Preparation and Application of Silver Nanoparticles on Silk for Imparting Antimicrobial Properties

M. L. Gulrajani, Deepti Gupta, S. Periyasamy, S. G. Muthu

Department of Textile Technology, Indian Institute of Technology Delhi, New Delhi 110016, India

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ABSTRACT: Silver nanoparticles were produced by a chemical reduction method that reduced silver nitrate with reducing agents such as hydrazine and glucose. The silver nanoparticles were characterized with transmission electron microscope, scanning electron microscope, and optical microscope. The effects of process parameters such as the stirring speed, temperature, type of reducing agent, and dispersing agent on the particle size were studied. The particle size decreased with an increase in the stirring speed and a decrease in the process temperature. Smaller particles were formed when the silver nitrate was reduced by glucose versus those that were formed by reduction with hydrazine. Silver nanoparticles with average sizes of 10 and 35 nm, produced by reduction with hydrazine at 5 and 40°C, were applied to silk by an exhaust method. Silk fabrics treated with 40 ppm silver hydrosol produced at 5°C and 60 ppm silver hydrosol produced at 40°C showed 100% antimicrobial activity against the gram-positive bacterium *Staphylococcus aureus*. The durability of the antimicrobial property of the treated silk fabric to washing was also examined and is presented. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 614–623, 2008

Key words: mixing; nanotechnology; particle nucleation; synthesis; TEM

INTRODUCTION

Various physicochemical methods have been investigated for the production of silver nanoparticles. Among the chemical methods,[1–10] the reduction of silver nitrate with various reducing agents such as ascorbic acid, glucose, and hydrazine has been extensively studied.[4,6,8,10,11]

The application of silver nanoparticles for imparting antimicrobial property to textiles has been recently investigated, and some commercial preparations are being produced for this purpose.[11–13]

The particle size and its distribution determine the minimal quantity of the particles on the fabric needed to obtain the required antimicrobial property. The size of the silver nanoparticles and its distribution are influenced by various process parameters. Some of the important parameters in consideration during the preparation of silver nanoparticles are the chemical nature of the surfactant (dispersing agent), the molar ratio of the surfactant to $AgNO_3$, the redox potential of the reducing agent, and the molar concentration, feed ratio, and stirring speed of the reactants.[1–10] Moreover, the temperature of the reduction medium also determines the final particle size, and it has been reported that when silver nitrate is reduced at the reaction temperature of 50°C, a particle size of less than 100 nm is formed.[1] Kim et al.[8] reported that of all the parameters, the concentration of the dispersant is the most influential parameter. Seo et al.[10] studied the type of reducing agent used for preparing silver nanoparticles with and without a surfactant. They found that particles with average sizes of 1 μm and 50 nm were formed without and with a surfactant, respectively, when hydrazine was used as a reducing agent. The main mechanism that influences the particle size is particle aggregation; therefore, the approach of almost all the aforementioned studies has been to minimize agglomeration. For example, Zhang et al.[9] treated silver nanoparticles with ionic liquids to stabilize and prevent agglomeration.

In this study, silver nanoparticles were produced by a chemical reduction method. The effects of process parameters such as the stirring speed, reaction temperature, and combinations of various reducing and dispersing agents on the particle size were investigated. Furthermore, in this study, an attempt was made to make antimicrobial silk fabrics by their treatment with silver nanoparticles. Silk possesses ionizable groups on the side chains of various amino acid residues, whose dissociation state depends on the surrounding pH conditions; since silk is amphoteric in nature.[14] Moreover, it has been reported that the silver nanoparticles develop negative charge around its surface.[15] Therefore, in this study, the effects of various parameters of the application medium, such as the pH, temperature, and

Correspondence to: M. L. Gulrajani (mlg54@hotmail.com).

time, on the silver nanoparticle uptake of silk were also studied.

EXPERIMENTAL

Materials

Degummed mulberry silk fabric (GSM-96, EPI-122, PPI-68, warp count = 3/7.5 tex, weft count = 2/2 tex) was used for the study. It was washed in distilled water at 60°C for 30 min and then dried in a stenter at 110°C for 3 min. The fabric was then kept in a desiccator for at least 12 h for conditioning at the standard relative humidity (65 ± 2%).

All the chemicals were procured from Mumbai, India. Silver nitrate was purchased from Merck. Hydrazine hydrate and D-glucose were procured from Qualigens Fine Chemicals. Poly(vinyl pyrrolidone) (PVP; molecular weight = 40,000) and ferric sulfate were obtained from Loba Chemie Pvt., Ltd. Potassium thiocyanate was procured from Sisco Research Laboratories Pvt., Ltd.

Preparation of the silver nanoparticles

For the preparation of the silver nanoparticles, 0.5*M* silver nitrate and 0.75*M* PVP were dissolved in 80 mL of deionized water. PVP (molecular weight = 40,000) was used as a dispersing and stabilizing agent, and the molar ratio of silver nitrate to PVP was maintained at 1 : 1.45 to get an optimum stabilizing effect of PVP with a minimum particle size.[16] Separately, 0.75*M* hydrazine was dissolved in 20 mL of deionized water. The hydrazine was taken 6 times in excess of silver nitrate by molar weight for the complete reduction of silver nitrate into silver.[17] The silver nitrate was slowly reduced to silver by the measured addition of hydrazine (3 ml/min) while the silver nitrate solution was stirred at 2500 rpm. The reaction was continued for 20 min at 40°C. Silver hydrosol thus formed was used for further characterization and application on silk. Each experiment was repeated at least three times, and hence the average particle size is presented for the study of various parameters such as the stirring speed, reducing and dispersing agents, and reaction temperature.

