

Effect of Acidic and Basic Conditions on the Plasmon Band of Colloidal Silver

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Abstract

Preparation of colloidal silver nanoparticles has been carried out by salt reduction method and confirmed by the appearance of plasmon band in the visible region. The prepared nanoparticles were subjected to acidic and basic environments. The plasmon band was studied as a function of time under the described conditions and hence used as a stability check of silver nanoparticles in different media. The mechanism of plasmon band disappearance of silver colloids was found to depend strongly on the pH of the medium.

Keywords: Colloidal silver, UV-visible spectroscopy, acidic and basic conditions, plasmon band

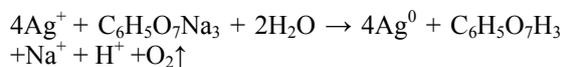
Introduction

The excellent conductivity of coinage metals has attracted the attention of many scientists [1]. Silver being one of the most conductive elements in the periodic table, an effective antifungal agent, easily affordable and having excellent antibacterial activity has been the focus of particular interest [2-4]. Silver nanoparticles are used in the manufacturing of odor resistant fabrics [5], surgical instruments, dressings, catalysis [6], optoelectronics and home appliances [6]. Moreover, it finds use in water treatment and power cells [7,8]. Recently, scientists have focused on the commercial use of silver nanoparticles such as the manufacturing of cheap and effective antibacterial paints, water filters, antibacterial surface coatings [9], superior electrocatalytic materials with piezo-electrics and many other advanced and sophisticated applications [10]. This requires an extensive study of the stabilities of silver nanoparticles under different possible conditions [11]. Various studies have revealed that silver nanoparticles are sensitive to acidic and basic

media but none of them reveal the limits up to which they are sensitive to the concentration of acids and bases and how they lose their stability as a function of time in extreme environments [3,4]. This study tries to explain the effect of such conditions on the stability of silver nanoparticles when prepared by citrate reduction.

Materials and methods

Colloidal silver nanoparticles were prepared by the salt reduction [12] in which silver nitrate was reduced by trisodium citrate.



A 200 ml solution of 0.01 M silver nitrate was magnetically stirred and heated until the temperature reached 368 K. 2 ml of 0.34 M trisodium citrate (TSC) was added which resulted in the appearance of a golden yellow color due to the formation of nanoparticles. The colloidal

solution of silver nanoparticles was removed from the hot plate just after the color change. The colloidal solution of the Ag-NPs was equally distributed among 15 test tubes (each test tube contained 15 ml of the NPs solution) and further divided into 3 groups i.e. group A, group R and group S for which the molarities of the base (NaOH) were 0.1 M (**Table 1**), 0.075 M (**Table 2**), 0.05 M (**Table 3**) respectively. As each group of NPs solution contained 5 members they were named according to the amount of base added as given in **Tables 1 - 3**.

A Cary WinUV spectrophotometer (model 50 conc serial: ACN-004 559 540) was used to study the plasmon band. After adding base to all the solutions their plasmon band was observed

periodically using UV-Vis spectrometer. Another experiment was performed using acidic concentrations, accordingly labeled and measured.

UV-Visible spectroscopy is extensively used for the studies of the metal nanoparticles showing plasmon bands. UV-Vis absorption spectra have proved their importance in order to confirm the existence of nano sized metal particles due to the surface plasmon resonance phenomenon in the metals. Ag-metal nanoparticles exhibit a plasmon band in the range of 350 nm to 550 nm. Samples were checked using UV-Visible spectroscopy for the study of changes in their plasmon band. All experiments were performed under normal laboratory conditions.

