New Approach to Antibacterial Treatment of Cotton Fabric with Silver Nanoparticle–Doped Silica Using Sol–Gel Process

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ABSTRACT: In this study, cotton fabric was successfully modified to have an antibacterial property through use of the sol–gel process. Dodecanethiol-capped silver nanoparticles, which have powerful antibacterial activity, were incorporated in silica sol. The starting materials were silver nitrate, tetraoctylammonium bromide, sodium borohydride, chloroform, 1-dodecanethiol, ethanol, tetraethylorthosilicate, and water. The cotton fabric was padded with dodecanethiol-capped silver nanoparticle–doped sol, dried at 60°C, and cured at 150°C. Scanning electron microscopy showed a uniform and continuous layer of doped sol on the fiber surface. The antibacterial effects of the treated cotton fabric against *Escherichia coli* were examined and found to be excellent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2938–2943, 2006

Key words: silicas; fibers; colloids; silver nanoparticles; thin-films

INTRODUCTION

Humans are prone to bacterial infections. Therefore, this research focused on discovering a textile treatment that would provide antibacterial protection. In previous research cotton fabrics were treated with polyethylene glycol,[1] zirconium complexes,[2] and metal and organometallic salts.[3] Other research was directed toward antibacterial material containing various natural and inorganic substances such as tea extracts, chitosan, copper, and zinc.[4] Recently, Parick et al. conducted a study to develop an antibacterial Ag/Na carboxymethyl cotton burn dressing.[5] They used the partial cation exchange of sodium by silver, which was achieved on a sodium carboxymethyl cotton gauze (nonwoven) treated with silver nitrate in an 85:15 ethanol/water medium.[5]

Silver or silver ions are known for their powerful antibacterial activity,[4] which is generally believed to result from the reaction of this heavy metal with proteins. The chemical reaction of silver atoms with the —SH groups of enzymes inactivates the protein.[4]

Jeon et al. prepared silver-doped thin silica film by the sol–gel process.[4] Silver was introduced as silver nitrate ($AgNO_3$), and tetraethylorthosilicate [TEOS, $Si(OC_2H_5)$] was used as a precursor for silica formation. The coated samples (microscopic glass substrates) were dried at 100°C for 30 min and cured between 200°C and 600°C. The authors reported that to achieve complete insertion of silver atoms into the silica network and to reduce the Ag^+ ions to Ag^0, the treatment temperature should reach 600°C.

Currently, functional finishes on textile fabrics are of critical importance in improving textile products by imparting them with multifunctional properties such as being antibacterial, providing UV protection, and being wrinkle-free. Sol–gel technology has emerged as a promising way to functionalize fabric surfaces. The sol–gel process has several advantages such as high purity, low temperature processing, ultrahomogeneity, and, most important, the possibility to incorporate additives such as nanoparticles into the first stage of the sol preparation without inhibiting formation of the silica network.

In this article, we report the results of our study using the sol–gel process to modify 100% cotton fabric with dodecanethiol-capped silver nanoparticle–doped silica sol in order to impart the cotton with an antibacterial property. Dodecanethiol-capped silver nanoparticles were prepared and introduced into the sol formulation. The cotton fabric was padded with do-

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decanethiol-capped silver nanoparticle–doped silica sol and then dried and cured. The treated cotton fabric showed very good antibacterial performance against *Escherichia coli*.

EXPERIMENTAL

Materials

The fabric used in this study was desized, scoured, and bleached 100% cotton fabric purchased from Testfabrics (Testfabrics Inc., West Pittiston, PA). The characteristics of the fabric were 79.4 ends, 65.4 picks, yarn count of 23.4 × 22 tex, and a weight of 161.98 g/m^2 (4.8 oz/yd^2).

The materials used in the synthesis of the dodecanethiol-capped silver particles were: silver nitrate ($AgNO_3$, purity > 99%), tetraoctylammonium bromide [$(C_8H_{17})_4NBr$, purity = 98%], chloroform (purity > 99%, ethanol stabilized), sodium borohydride (purity > 98%), water (HPLC grade, residue after evaporation < 1 ppm), and 1-dodecanethiol (98%). All were purchased from Fisher Scientific (Houston, TX) except 1-dodecanethiol, which was purchased from Avocado Research Chemicals (Lancashire, UK).