Application of the silver nanoparticles on silk

Silver nanoparticles were applied to the silk fabric by an exhaust method with a shaker bath (SW 22, Julabo, Germany). The major parameters of application, that is, the pH, temperature, and time, were studied. The beakers containing silver solutions were kept in the shaker bath. Then, the respective parameters were monitored, that is, the pH and temperature, with a pH meter and a thermometer. For adjusting the pH, a weak alkali agent was used as the silver hydrosol itself has an acidic pH. For adjusting the temperature, the thermostat control in the shaker machine was used. Once the required pH and temperature of the silver hydrosol in the bath were achieved, the silk sample was entered and treated for 30 min at 150 rpm of the shaker shaft. For all other experiments, generally the treatment was carried out at 40°C for 30 min. The treated fabrics were then dried at room temperature without any rinsing.

Estimation of the silver content

The amount of silver present in the silver hydrosol was calculated by a modified method of estimating silver (Volhard's thiocyanate method).[18] This method is based on the greater affinity of silver ions than ferric ions for thiocyanate. The following procedure for the estimation of the silver content was used.

The thiocyanate reagent was prepared by the dissolution of 9.2 mg of potassium thiocyanate in 20 mL of deionized water.

The ferric indicator was prepared from 100 mL of a saturated solution of ferric sulfate, and a sufficient amount of nitric acid was added to clear up the solution to produce a pale yellow color.

A standard silver solution was prepared in such a manner that 50 mL of the standard solution contained 0.25 g of Ag.

A standard silver solution (20 mL) was titrated against potassium thiocyanate in the presence of 10 mL of the ferric indicator until the point at which a permanent faint red color appeared. The volume of thiocyanate required was denoted V_s.

To estimate the silver content in silver hydrosol, 20 mL of the solution was titrated against potassium thiocyanate in the presence of 10 mL of the ferric indicator until the point at which a permanent faint red color appeared. The volume of thiocyanate required was denoted V_1.

The silver content (ppm) was calculated as follows:

$$\text{Silver content} = (5000 \times V_1)/V_s$$

Characterization

For initial optimization, the size and distribution of the silver nanoparticles were characterized with Leica DMLP optical microscope attached to a JVC TK-c1380 color video camera. The size and morphology of the silver nanoparticles were examined with transmission electron microscopy (TEM; Philips). The determination of the mean particle size and the standard deviation of the particle population from scanning electron micrographs are reported in the literature.[19] Similarly, in this study, the average

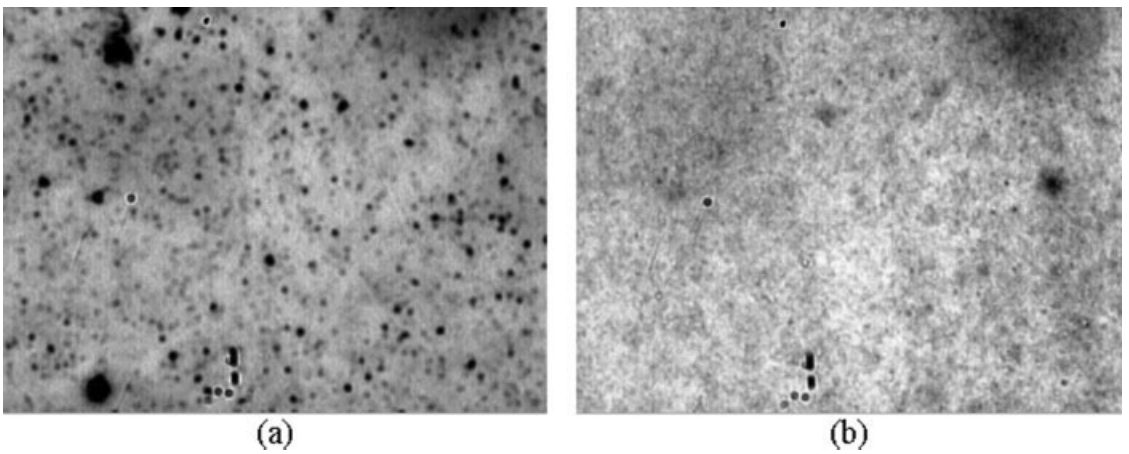

Figure 1 Optical micrographs of silver nanoparticles prepared at (a) 700 and (b) 2500 rpm.

particle size and standard deviation of the population were analyzed by image analysis with TEM micrographs.

The scanning electron microscopy (SEM) analysis of silver-nanoparticle-coated silk was performed with a high-resolution (up to 3 nm) scanning electron microscope (EVO 50, Zeiss, Hi-Tech Instruments Sdn. Bhd. Puchong Selangor, Malaysia) at a 23,000 × magnification.

The color (*K* (absorption) /*S* (scattering in Kubelka-Monk equation) value) of the treated silk fabric was measured with a Gretag Macbeth Colour-Eye 7000A (New Windsor, NY) spectrophotometer with a D_{65} illuminant and 10° observer. To establish the significance due to changes in the bath temperature during the application of silver nanoparticles to silk, the *t* test analysis statistical technique, that is, a significance test of the mean of small samples, was used.[20]

The silver-nanoparticle-coated silk fabrics were tested for antimicrobial activity by a colony count method according to AATCC 100, a standard test method for determining the antimicrobial activity of immobilized antimicrobial agents. According to this method, a sterilized test sample of 1″ × 1″ was placed in a 10-mL liquid culture containing a 10-μL microbe culture. Then, the samples were incubated for 24 h at 37°C. From the incubated samples, a 100-μL solution was taken and diluted with the appropriate dilution factor (10^6), and the final diluted microbe solution was plated and distributed onto an agar plate. All the plates of the control untreated and treated fabrics were incubated for 22–24 h, and the colonies that formed were counted with a colony counter. An evaluation of the antimicrobial activity was carried out by a comparison of the reduction percentage of microbes in the control and treated fabrics.