Table 1 Group A (0.1 M acid/base stock solution).

| Sample name | Amount of base/acid added (ml) | Final concentration of acid/base (M) $\times 10^{-3}$ |
|-------------|--------------------------------|---|
| A1 | 0.1 | 0.66 |
| A2 | 0.2 | 1.3 |
| A3 | 0.3 | 2.0 |
| A4 | 0.4 | 2.6 |
| A5 | 0.5 | 3.2 |

Table 2 Group R (0.075 M acid/base stock solution).

| Sample name | Amount of base/acid added (ml) | Final concentration of acid/base (M) $\times 10^{-3}$ |
|-------------|--------------------------------|---|
| R1 | 0.1 | 0.50 |
| R2 | 0.2 | 1.0 |
| R3 | 0.3 | 1.5 |
| R4 | 0.4 | 2.0 |
| R5 | 0.5 | 2.5 |

Table 3 Group S (0.05 M acid/base stock solution).

| Sample name | Amount of base/acid added (ml) | Final concentration of acid/base (M) $\times 10^{-3}$ |
|-------------|--------------------------------|---|
| S1 | 0.1 | 0.33 |
| S2 | 0.2 | 0.66 |
| S3 | 0.3 | 0.98 |
| S4 | 0.4 | 1.3 |
| S5 | 0.5 | 1.6 |

Results and discussion

Appearance of plasmon band

Figure 1 shows the UV-Visible spectrum of 0.1 M $\text{AgNO}_{3(\text{aq})}$ solution where 0.34 M TSC is used as a solvent. The appearance of the plasmon

band is consistent with the formation of colloidal silver nanoparticles. The λ_{max} value of 437 nm corresponds to the average size of 45 nm which is already established in literature.

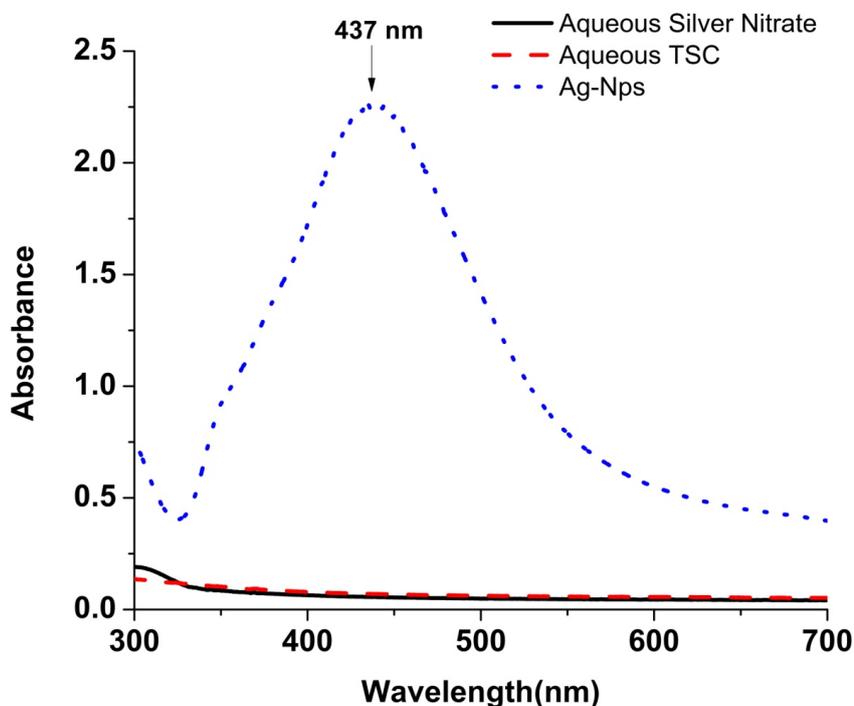


Figure 1 UV-Visible spectra of aqueous silver nitrate solution of known molarity (0.1 M) and of TSC 0.34 M and the plasmon band.

Effect of base on the plasmon band of Ag-NPs in solution

When a basic solution of NaOH was added to the NPs solution, the first observation was an immediate color change of solutions i.e., solutions became blackish and there was an abrupt increase in the absorbance values (color of Ag-NPs solution turned blackish from greenish yellow). It was

observed that the higher the concentration of base in the solution the darker the color of the solution and the rate of color change was also faster. This may indicate a faster structural change in the nanoparticles. There is a very small blue shift (8 nm) in the wavelength of the maximum absorbance.