The materials used in the sol–gel process, purchased from Fisher Scientific (Houston, TX), were tetraethylorthosilicate ([$Si(OC_2H_5)_4$, purity > 95%], ethanol (absolute, 200 proof), and 1*N* nitric acid solution. Deionized water passed through a reverse osmosis unit was used in the synthesis of the sol. All chemical reagents were used as received.

Methods

Synthesis of dodecanethiol-capped silver nanoparticles

Silver nanoparticles capped with dodecanethiol (Ag-NP) were prepared by two-phase arrested precipitation using the wet-chemistry method of oil/water/surfactant microemulsions.[6–10] In a typical experiment, 30 mL of aqueous silver ion solution (0.03*M* $AgNO_3$) was mixed with 20.4 mL of a chloroformic solution of the phase transfer catalyst [0.2*M* tetraoctylammonium bromide, $(C_8H_{17})_4NBr$] and stirred vigorously for 1 h. The silver ions migrated into the organic phase, which was subsequently collected, and then dodecanethiol (0.0002 g) was added. The mixture was stirred for 15 min, then 24 mL of aqueous sodium borohydride (0.43*M*) was injected slowly, after which the reaction mixture was stirred for 8 h. The nanoparticle-rich organic phase was collected and subsequently used in the sol–gel synthesis. The synthesized dodecanethiol-capped silver nanoparticles were typically 1–5 nm in size.[10]

Sol–gel synthesis

The sol was prepared by mixing the precursor tetraethylorthosilicate (40 mL) with alcohol (40 mL) and water (13 mL) in a molar ratio of 1 : 1 : 4, respectively. The ethanol–water mixture was added dropwise to prevent rapid hydrolysis. After its addition was complete, the dodecanethiol-capped silver nanoparticle–rich organic solution was added dropwise to make the desired concentration (1, 3, 5, 10, or 15 mL). The pH of the solution was adjusted to a pH of 1–2 using nitric acid, and the reaction mixture was stirred for 45 min.

Fabric treatment

Fabric samples were dipped into the sol, soaked for 5 min, and passed through a two-roller laboratory padder (BTM 6-20-190) at a speed of 4 yd/min and an air pressure of 2.76×10^5 Pa. The padded fabric samples were dried at 60°C for 10 min by passing through a Benz Dry-Cure Thermosol Oven (IT500 with an 18-in working width) at 0.3 yd/min in order to evaporate the solvent (ethanol) and cured in the same oven at 150°C for 5 min. The samples were then conditioned at 21°C ± 1°C and 65% ± 2% relative humidity for at least 24 h before performing any analysis. Three specimens were treated for each amount of Ag-NP.

Scanning electron microscopy

Morphological changes as a result of the sol–gel treatment of cotton fabric were investigated using scanning electron microscopy (SEM). The fabric samples were mounted on an aluminum stub and coated with a layer of gold by thermal evaporation in a vacuum-coating unit. They were then examined in a scanning electron microscope (Hitachi S570) with an accelerating voltage of 6 KV.

Thermogravimetric analysis

Changes in thermogravimetric weight loss as a result of the sol–gel treatment of the cotton fabric samples and a control were investigated using thermogravimetric analysis (TGA), which was performed using a Pyris1 TGA instrument equipped with an autosampler (Perkin–Elmer, Shelton, CT). The thermograms were recorded between 30°C and 600°C at a heating rate of 10°C/min with nitrogen flow of 20 mL/min. Three replications were performed from each sample. Pyris software (Perkin–Elmer, Shelton, CT) was used to calculate the percent weight loss of each sample.

