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pH effect on the aggregation of silver nanoparticles synthesized by chemical reduction

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Silver colloidal nanoparticles were prepared according to the chemical reduction method in which the ascorbic acid was used as a reducing agent and sodium citrate as a stabilizing agent. The absorption spectra of all prepared samples obtained using the UV-Vis spectrophotometer showed a surface plasmon peak at a wavelength of about 420 nm. The size of the silver nanoparticles was controlled by changing the pH values of the reaction system. At high pH, smaller size silver nanoparticles were obtained compared to low pH values. This difference can be attributed to the difference in the reduction rate of the precursor. In addition to the inverse proportionality between the size and the pH value it is clear that increasing the pH value enables us to obtain spherical nanoparticles while at low pH, rods and triangular particle shapes were formed. Poor balance between nucleation and growth processes could be the cause of this result.

Keywords: *silver nanoparticles; pH; chemical synthesis*

1. Introduction

In the last few years, nanoparticles science and technology have been widely developed due to fascinating physical, chemical and optical properties of these species. Most of their properties are related to high surface to volume ratio of nanoparticles as well as some quantum size effects. Every particle having a dimension in the range between 1 to 100 nm can be defined as a "nanoparticle".

Metal nanoparticles, such as silver and gold nanoparticles, are widely used in various fields such as medicine, biology, chemistry, physics and electronics. This widespread use results from unique properties such as thermal, magnetic, electronic, electrical and optical properties compared to bulk phase [1].

Many researchers have prepared and characterized silver nanoparticles (AgNPs) using different methods such as chemical methods, gamma radiation, laser ablation and electrochemical methods [2–5]. Others have studied the possibility of controlling their shape and size through investigating factors that affect their dimensions. Hongli *et al.* observed the changes in color of colloidal silver solutions at different pH values [6]. Under high pH, the color of silver solution was changed from colorless to yellow and then brown. Under low pH, the color was changed from colorless to yellow and then blue turbid. Dong *et al.* showed that the shape of AgNP particles depended on the pH value when they used citrate ($Na_3C_6H_5O_7$) as a reducing as well as a stabilizing agent and they found that the shape of AgNPs at high pH was a mixture of spherical and rod-like particles while at low temperature the shape was triangular and polygonal [7]. Mazumdar *et al.* studied the possible toxicity of silver nitrate solutions and sodium borohydride solutions ($AgNO_3/NaBH_4$) on the seeds of three plant species since they were used as raw materials for nanoparticle synthesis [8]. Qin *et al.* studied the size and shape of AgNPs by changing the pH value of the solution and observed that the size became smaller and the shape more spherical as the pH increased [9].

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In this study, silver colloidal nanoparticles have been prepared according to the chemical reduction method in which the ascorbic acid was used as a reducing agent and sodium citrate as a stabilizing agent. The effect of pH on the color, shape and size of silver nanoparticles was investigated.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$), trisodium citrate ($Na_3C_6H_5O_7$), ascorbic acid ($C_6H_8O_6$), sodium hydroxide (NaOH), nitric acid (HNO_3), acetic acid ($C_2H_4O_6$) and deionized water were used in the experiment. All chemicals were produced by Sigma Aldrich (India), Merck (India) and Acros (USA).

2.2. Procedures

A 0.1 M $AgNO_3$ solution was prepared by adding 16.987 mg of $AgNO_3$ to 1 ml deionized water. A 100 ml of an aqueous solution containing ascorbic acid ($C_6H_8O_6$) 6×10^{-4} M and trisodium citrate ($Na_3C_6H_5O_7$) 3×10^{-3} M was prepared, and the solution was adjusted to different pH values by adding of 0.2 mol/l of citrate acid or 0.1 mol/l of NaOH solution.