To study the durability for washing, the treated silk fabrics were subjected to washing cycles according to the ISO 105 C-01 procedure. For one washing cycle, the samples were treated with 5 gpl nonionic detergent (Lissopol-N) at 40°C for 30 min. After a required number of such washing cycles, the antimicrobial property was studied.

RESULTS AND DISCUSSION

The silver nanoparticles were produced by a chemical reduction method, and the effects of various process parameters such as the stirring speed of the reactants, reaction temperature, and combinations of various reducing and dispersing agents on the particle size were studied, and the results are discussed next.

Effect of the stirring speed

In the process of silver nanoparticle formation by a chemical reduction method, the silver ions are reduced to their atomic state, and therefore the nanoparticle is made of a small number of atoms depending on its particle size:

$$4Ag^+ + N_2H_4 \longrightarrow 4Ag^0 + N_2 + 4H^+ \qquad (1)$$

Figure 1 shows optical micrographs of silver nanoparticles produced at two different stirring speeds, that is, 700 and 2500 rpm. Clusters of silver nanoparticles are present, and the cluster size varies with the stirring speed. The average cluster sizes were found to be 510 and 370 nm for those silver hydrosols produced at stirring speeds of 700 [Fig. 1(a)] and 2500 rpm [Fig. 1(b)], respectively.

The probable reason for the observed decrease in the cluster size with increasing stirring speed may be the better dispersion of particles being formed. The silver nanoparticles prepared at 700 and 2500 rpm were further studied under TEM, and the results are shown in Figure 2(a,b), respectively. The average sizes of the particles produced at 700 and

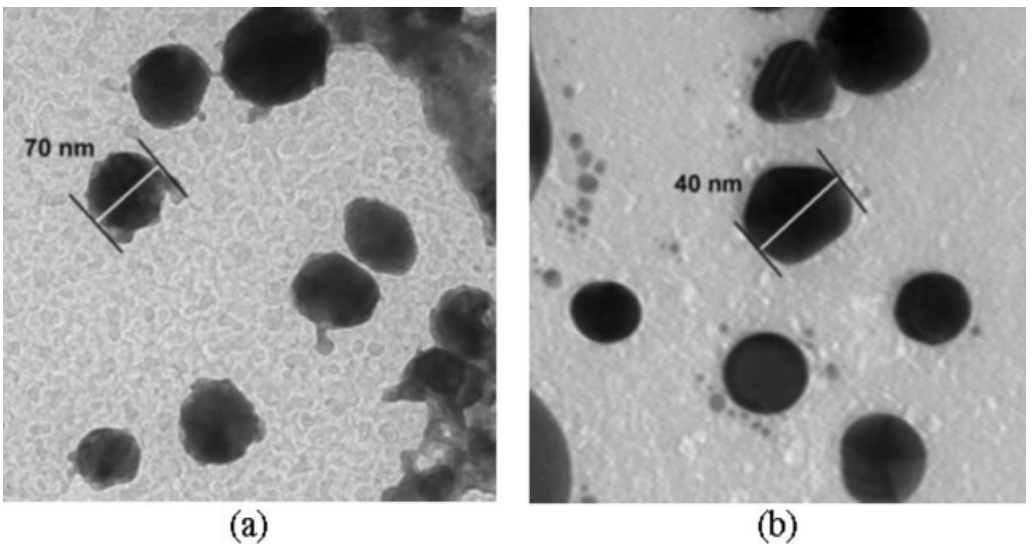

Figure 2 Transmission electron micrographs of silver nanoparticles formed at (a) 700 (175,000×) and (b) 2500 rpm (230,000×).

2500 rpm were 72 and 37 nm with 5.78 and 3.41 nm standard deviations, respectively. From these TEM results, it can be inferred that with an increase in the stirring speed, the particle size decreases because of better dispersion, which minimizes particle agglomeration.[6] The general problem of reducing aqueous soluble silver salts with a reducing agent is the tendency of particle agglomeration, which leads to a large particle size with an irregular shape. Various studies on preventing particle agglomeration and thus reducing the size of nanoagglomerates have been carried out.[9,16,21,22] The fundamental approach in all the cases is preventing metal particle nucleation via coordinate bond formation with metal ions and hydrophobic and hydrophilic interactions of a surfactant.[23] Thus, a high stirring speed may well disperse the particles being reduced, facilitating the interaction of individual particles with the surfactant and thereby reducing the particle size. In other words, an increase in the stirring speed may disturb the metal ion nucleation and prevent agglomeration.

Effect of the reducing and dispersing agent

Under identical conditions of an experiment, at a fast reduction rate, the possibility of particles coalescing is high because less time is available for the particles being formed to get dispersed in the medium before meeting with another particle, and hence it may lead to agglomeration. Therefore, the type of reducing agent used and the rate at which it is added to the silver nitrate play a major role in determining the final particle size. Similarly, the kind of dispersing agent used in the medium may also have a significant role in the particle agglomeration mechanism and thus influence the particle size. Therefore, two different types of reducing agents, that is, glucose (low reducing power) and hydrazine (high reducing power), and two different types of dispersing agents, that is, an oligo condensate of naphthalene sulfonic acid (OCNS; a relatively poor dispersing agent) and PVP, were chosen to study their effects on the particle size. The results of this study are presented in Figure 3.

It can be observed from Figure 3 that the silver nanoparticles produced in the presence of OCNS with glucose and hydrazine have comparatively large particles with average particle sizes of 70 nm for glucose and 85 nm for hydrazine (Table I). However, when PVP is used as a dispersing agent, the particle size of the silver nanoparticles decreases significantly [Fig. 3(b,d)], with particle sizes of 20 and 35 nm for glucose and hydrazine used as reducing agents, respectively (Table I).