FTIR measurements

FTIR was used to monitor the changes resulting from the sol–gel treatment of cotton fabric. Spectrum-One

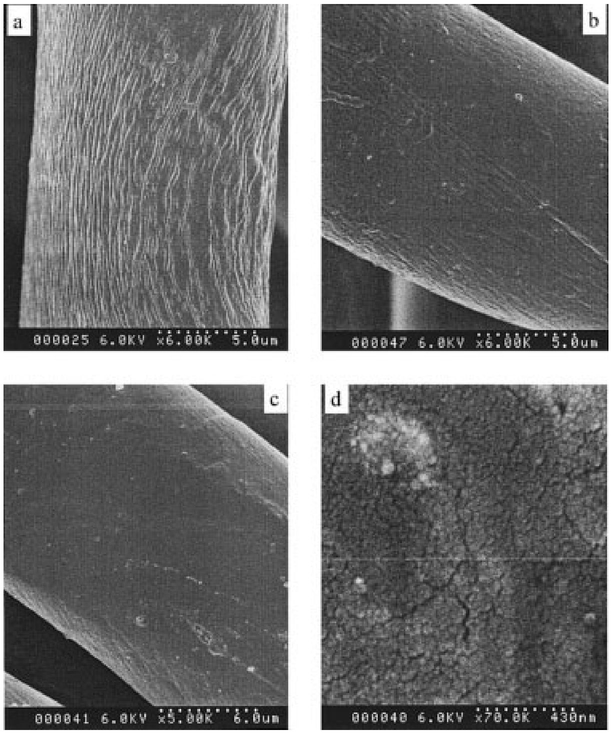

Figure 1 (a) SEM micrograph of untreated cotton fabric. (b) SEM micrograph of cotton fabric treated with sol only. (c) SEM micrograph of cotton fabric treated with sol doped with dodecanethiol-capped silver nanoparticles. (d) SEM micrograph of cotton fabric treated with sol doped with dodecanethiol-capped silver nanoparticles at higher magnification.

(from Perkin–Elmer) equipped with a universal attenuated total reflectance Fourier transform infrared (UATR-FTIR) was used to acquire the FTIR spectra of the treated fabrics. The UATR consists of a ZnSe crystal that allows collecting the FTIR spectra directly from the sample without any special sample preparation. Cotton fabric samples were placed on the top of the ZnSe crystal, and a pressure was applied to it to ensure good contact with the incident IR beam and to prevent the loss of IR incident radiation. The IR spectra were collected using 32 scans with 4 cm^{-1} spectral resolution between 650 cm^{-1} and 4000 cm^{-1}.

Antibacterial test

LBB735, a wild-type *E. coli* K12 strain, was used for all antibacterial testing. The bacterial cultures were grown in Luria Bertani media (with 0.5% NaCl)[11] in a gyratory shaking water bath (New Brunswick Scientific, Edison, NJ) at 250 rpm at 37°C. The cloth squares to be tested were autoclaved for sterilization. Growth tests were conducted by adding 20 mL of an exponentially growing culture of *E. coli* to a 300-mL side-arm flask containing 5 × 5 cm of sterile cloth and then monitoring growth by measuring the optical density at 600 nm (OD_{600}) relative to time.

RESULTS AND DISCUSSION

Figure 1(a–d) shows the morphological changes induced by the treatment of the cotton fabric with a silica sol doped with dodecanethiol-capped silver nanoparticles. In contrast to the SEM micrographs of the untreated cotton fabric [Fig. 1(a)], the SEM micrographs of the treated cotton fibers showed a smoother surface coated with a continuous layer of the doped sol [Fig. 1(b)]. As expected, a comparison of the micrographs of the fabric treated with sol only, that is, without nanoparticles, and with those of the doped sol did not show any significant morphological differences [Fig. 1(b,c)]. At higher magnification, a uniform film was observed on the fiber surface [Fig. 1(d)]. Small cracks caused by drying appeared on the surface of the treated fabric.

The statistical analysis showed a significant effect of dodecanethiol-capped silver nanoparticles on the percent add-on of the fabric (Table I and Fig. 2). On average, adding 15 mL of dodecanethiol-capped silver nanoparticle–rich organic phase increased the percent add-on by 13%.