The aqueous solution was placed over a heater which was switched on simultaneously with a stirrer and a condenser. When the temperature reached around 100 °C, the solution started to boil and the $AgNO_3$ solution was added drop by drop through the upper opening at the ratio 1 ml $AgNO_3$ solution: 100 ml aqueous solution of sodium citrate and ascorbic acid. The color of the solution changed to light yellow after adding $AgNO_3$ solution under low pH to blue turbid under high pH. The first change appeared within 5 – 10 minutes after adding $AgNO_3$ solution. Boiling must have been continued for almost 1 hour at a fixed temperature of about 100 °C [10].

3. Results and discussions

The prepared colloidal silver nanoparticles were investigated using different analysis tools. The particle size analyzer was used to investigate the size of the prepared nanoparticles. Fig. 1 shows the size distribution in one of the prepared samples. It is clear that most of the prepared nanoparticles have the radii less than 70 nm and about 45 % of them have the radius below 51 nm.

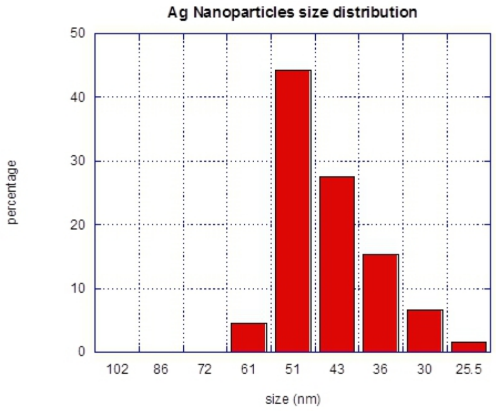

Fig. 1. Size distribution of silver nanoparticles.

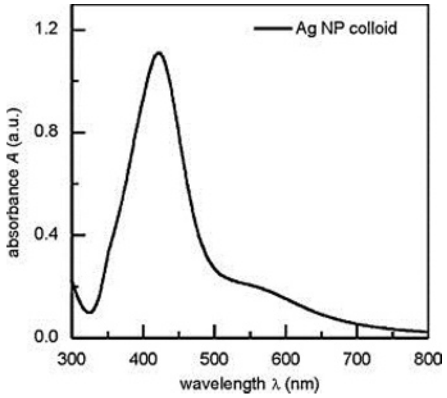

Fig. 2. Absorption spectra of silver nanoparticles.

The UV-Vis spectrophotometer was used to obtain the absorption spectra of the prepared samples. Usually, these spectra give the indication about the formation of colloidal silver nanoparticles as well as the quality of the tested samples.

The measurement showed that silver nanoparticles had an absorption peak around the wavelength of 410 nm. This is a characteristic property of silver nanoparticles and corresponds to the surface plasmon resonance. A typical absorption spectrum of silver nanoparticles colloid is shown in Fig. 2.

Transmission electron microscope TEM imaging technique was used to determine the shape and size of the nanoparticles that were formed under the influence of different pH values.

3.1. pH effect on the size of AgNPs

There are many factors that affect the size and shape of silver nanoparticles. In this part, we will address the impact of the pH on the size of AgNPs by monitoring size variations as a result of changing the pH of the solution.

Absorption spectra at different values of the pH (7, 8, 9, 10, and 11) are presented in Fig. 3. A general trend is that the surface plasmon resonance peak shifts toward the short wavelength region as well as becomes narrower when the pH value increases.

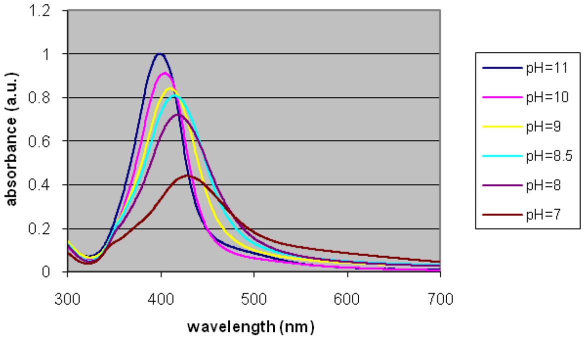

Fig. 3. Absorption spectra of AgNPs at different pH values.