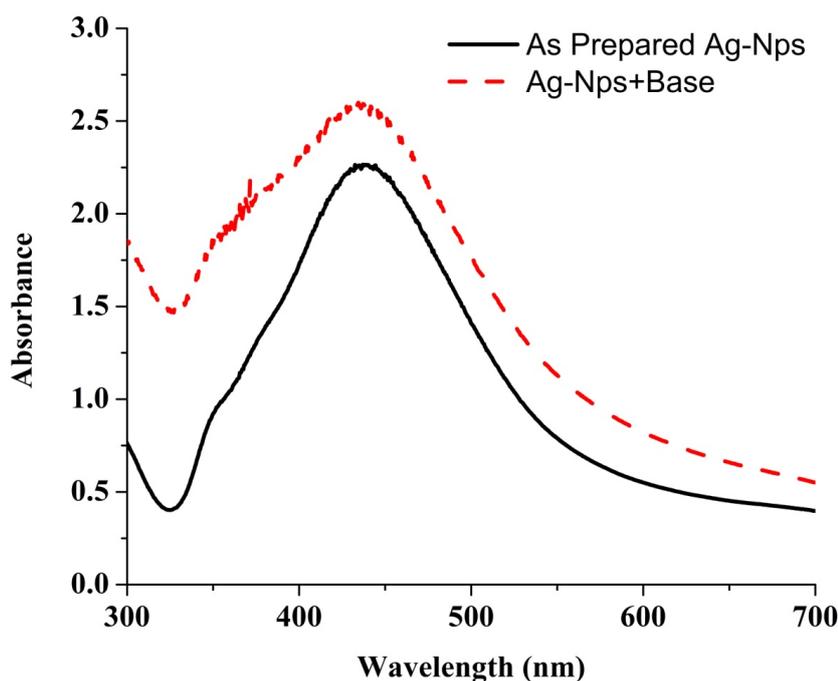


Figure 2 UV-Visible spectra of Ag-NPs before and after adding the base.

In **Figure 2**, increase in the absorbance value corresponds to the formation of new nucleation sites. In the presence of base an increase in the width of the peak was observed which may be due to an increase in the range of particle sizes.

The addition of base has two peculiar effects on the spectra of Ag-NPs i.e., (i) an initial dip in the absorbance value (ii) the unevenness of the spectrum. Overall there is a gradual decrease in the absorbance which can be clearly seen in **Figures 3a - 3c**. The initial dip in the spectra can be correlated to the dissolution of silver nanoparticles into Ag^+ ions in the form of $\text{Ag}^+\text{OH}(\text{aq})$ which ultimately deposit on the glass wall of the test tubes forming a mirror. In the mean time a restructuring follows which actually resists the dissolution of more nanoparticles. There might be a formation of AgOH layer on the surface of the silver nanoparticle which slowly dissolves with the passage of time resulting in slow degradation in

the second stage of the process. This rearrangement is depicted from the regain of the high absorbance in the case of a basic medium. After this regain, the absorbance starts to fall gradually with time in a very regular fashion. Such a behavior is clearly pictured in **Figure 3**. This can be correlated to the preferential formation of $\text{AgOH}(\text{aq})$ as compared to the citrate capped colloids of silver. Moreover, the higher concentration of base resulted in a darker solution and the rate of color change was faster too which is due to the fast transformation of Ag-NPs to $\text{AgOH}(\text{aq})$. This also indicated more rapid structural changes in the nanoparticles surface.

This can be further explained chemically as the preferential affinity of Ag-NPs for the formation of hydroxide instead of remaining capped by the citrate which again has a tendency to take on the more readily available cations of the strong alkali.