Figure 3 shows percent weight loss versus treatment temperature for the untreated cotton fabric and the cotton fabric treated with silica sol containing 15 mL of a dodecanethiol-capped silver nanoparticle–rich organic phase. The statistical analysis showed a significant effect of the treatment with the sol doped with dodecanethiol-capped silver nanoparticles on the percent residue at 600°C ($df = 3$, $F = 567.0$, $p = 0.000001$). The percente residue at the end of the thermal treatment (600°C) of the control fabric averaged 22%. However, it averaged 34% for the treated fabric.

TABLE I
Variance Analysis of Effect of Amount of Silver Nanoparticles on Percent Add-on

Parameter	*df*[a]	*F*[a]	Probability	Percent add-on[b]
Intercept	1	51,913.71	0.0000001	
[Ag-NP] (mL)	5	27.12	0.0000001	
0				9.57 d
1				9.28 d
3				9.97 c
5				9.93 c
10				10.40 b
15				10.81 a
Error	17			

[a] df, degrees of freedom; F, variance ratio.
[b] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman-Keuls tests).

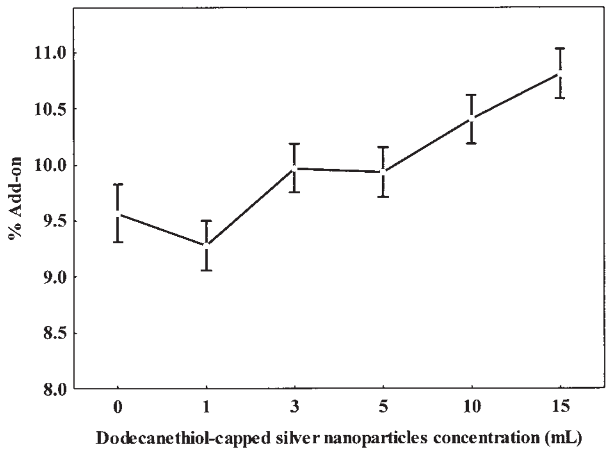

Figure 2 Percent add-on versus concentration of dodecanethiol-capped silver nanoparticles.

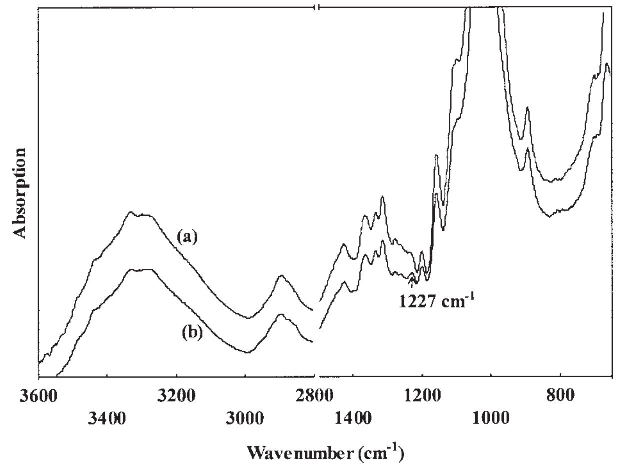

Figure 4 UATR-FTIR spectra of (a) control fabric and (b) treated fabric with a sol containing a dodecanethiol-capped silver nanoparticle–rich organic phase (15 mL).

Figure 4 shows the FTIR spectra of the untreated cotton fabric and the cotton fabric treated with silica sol containing 15 mL of a dodecanethiol-capped silver nanoparticle–rich organic phase. The peak at 1227 cm^{-1} could be attributed to the asymmetric stretching of ≡Si—O—Si≡.

The antibacterial performance of the treated fabric against *E. coli* was assessed by measuring the optical density at 600 nm of the medium containing the bacteria culture and the fabric at different times (Fig. 5). There were significant differences in antibacterial effects between the untreated cotton fabric, the cotton fabric treated only with the sol, and the cotton fabric treated with the sol doped with a dodecanethiol-capped silver nanoparticle–rich organic phase. As expected, the untreated fabric did not show any antibacterial activity; and optical density showed a 20-fold increase; therefore, in the bacteria population for a 215-min period (optical density at $t = 0$ was 0.07, and optical density at $t = 215$ min was 1.5). However, when the fabric was treated with a sol containing 15 mL of the dodecanethiol-capped silver nanoparticle–rich organic phase, the density of the bacteria dropped by 40% (optical density at $t = 0$ was 0.1, optical density at $t = 185$ min was 0.06). This behavior indicates that not only did the treated fabric have an inhibitory effect on *E. coli* growth, but also suggests the treated fabric had bactericidal activity (Fig. 6).