A noticeable observation is that the particles formed with glucose are smaller than those formed with hydrazine as a reducing agent for both dispersing agents. As hydrazine is a powerful reducing agent, it reduces the silver nitrate to silver atoms at a much faster rate than glucose. Therefore, the particles may tend to agglomerate very fast, resulting in the formation of comparatively large particles of 35 and 85 nm with PVP and OCNS as dispersing agents, respectively. The observed difference in the average particle size with dispersing agents can be attributed to the ability to disperse the particles. Lone pairs of both nitrogen and oxygen atoms in the polar groups of one PVP unit occupy two *sp* orbitals of the silver ion and form a coordinative bond.[16] Therefore, PVP acts as both a dispersing and protecting agent and hence helps in forming small particles,

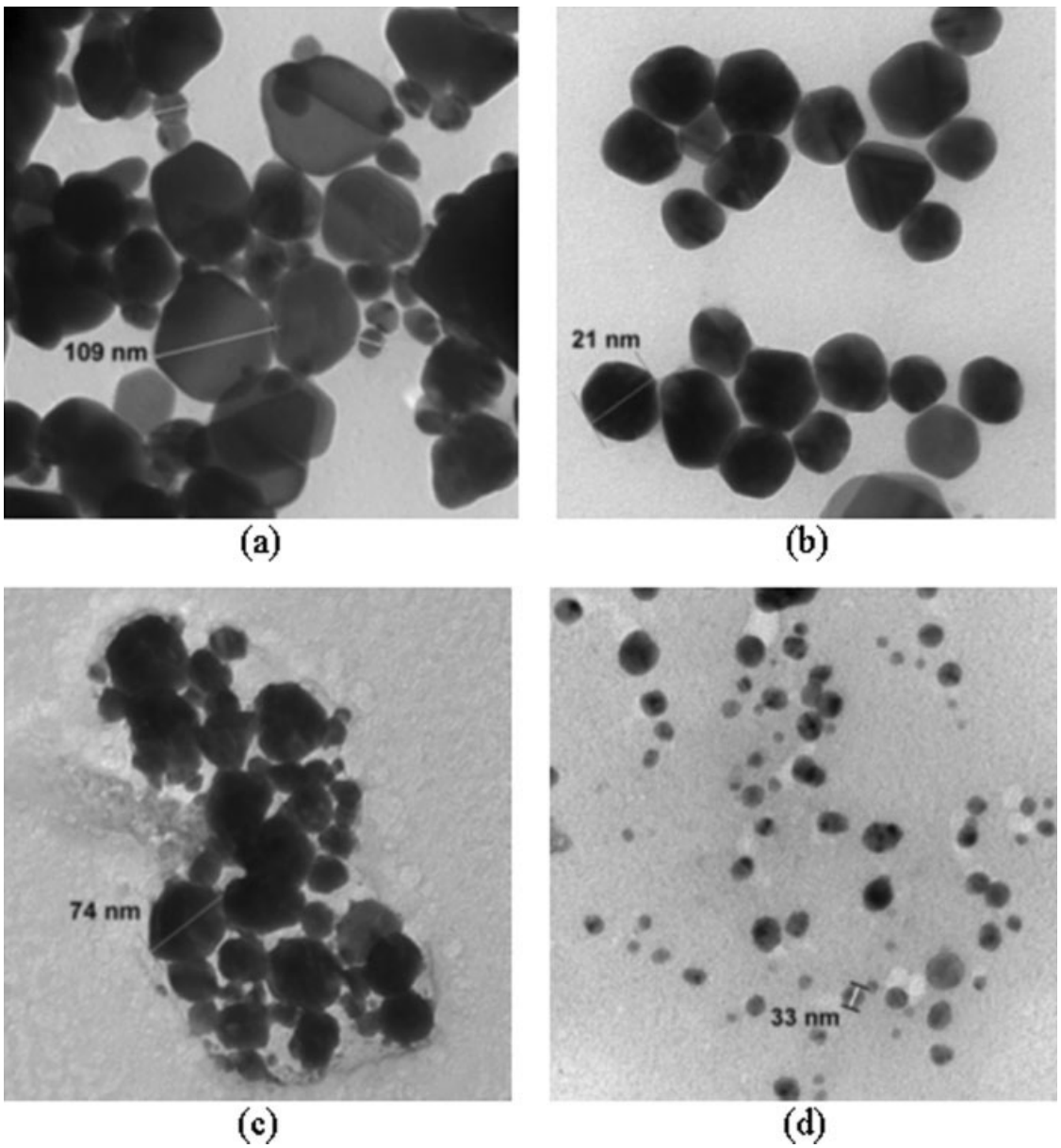

Figure 3 Transmission electron micrographs of silver nanoparticles prepared with hydrazine with (a) OCNS (175,000×) and (b) PVP (230,000×) and with glucose with (c) OCNS (110,000×) and (d) PVP (100,000×).

such as 20 nm with glucose and 35 nm with hydrazine. This is further evidenced by the study of population standard deviations in Table I. It can be observed from the table that the standard deviation is very large, that is, 5.72 and 6.71 nm for those particles prepared with OCNS, whereas with PVP, it is reduced drastically, that is, 1.69 and 2.58 nm, indicating better particle distribution when PVP is used.

TABLE I
Effect of the Reducing Agent and Dispersing Agent on the Particle Size

Reducing agent	Average particle size (nm)	Standard deviation (nm)
Glucose with OCNS	70	5.72
Glucose with PVP	20	1.69
Hydrazine with OCNS	85	6.71
Hydrazine with PVP	35	2.58

Effect of the reaction temperature

One of the important process parameters in preparing silver nanoparticles is the reaction temperature as it affects the kinetics of the atoms and molecules significantly and hence the particle size. Figure 4 shows transmission electron micrographs of silver nanoparticles produced with hydrazine at two different temperatures, that is, 5 and 40°C.