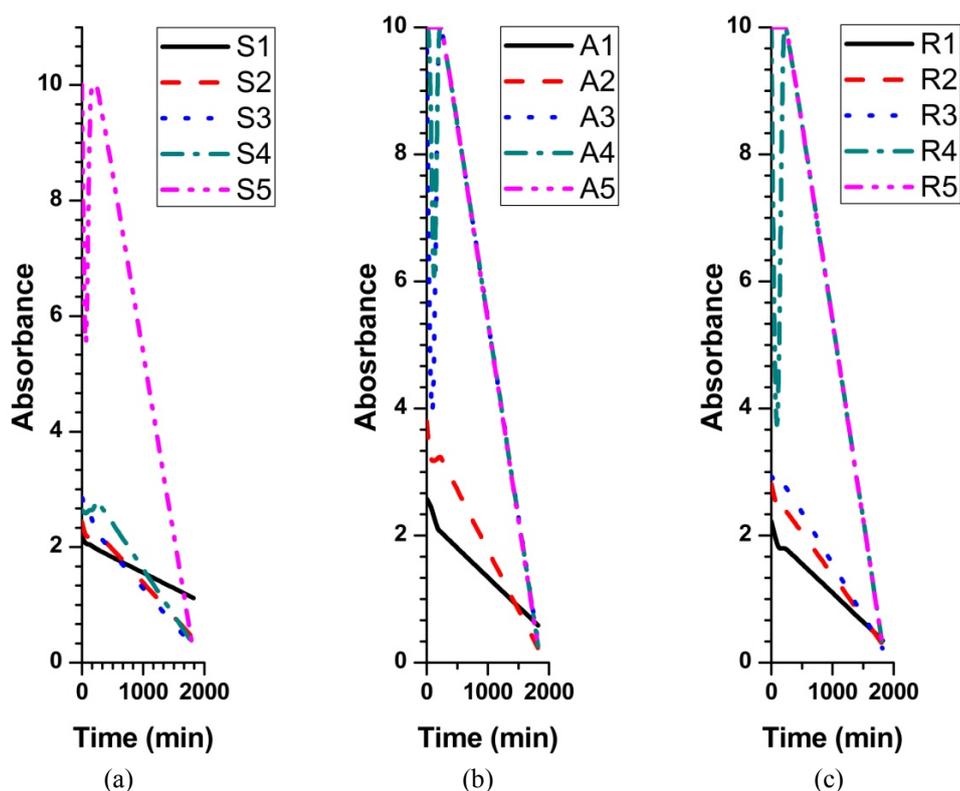


Figure 3 Summary of the results of addition of base to the as-prepared Ag-NPs solutions.

Initially this results in the development of nucleation sites along with the instability that causes the nanoparticles to combine and form larger agglomerates. This is evident from the elevation of the baseline of the UV-Vis spectrum and the reduction in the plasmon band absorbance value. However, samples A1, S1, S2, R1 Ag-NPs

remained relatively stable for longer than 24 h and the plasmon band was present although the peak height revealed low concentrations of nanoparticles. The concluding observation was the presence of a clear solution and the formation of mirror on the glass walls of the test tube.

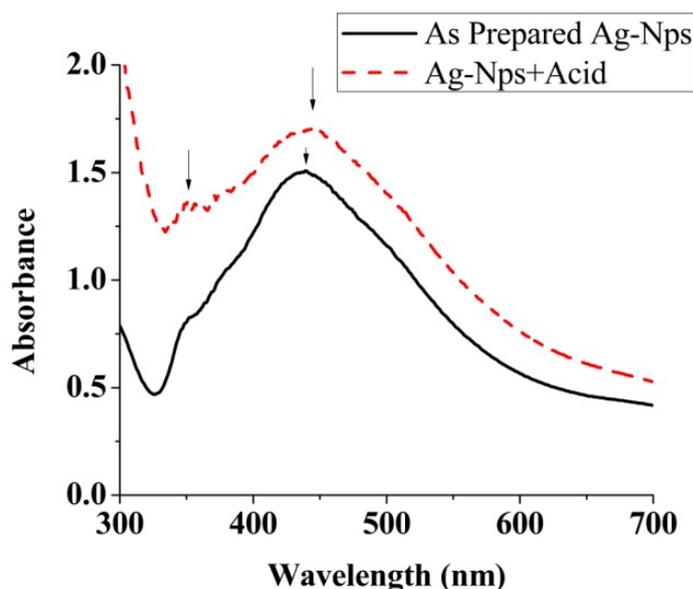


Figure 4 Plasmon band of the as-prepared Ag-NPs and effect of adding acid. Spectra were recorded just after the addition of acid.