The analysis of the slopes of the bacterial growth curves, optical density versus time, showed negative slopes for the growth curves of the fabric treated with the sol containing 10 or 15 mL of dodecanethiol-capped silver nanoparticles (Table II). No significant

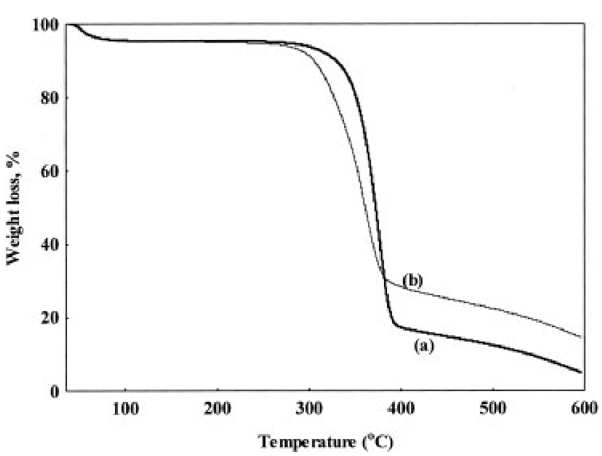

Figure 3 Thermogravimetric weight loss curves of: (a) control fabric and (b) treated cotton fabric with a sol containing a dodecanethiol-capped silver nanoparticle–rich organic phase (15 mL).

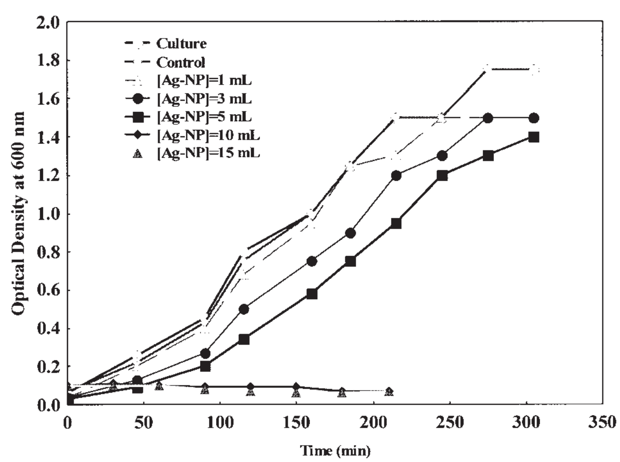

Figure 5 Antibacterial performance of the control and treated cotton fabric with a sol containing different amounts of a dodecanethiol-capped silver nanoparticle–rich organic phase.

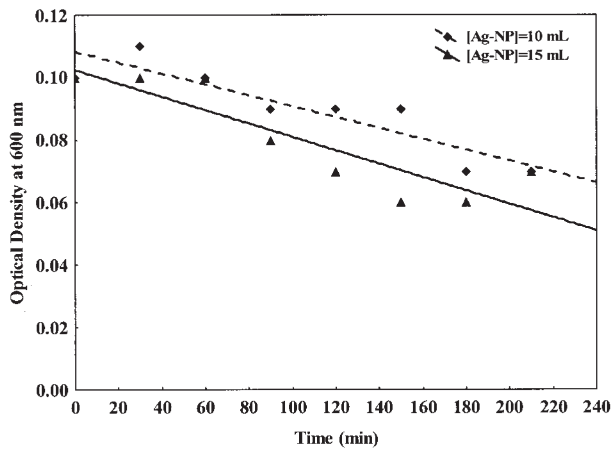

Figure 6 Antibacterial performance of cotton fabric treated with a sol containing 10 and 15 mL of a dodecanethiol-capped silver nanoparticle–rich organic phase.