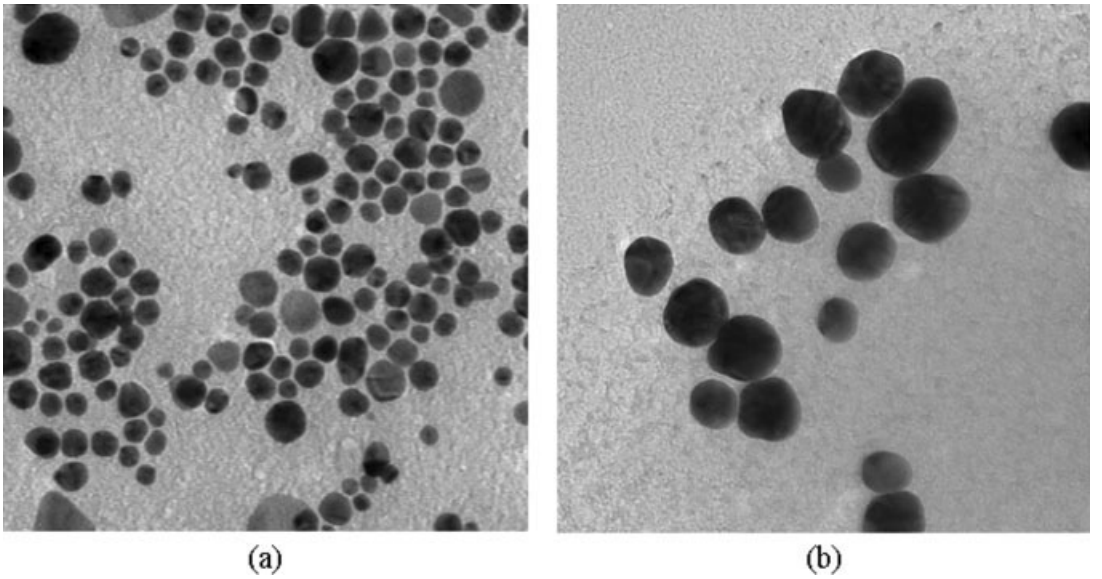

Figure 4 Transmission electron micrographs (230,000×) of silver nanoparticles prepared (a) at 5°C and (b) at 40°C.

It can be observed from the figure that the particles formed at 5°C are smaller than those formed at 40°C. The measured average sizes of the silver nanoparticles produced at 5 and 40°C are 10 and 35 nm, respectively. Because of a decrease in the process temperature from 40 to 5°C, the interaction of hydrazine with the silver nitrate may be reduced, and this results in the formation of smaller nanoparticles of silver. The calculated population standard deviations of the silver nanoparticles produced at 5 and 40°C are 1.03 and 2.58 nm, respectively. This indicates that at a reduction temperature of 5°C, both the particle size and the particle distribution are reduced; this is further confirmed in Figure 5. Figure 5(a–c) shows the UV–vis spectra of the silver hydrosols (50 ppm) prepared at 5 and 40°C with PVP as the dispersing agent and at 40°C with OCNS as the dispersing agent, respectively. The shape of the curve indicates the particle size and its distribution. The sharp peak with a narrow width of the curve [Fig. 5(a)] indicates the formation of small particles with a narrow size distribution at 5°C, whereas the blunt and large width of the curve [Fig. 5(c)] indicates the large particles with a wide distribution at 40°C with OCNS as the dispersing agent.

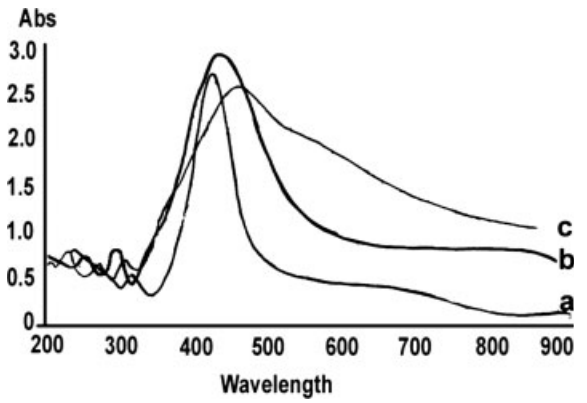

Figure 5 UV–vis spectra of the silver hydrosols prepared at (a) 5 (PVP), (b) 40 (PVP), and (c) 40°C (OCNS).

Application on silk: the effect of the pH of the application medium

As a protein fiber, *Bombyx mori* silk is amphoteric in nature because of ionizable groups present as end groups and on the side chains of various amino acid residues. Their dissociation state depends on the pH of the surrounding medium.[14] This characteristic of silk facilitates attracting and binding the charged metal ions.[24–26] When immersed in an aqueous solution of metal salts, silk exhibits the tendency to absorb metal cations, and the rate and extent of uptake depend on various factors, such as the kind of metal and its valence state, solution pH, time, and temperature. Therefore, the effect of the pH of the application medium on the silver nanoparticle uptake on the fabric was studied. On the absorption of silver nanoparticles, the fabric acquires a yellowish-green tinge that can be quantified by the measurement of the K/S value of the treated fabric.