Assuming that the shift in the surface plasmon resonance peak indicates a change in the size of AgNPs and hence any shift of the peak toward the shorter wavelength is accompanied by a decrease in the size of the prepared AgNPs, we conclude that raising the pH of the solution results in the formation of nanoparticles with smaller size and vice versa. On the other hand, the broadening of the surface plasmon resonance peak indicates the existence of a wider range of sizes in the solution.

Fig. 4 shows the relationship between the maximum absorption and the pH value which is almost directly proportional. Fig. 5 shows that the relationship between the size of AgNPs and the pH value is inversely proportional. The effects of the pH value on the AgNPs size, absorption peak and wavelength are listed in Table 1.

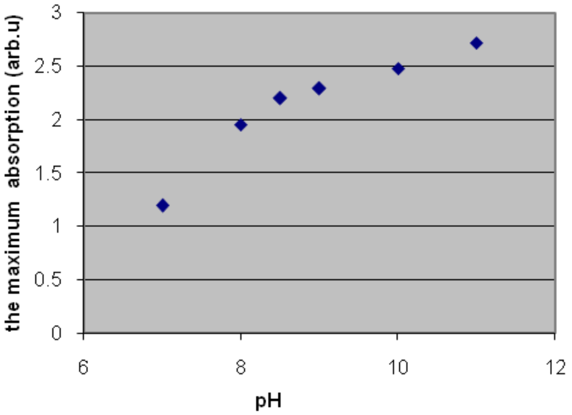

Fig. 4. Relationship between the pH values and the maximum absorption.

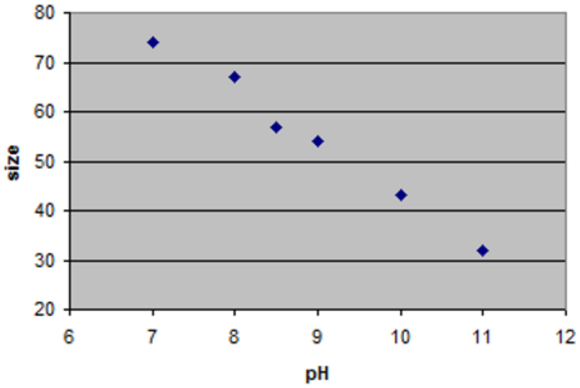

Fig. 5. Relationship between the pH values and the size of AgNPs.

Fig. 6 presents the results of all TEM measurements of the prepared samples at different pH values. It is clear that as the pH value increases, the sizes of the particles decrease and the shape becomes more spherical. It is worth mentioning that the results of the TEM imaging are in good agreement with the results obtained from the absorption spectra of the same samples.

According to Fig. 6, the particles prepared under low pH (7, 8 and 8.5) are mostly irregular in shape. Irregularity in the shape of particles can be attributed to the slow reduction rate of the precursor in addition to the poor balance between nucle-

Table 1. The wavelength, absorption peaks and radius of AgNPs at different pH values.

pH ± 0.01	The peak absorption (arb.u.)	The wavelength (nm) ± 0.3	The size of AgNPs
7.00	1.193	428.0	74.00 ± 3.11
8.00	1.955	418.5	67.00 ± 1.59
8.50	2.197	416.0	57.00 ± 1.37
9.00	2.287	410.5	54.00 ± 1.95
10.00	2.476	404.0	43.00 ± 1.87
11.00	2.716	397.0	32.00 ±1.55

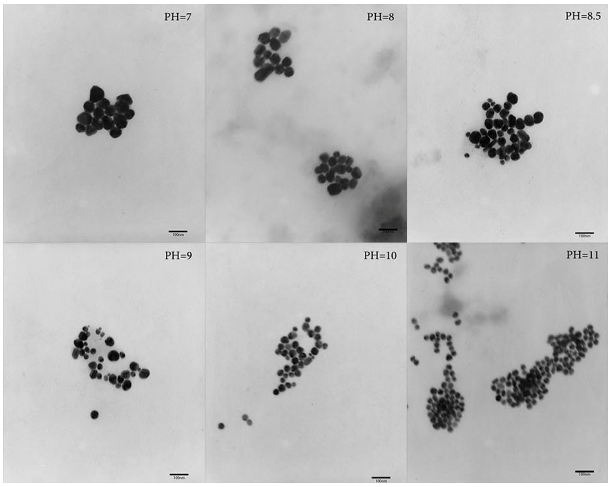

Fig. 6. TEM image of nanoparticles at different pH values.