Effect of acid on the surface plasmon band of Ag-NPs

After adding the acid to the as-prepared Ag-NPs solution, a small red shift (10 nm) is seen in the spectra shown in **Figure 4**. This indicates an increase in the size of the nanoparticles and the increase in the absorbance value represents the formation of new nucleation sites i.e. an increase in the concentration of the NPs. Another visible change in the plasmon resonance band is the second maximum which is due to the presence of two main particle sizes.

After adding different concentrations of acid the response of the solutions was different. The visible spectra showed a decrease in the concentration of the nanoparticles and ultimately a change in size due to accelerated growth of the particles. The growth of the particle is proved by ultrasonification of the resulting precipitate which could not be re-dispersed even when put to the process for long time in the same medium initially used for the dispersion of Ag-NPs. The sample S1 has the lowest concentration of acid so it did not show any appreciable disappearance of nanoparticles even after 24 h. Similarly samples A1, R1, S1, S2 i.e., concentration of acid $< 10^{-3}$ M

retained their plasmon band for significant lengths of time i.e., even after 24 h which shows that Ag-NPs were stable in low acid concentrations as depicted in **Figure 5**. The calculation of acid concentration in solutions showed that nanoparticles became unstable in acidic medium when the concentration of acid is $\geq 10^{-3}$ M. Any lower concentration of acid will be unable to completely destabilize the Ag-NPs before 24 h. However, higher concentrations clearly changed the nano domains of the Ag-NPs.

According to Murali *et al.* [13] electrostatic repulsive interactions between flocculated clusters are responsible for the stability of Ag-NPs, and the capping agent enhances these forces and hence, stabilizes the nanoparticles. With the addition of acid, the pH value of capped Ag-colloidal solution decreases and creates holes (for electrons due to addition of H^+ ions to the solution) in hydrosol. This decrease in electrostatic repulsion produces appreciable damping and red shift in the absorption spectra. Increase in size distribution is also evident from spectra in **Figure 4**. All the plots of absorbances at different concentrations vs. time other than $\leq 10^{-3}$ M are able to rapidly increase the size of Ag-NPs.

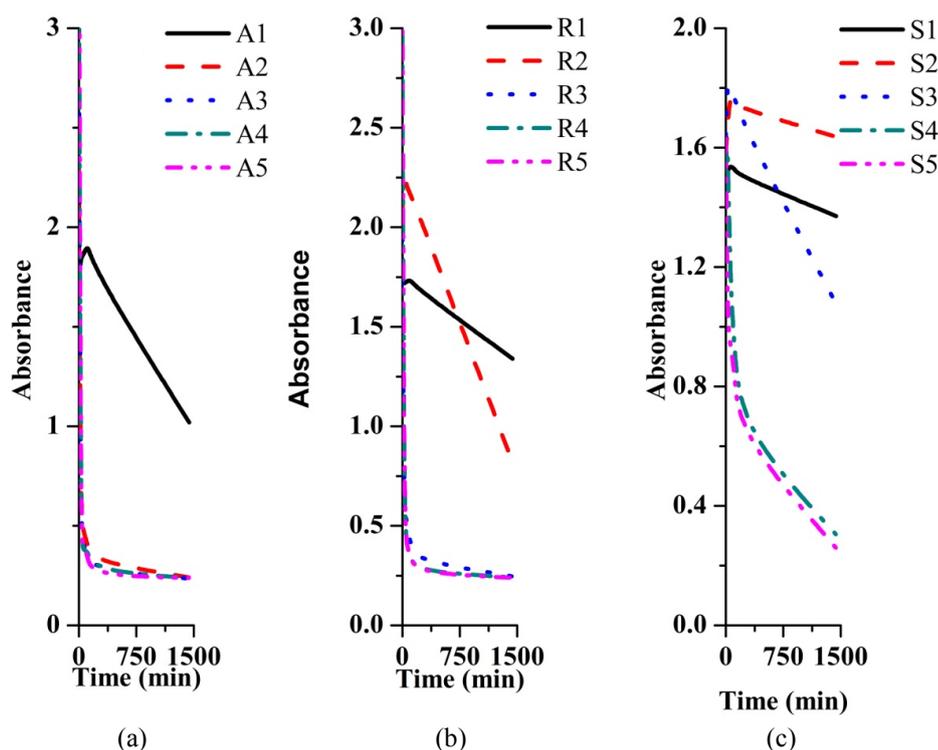


Figure 5 Plot of absorbances of Ag-NPs plasmon band subjected to different acidic environments.