It can be observed from Figure 6 that the K/S value of the treated fabric is 1.431 and 1.978 at acidic pHs of 3 and 4, respectively, indicating a good uptake of silver nanoparticles by the fabric. However, at an alkaline pH, that is, 10, K/S is 0.3, which is very close to the K/S value of the untreated fabric, indicating very poor uptake of the particles. Francis and George[15] reported that the silver nanoparticles generate a negative potential (−35 mV) around the

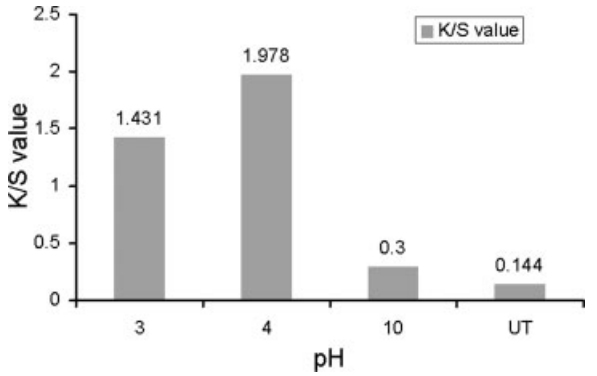

Figure 6 Effect of pH on the particle uptake (measured by the *K/S* value) on silk fabric.

surface when dispersed in water. Therefore, the low uptake of the silver nanoparticles by the fabric at an alkaline pH can be attributed to the negative–negative repulsion effect as the silk fabric develops more negative charge because of its amphoteric nature. However, because of the same amphoteric nature, the silk fabric develops more positive charges at an acidic pH and hence attracts the negatively charged silver nanoparticles; this results in high uptake.

Effect of the temperature of the application medium

As discussed in the previous section, the silver nanoparticle uptake by the fabric may also depend on the exhaustion bath temperature. Table II shows the effect of the temperature on the silver nanoparticle uptake measured in terms of the *K/S* value of the treated silk fabric.

It can be observed from the table that the *K/S* value decreases with the increase in the application temperature, indicating a decrease in the silver nanoparticle uptake. The absorption of silver nanoparticles by the silk fabric may be an exothermic reaction, and hence the increase in the process temperature results in poor particle uptake. Experiments at each temperature were repeated five times, and so to study the significance of the temperature effect, two successive readings were analyzed with the *t* test statistical technique, that is, a significance test between means of two small samples.[20] The calculated standard deviation and *t* values of successive readings are presented in Table II. It can be observed from the table that all the calculated *t* values are greater than the actual *t* value at a 1% level of significance for a degree of freedom of 8, that is, 3.355. Therefore, it can safely be inferred that at each temperature level, there is a significant difference in the silver nanoparticle uptake.

TABLE II
Effect of the Bath Temperature on the Particle Uptake by the Silk Fabric

Temperature (°C)	*K/S* value	Standard deviation	*t* value between successive readings
40	1.784	0.0054	14.15
50	1.724	0.0078	5.81
60	1.631	0.0100	6.51
70	1.593	0.0084	17.27
80	1.479	0.0122	6.37
90	1.423	0.0154	—

The *t* value at a 1% level of significance for a degree of freedom of 8 is 3.355. The *K/S* value of untreated silk fabric is 0.144.

Effect of the time of exhaustion

Figure 7 shows the effect of the time of exhaustion of silver nanoparticles on silk fabric in terms of the color value (*K/S*) of the fabric after treatment. It can be observed from the figure that the color value (*K/S*) increases from 10 to 30 min and then almost stabilizes. This phenomenon can be attributed to the charging pattern of the silk substrate and the ζ potential of the silver nanoparticles. Because the fabric has a positive charge and the particles have a negative charge, there exists a strong affinity between them. Therefore, up to an exhaustion period of 30 min, the rate of uptake is very high; however, beyond that, the curve becomes asymptotic.

From these studies, it can be inferred that the optimized application conditions for applying silver nanoparticles to silk fabric by an exhaust method are an acidic pH of 4, a temperature of 40°C, and a treatment time of 30 min.

Antimicrobial study

The silk fabric was treated with silver nanoparticles by an exhaust method under optimized conditions for imparting antimicrobial activity. The treated samples were tested for antimicrobial activity against the

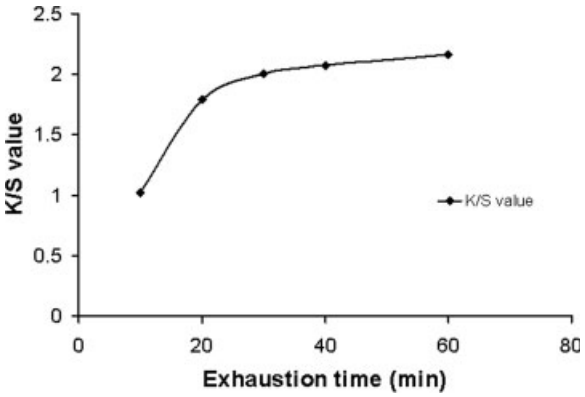

Figure 7 Effect of the time of application on the particle uptake.

TABLE III
Antimicrobial Activity of Silk Treated with Silver Nanoparticles

	Silver at 40°C with hydrazine		Silver at 5°C with hydrazine	
Concentration of silver hydrosol (ppm)	Average colony count	Antimicrobial activity (%)	Average colony count	Antimicrobial activity (%)
500	0	100	0	100
400	0	100	0	100
300	0	100	0	100
200	0	100	0	100
150	0	100	0	100
100	0	100	0	100
75	0	100	0	100
50	7	92	0	100
25	35	61	16	81
60	0	100	0	100
40	0	100	0	100