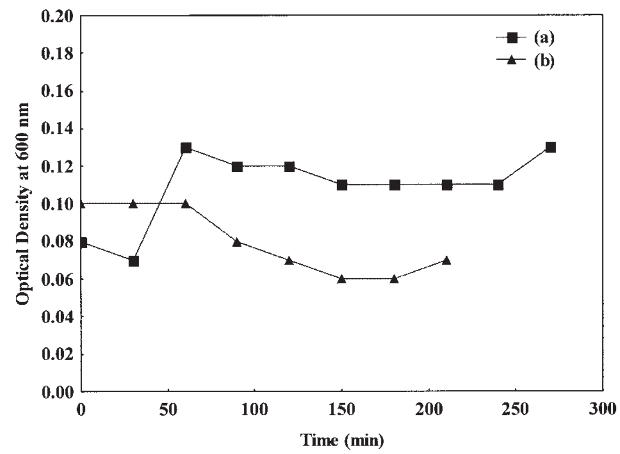

Figure 7 Antibacterial performance of: (a) fabric treated with sol containing silver nitrate and (b) fabric treated with sol containing a dodecanethiol-capped silver nanoparticle–rich organic phase (15 mL).

differences were observed between the culture, the control, and the fabrics treated with the sol containing 1, 3, or 5 mL of dodecanethiol-capped silver nanoparticles. Therefore, to obtain high antibacterial performance, the optimum amount of dodecanethiol-capped silver nanoparticles in the silica sol is at least 10 mL.

These results are in agreement with previous research that showed the inhibitory and killing effects of silver ions on *E. coli* and *Staphylococcus aureus*.[4] Jeon et al. investigated the preparation and antibacterial effects of silver-doped silica thin films by the sol–gel process.[4] They reported that the thin film had to be subjected to thermal treatment at 600°C in order to reduce Ag^+ to Ag^0. In our study, the treated fabric with silica doped with a dodecanethiol-capped silver nanoparticle–rich organic phase was treated only at 150°C and showed excellent antibacterial performance.

Attempts were made to incorporate silver nitrate in the silica sol in a molar ratio of 1 : 3.8 : 4 : 0.007 tetraethylorthosilicate/ethanol/water/silver nitrate. Although the sol was clear, the cured white fabric turned dark brown. This could be attributed to the reduction of Ag^+ ions to Ag^o during the curing at 150°C. The antibacterial test of the treated fabric showed excellent antibacterial activity against *E. coli,* as shown in Figure 7. To avoid the fabric changing color because of the reduction of the Ag^+ ions during drying, it was necessary to reduce the Ag^+ ions before applying them to the fabric. Further investigations of adding $AgNO_3$ to the sol and reducing the Ag^+ ions using sodium borohydride are being conducted. Note that, as shown in Figure 7, in contrast to dodecanethiol-capped silver particles (which show bactericidal effects), silver nitrate treatment seems to have only inhibitory effects on *E. coli.*

CONCLUSIONS

The sol–gel method was used to synthesize dodecanethiol-capped silver nanoparticle–doped silica sol. Woven cotton fabrics treated with this doped sol were tested for antibacterial activity and showed excellent antibacterial performance against *E. coli*. The treated fabrics could be successfully used as disposable bandages. However, further investigations will study the

TABLE II
Statistical Analysis of the Curves of Optical Density Versus Time Showing Slopes, Confidence Interval Limits, and Adjusted Coefficients of Correlation

Treatment	Slope	+95% Confidence Limits	−95% Confidence Limits	R^2
Culture	0.006095	0.005331	0.006859	0.974
Control fabric	0.006172	0.005377	0.006967	0.973
[Ag-NP] = 1 mL	0.005505	0.004522	0.006489	0.948
[Ag-NP] = 3 mL	0.005487	0.004786	0.006188	0.973
[Ag-NP] = 5 mL	0.005037	0.004296	0.005778	0.965
[Ag-NP] = 10 mL	−0.000175	−0.000255	−0.000094	0.794
[Ag-NP] = 15 mL	−0.000214	−0.000325	−0.000104	0.753

durability of the treatment after repeated laundering as well as the antibacterial efficiency of the treated fabric against other types of bacteria.

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