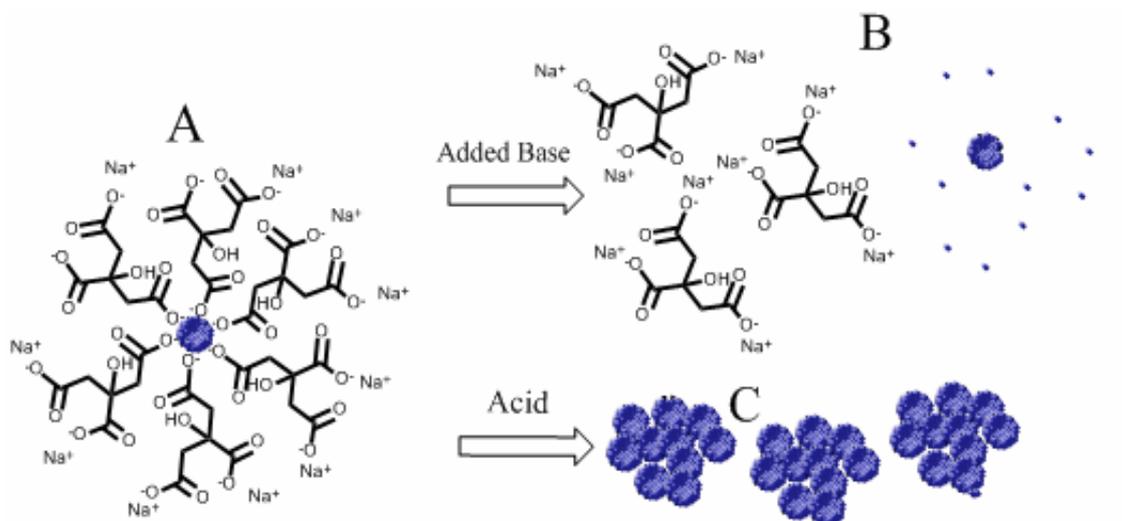
Increasing concentrations of acid results in rapidly decreasing plasmon band, unstable Ag-NPs

After complete disappearance of the plasmon band in visible spectra the solutions became clear and black residues were there in the bottom of the test tubes. The clearness of the solutions and that residue can be explained as follows. When acid was introduced into the Ag-NPs solutions they started to grow in their sizes which are evident from the red shift in the visible spectra and after some time they grew large enough to cross the lower limit of 10^{-9} m and entered larger sizes. As the plasmon band represents the existence of nano sized silver particles so with the extinction of nano size silver particles the plasmon band also disappeared and particles settled down in the bottom of the test tubes.

While disappearing, the acidic and basic samples followed different mechanism. In the basic medium, particles decrease their size and form Ag^+ ions while in acidic medium, particles grow in size to cross this limit. In the basic medium, particles decreased their size and stabilize themselves by sticking to the walls of test tubes and the end product was a clear solution with a silvering of the walls of the test tubes. In the case of acidic medium particles grow in size and became larger and thus settle at the bottom of the test tube.

Conclusions

Ag-NPs are unstable in both acidic and basic media however the mechanism which leads to this instability is very much different in the two mediums.



Scheme 1

Ag-NPs (**Scheme 1**) spontaneously convert to Ag^+ ions i.e., shown by small blue dots in **Scheme 1** under basic conditions i.e., in the form of $\text{Ag}^+\text{OH}(\text{aq})$ which ultimately deposits on the wall of test tube. In acids (**Scheme 1**) the nanoparticles aggregate and grow in size resulting in precipitates at the bottom of the test tube. In acidic conditions we conclude that “Stable Ag-NPs < concentration of acid 10^{-3} M \leq Unstable Ag-NPs”.

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