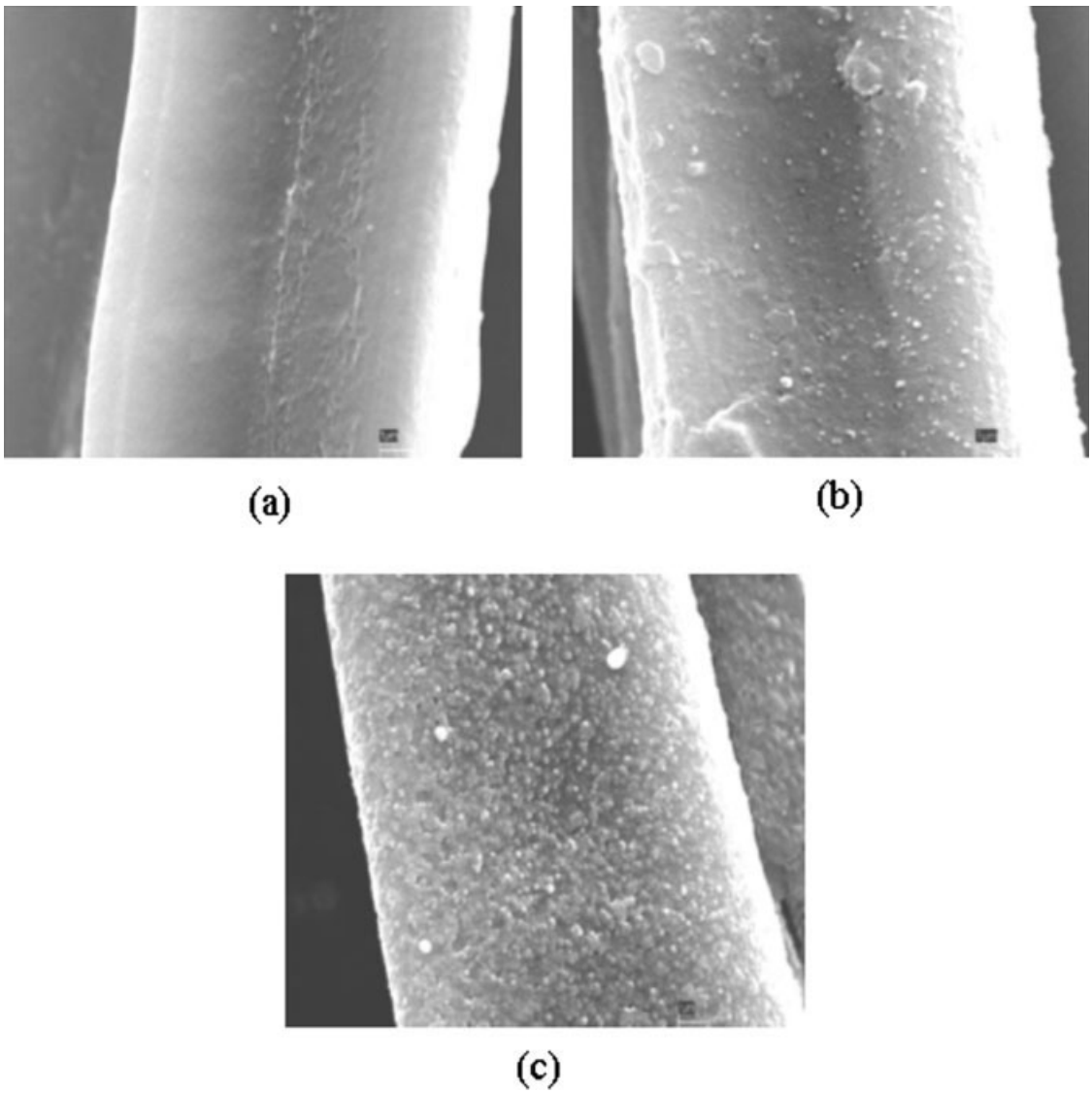

Figure 8 SEM micrographs of silk treated with silver nanoparticles: (a) untreated, (b) treated at 40 ppm, and (c) treated at 200 ppm.

TABLE IV
Washing Stability of the Treated Silk Fabrics

	Antimicrobial activity (%)	
Washing cycle	Silk treated with particles (silver at 40°C) at 60 ppm	Silk treated with particles (silver at 5°C) at 40 ppm
Before wash	100	100
First wash	100	100
Second wash	100	100
Third wash	100	100
Fourth wash	100	100
Fifth wash	100	100
Seventh wash	89	91
Tenth wash	78	84

gram-positive bacterium *Staphylococcus aureus*. Table III presents the results of the antimicrobial activity of silk fabric treated with various concentrations of silver nanoparticles prepared at reaction temperatures of 40 and 5°C with hydrazine and PVP as reducing and dispersing agents, respectively. It can be observed from the table that up to a concentration of 75 ppm, the fabric treated with nanoparticles produced at 40°C showed 100% antimicrobial activity, whereas it extended up to 50 ppm in the case of 5°C particles.

Upon further study, it was found that the silk samples treated with 40 ppm silver hydrosol, produced by the 5°C method, showed 100% antimicrobial activity. However, in the case of silver hydrosol produced by the 40°C method, the samples needed to be treated with 60 ppm to have 100% antimicrobial activity. This may be because the silver particles produced by the 5°C method had an average particle size of 10 nm, whereas the particles produced by the 40°C method had an average particle size of 35 nm. Therefore, because of the large available surface area, the particles produced by the 5°C method showed better antimicrobial activity.

To examine the morphology of the silver-nanoparticle-treated silk, silk fabric treated with two extreme concentrations, that is, 40 and at 200 ppm, of the 5°C method particles was observed with SEM. The micrographs are presented in Figure 8, and the presence of silver nanoparticles over the treated silk surface can be seen at both concentrations; in particular, at 200 ppm, the particle concentration is quite high [Fig. 8(c)].

To study the stability of the antimicrobial property, the silk fabric treated with silver nanoparticles was subjected to a number of washing cycles according to the standard procedure explained in the Experimental section. Table IV presents the antimicrobial activity of silk fabric treated with silver nanoparticles produced by the 40 and 5°C methods at concentrations of 60 and 40 ppm, respectively, at the end of every washing cycle up to 10 washing cycles.

