The kinetic study and the comparison on the stability of silver nanoparticles at higher concentration of $AgNO_3$ 2.0mM (A) and at lower concentration of $AgNO_3$ 0.20mM (B) using UV-Vis Spectrophotometer.

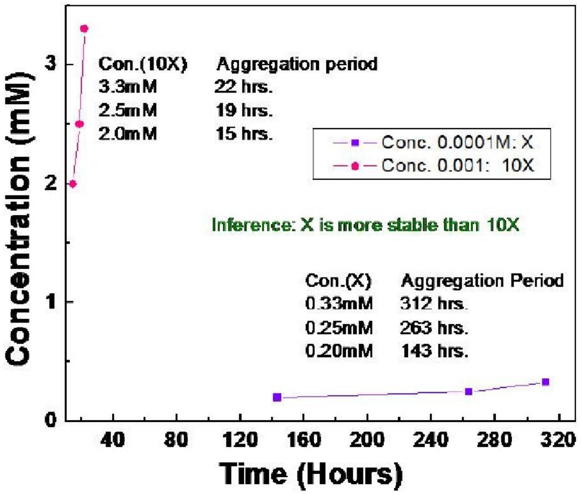

Figure 6 : Graphical summary of the kinetic study and the comparison of the stability of silver nanoparticles at higher concentration range of $AgNO_3$ (3.3-2.0mM) and at lower concentration range of $AgNO_3$ (0.33-0.20mM) using UV-Vis Spectrophotometer.

Figure 6 shows the aggregation periods observed for different $AgNO_3$ concentrations, it is self explanatory and gives a clear idea about kinetic study and the comparison of the stability of Ag NPs at higher concentration range of $AgNO_3$ (3.3-2.0mM) and at lower concentration range of $AgNO_3$ (0.33-0.20mM). However it was even observed that at higher $AgNO_3$ concentration (10X), the aggregation period increases with increase in the $AgNO_3$ concentration, i.e. Ag NPs synthesized at 2.0mM aggregates faster than 3.3mM and similar results were observed for lower $AgNO_3$ concentration (X) as shown in Figure 6.

With respect to the above noted observation the gap between aggregation periods for the successive $AgNO_3$ concentrations should increase, however it was observed that as the concentration is increasing the gap between the aggregation periods is decreasing i.e. the gap between 3.3mM and 2.5mM $AgNO_3$ should have been much greater than the gap observed between 2.5mM and 2.0mM. Similar results were observed at lower $AgNO_3$ concentration (X) also.

CONCLUSION

Silver nanoparticles were synthesized using sodium borohydride as reducing and capping agent. In order to check the stability of silver nanoparticles at various $AgNO_3$ concentrations, we carried out preliminary experiments at two higher concentrations $1x10^{-1}M - 1x10^{-2}M$ and two lower concentrations $1x10^{-5}M - 1x10^{-6}M$, however we observed too fast reaction at higher concentrations and too slow reaction at lower concentrations, hence we elected optimum range of concentration $10^{-3}M$ and $10^{-4}M$ as the working range for our study. The reaction kinetics were studied at different $AgNO_3$ concentrations and observed that the stability of Ag NPs depends upon the initial $AgNO_3$ concentration and reducing agent. It was concluded that Ag NPs synthesized at lower $AgNO_3$ concentrations were highly stable compared to the Ag NPs at higher $AgNO_3$ concentrations. As the selection of initial $AgNO_3$ concentration is crucial step for synthesizing stable Ag NPs, this experiment can be proved as a useful study for selection of appropriate $AgNO_3$ concentration.

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