ation and growth processes. On the other hand, the AgNPs prepared under high pH (10 and 11) are more regular and smaller compared to the previous samples prepared at lower pH values. The average radii of particles are around (43.00 ± 1.87, 32.00 ± 1.55) nm, respectively, and the shape of silver nanoparticles is spherical. The spherical shape of silver nanoparticles can be attributed to the balance between the nucleation and growth processes as well as to the increase in reduction rate of the silver precursor (Ag^+).

3.2. The effect of the pH on the color of AgNPs

Fig. 7 shows the variation in the color after adding silver nitrate solution ($AgNO_3$) to the ascorbic acid and citrate solution. With increasing the pH values the color of the solution changes from colorless to yellow and then to brown, while it changes from colorless to blue turbid as the pH values decrease.

Fig. 7. The color of AgNPs colloids at different pH values.

The variation in color can be attributed to the surface plasmon resonance since the strong interaction between silver nanoparticles and light results in collective oscillations of conduction electrons on the surface when excited by light at specific wavelengths.

4. Conclusions

Silver colloidal nanoparticles were prepared according to the chemical reduction method in which the ascorbic acid was used as a reducing agent and sodium citrate as a stabilizing agent. The absorption spectra of all prepared samples obtained using the UV-Vis spectrophotometer showed a surface plasmon peak at a wavelength of about 420 nm. This peak is a characteristic property of silver nanoparticles.

The relationship between the average size of silver nanoparticles and the pH values of the solution was investigated. It has been found that as the pH value increases, the surface plasmon peak shifts to left indicating a decrease in the size of the prepared nanoparticles. Moreover, this shift in the peak is accompanied by a decrease in the width of the peak indicating size uniformity.

TEM images obtained using the transmission electron microscope confirmed the results obtained using the UV-Vis spectrophotometer regarding the dependence of the size on the pH value. In addition to the inverse proportionality between the size and the pH value, it is clear that increasing the pH value produced a spherical nanoparticles while at low pH, rods and triangular particles were obtained. This result can be attributed to the poor balance between nucleation and growth processes.

References

[1] MYERS D., *Surfaces, Interfaces, and Colloids: Principles and Applications*, 2nd Ed., Wiley VCH, New York, 1999.

[2] PILLAI Z.S., P.V. KAMAT, *J. Phys. Chem. B*, 108 (2004), 945.

[3] LIU Y., CHEN S., ZHONG L., WU G., *Radiat. Phys. Chem.*, 78 (2009), 251.

[4] TSUJI T., IRYO K., WATANABE N., TSUJI M., *Appl. Surf. Sci.*, 202 (2002), 80.

[5] MA H.Y., YIN B.S., WANG S.Y., JIAO Y.L., PAN W., HUANG S.X., CHEN S.H., MENG F.J., *Chem. Phys. Chem.*, 5 (2004), 68.

[6] QU J., CHANG Y., MA Y., ZHENG J., LI H., QU Q., REN C., CHEN X., *Sensor. Actuat. B-Chem.*, 174 (2012) 133.

[7] DONG X. et al., *J. Phys. Chem. C*, 113 (2009), 6573.

[8] MAZUMDAR H., AHMED G., *Int. J. Chem. Tech. Res.*, 3 (2011), 1494.

[9] QIN Y., JI X., JING J., LIU H., WU H., YANG W., *Colloid. Surface. A*, 375 (2010), 172.

[10] LEE P.C., MEISEL D., *J. Phys. Chem. B*, 86 (1982), 3391.

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