It can be observed from Table IV that up to five washing cycles, the fabric shows 100% antimicrobial activity; however, beyond seven washing cycles, it decreases, probably because of a significant loss of silver nanoparticles from the fabric. Nevertheless, even up to 10 washing cycle, the fabric shows 80% antimicrobial activity, which would be sufficient for practical applications. Moreover, in this particular study, the silk fabric was treated with silver hydrosol of minimum concentrations of 60 and 40 ppm. However, if it is treated with higher concentrations of silver hydrosols, the stability to washing can be increased considerably.

CONCLUSIONS

The silver nanoparticles were produced by the reduction of silver nitrate with hydrazine and glucose as reducing agents and with PVP as a dispersing and protecting agent. It was found that with an increase in the stirring speed, the particle size decreased, and the average particle sizes were 72 and 37 nm at stirring speeds of 700 and 2500 rpm, respectively. The particle size was greatly influenced by the type of reducing agent and dispersing agent used. When glucose and PVP were used as reducing and dispersing agents, respectively, silver nanoparticles of 20 nm were produced. However, the use of hydrazine and an oligo condensate of OCNS as reducing and dispersing agents resulted in a larger particle size. When the reduction process was conducted at 5°C with hydrazine and PVP, silver nanoparticles of 10 nm were produced, whereas 35 nm was achieved at 40°C.

The optimum conditions for the application of silver nanoparticles to silk by an exhaust method were established to be an acidic pH of 4, a temperature of 40°C, and a time of 20–30 min. Finally, it was found that the silk fabric treated with 40 ppm silver hydrosol produced at 5°C and with 60 ppm silver hydrosol produced at 40°C showed 100% antimicrobial activity against the gram-positive bacterium *S. aureus*. The study of the washing stability of the silk fabric treated with silver hydrosols of minimum concentrations, that is, 60 and 40 ppm, showed 100% antimicrobial activity up to five washing cycles and around 80% activity after 10 washing cycles.

References

1. Chen, W.; Yan, J.; Song, N.; Li, Q.; Yang, B.; Dai, Y. Guijinshu 2006, 27, 14.
2. Wei, Z.; Xia, T.; Feng, W.; Wang, Q.; Dai, J.; Yan, P. Guijinshu 2006, 27, 1.
3. Choi, N. K.; Seo, D. S.; Lee, J. K. Mater Forum 2005, 29, 394.

4. Wang, H.; Qiao, X.; Chen, J.; Wang, X.; Ding, S. Mater Chem Phys 2005, 94, 449.
5. Li, G.; Luo, Y.; Yao, W.; Zhu, L.; Tan, H. Chem J Internet 2005, 7, 071001pe.
6. Wang, H.; Qiao, X.; Chen, J.; Ding, S. Colloids Surf A 2005, 256, 111.
7. Li, X.; Han, Y.; Yin, W. Kuangye 2004, 13, 51.
8. Kim, K. D.; Han, D. N.; Kim, H. T. Chem Eng J 2004, 104, 55.
9. Zhang, S. M.; Zhang, C. L.; Zhang, J. W.; Zhang, Z. J.; Dang, H. X.; Wu, Z. S.; Liu, W. M. Wuli Huaxue Xuebao 2004, 20, 554.
10. Seo, W. S.; Kim, T. H.; Sung, J. S.; Song, K. C. Hwahak Konghak 2004, 42, 78.
11. Lee, W. F.; Tsao, K. T. J Appl Polym Sci 2006, 100, 3653.
12. Tarimala, S.; Kothari, N.; Abidi, N.; Hequet, E.; Fralick, J.; Dai, L. L. J Appl Polym Sci 2006, 101, 2938.
13. Jiang, H.; Manolache, S.; Wong, A. C. L.; Denes, F. S. J Appl Polym Sci 2004, 93, 1411.
14. Arai, T.; Freddi, G.; Colonna, G. M.; Scotti, E.; Boschi, A.; Murakami, R.; Tsukada, M. J Appl Polym Sci 2001, 80, 297.
15. Francis, S. K.; George, M. Ions, Atoms and Charged Particles. http://www.silver-colloids.com/Papers/IonsAtoms&ChargedParticles.PDF.
16. Zhang, Z.; Zhao, B.; Hu, L. J Solid State Chem 1996, 121, 105.
17. Ulrich, N.; Amelie, C.; Karin, P.; Siegfried, S. Langmuir 2000, 16, 9087.
18. Howell, N. F. Standard Methods of Chemical Analysis—The Elements, 6th ed.; Van Nostrand: Princeton, NJ, 1962; Vol. I, p 543.
19. Dongjo, K.; Sunho, J.; Jooho, M. Nanotechnology 2006, 17, 4019.
20. Booth, J. E. Principles of Textile Testing: An Introduction to Physical Methods of Testing Textile Fibres, Yarns and Fabrics; Temple Press, London, 3rd ed.; 1996; Chapter 2, p 45.
21. Radziuk, D.; Skirtach, A.; Sukhorukov, G.; Shchukin, D.; Moehwald, H. Macromol Rapid Commun 2007, 28, 848.
22. Lee, H. Y. Chawon Rissaikuring 2006, 15, 19.
23. Hirai, H.; Nakao, Y.; Toshima, N. J Macromol Sci Chem 1979, 13, 727.
24. Nakamura, Y.; Kurose, A.; Shimizu, F.; Shirai, H.; Hojo, N. Sen-I Gakkaishi 1985, 41, T-353.
25. Chen, W.; Koyama, T.; Hanabusa, K.; Shirai, H. Sen-I Gakkaishi 1995, 51, 176.
26. Shimizu, Y.; Takagishi, T. J Seric Sci Jpn 1997, 66, 1.