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ORIGINAL PAPER

Antimicrobial finishing of cotton textile based on water glass by sol–gel method

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Abstract A low temperature and cost-effective process for antimicrobial finishing of cotton textiles has been developed by sol–gel method. The antimicrobial treatment was performed by treating cotton textile with silica sols from water glass and then with silver nitrate solution. The antimicrobial activity was determined by using *E. coli* as a model for Gram-negative bacteria. The results showed that the treated textile has an excellent antimicrobial effect and laundering durability. SEM analysis showed coarse surface morphological change on the water glass treated cotton textile. The residual concentration of silver ion on fabrics was informed by ICP-MS. XPS results indicated that two different states of silver were present on the surface of the antimicrobial textile.

Keywords Antimicrobial finishing · Water glass · Cotton fabric · Sol–gel · Silver ion

1 Introduction

Textiles, especially those made of natural fibers, are an excellent medium for the growth of microorganisms when the basic requirements such as nutrients, moisture, oxygen, and appropriate temperature are present. The large surface area and ability to retain moisture of textiles also assist the growth of microorganisms on the fabric. Therefore, there is a great demand for antimicrobial finishes of textiles to control the growth of microorganisms, such as bacteria, fungi or mildew, and prevent the textile from deterioration of strength and quality, staining, odors, and health concerns caused by microorganisms [1].

Antimicrobial properties can be imparted to textile materials by chemically or physically incorporating antimicrobial agents onto fibers or fabrics. Ionic silver compounds, a well-known antimicrobial agent which is capable to inhibit and kill bacteria and fungi [2], is unique in comparison with other antimicrobial agents because it has no toxicity and carcinogenic activities [3]. However, silver ions must be sufficiently anchored on the textiles in order to provide durability of antimicrobial properties.

The sol–gel method could be an effective procedure to entrap organic and inorganic compounds with various functionalities on different surfaces. There are several potential advantages of sol–gel technique for functional finishing of textiles, such as ordinary processing conditions, fast throughput and no damage to the substrate materials, etc [4, 5].

There are literatures on the immobilization by sol–gel method with silver as antimicrobial agent [6–8]. The most commonly matrix used for antimicrobial coatings are sol–gel-based inorganic oxides such as silica and alumina [9, 10]. However, there still remain some drawbacks of the conventional sol–gel process, such as using expensive alkoxysilane precursors, demanding adscititious water and acid. An alternative economic route for the preparation of silica sol has been reported by using water glass as precursor, which is much cheaper than silicon alkoxides [11–13]. However, ion exchange or organic phase extraction was still used in these reported processing [11–13].

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The aim of this work was to prepare an antimicrobial textile using water glass as the precursor for silica sol, and ionic silver as antimicrobial agent was entrapped in silicon oxide matrix. The antimicrobial finishing was performed in aqueous phase, and no any organic solvent was needed during processing.

2 Experimental

2.1 Materials

Water glass (an industrial product, the molar ratio of SiO_2 to Na_2O is 1.8 or 2.3) was purchased from Yueda Chemicals Factory (Shanghai, China) and used as received. The following reagents used were of analytical grade: silver nitrate (Shanghai chemical reagent Co.), H_2SO_4 (Shanghai chemical reagent Co.). Scoured and bleached cotton fabric ($20^s \times 16^s$, 128×60, from Wuxi bleaching and dyeing factory) was treated first with a solution containing 1.5 g sodium carbonate in 1 dm^3 of water, and then washed with distilled water. Finally, 100% cotton fabric was dried and cut into square 15×15 cm pieces. *Escherichia coli* (*E. coli*), a gram-negative bacterium, was selected due to its popularity of being selected as a test organism and its resistance to common antimicrobial agents. The gram-negative *E. coli* was supplied by China General Microbiological Culture Collection Center (CGMCC).

2.2 Sample preparation

The silica sol was prepared by acidifying water glass solution with 0.05 M H_2SO_4 solution to pH 11.0. The solution was then stirred for 10 min.

The cotton sample was impregnated in the silica sol bath, and padded (P-BO Padder, Okazaki Machine Co., Guangzhou, China) to keep the wet pickup of 70% (based on the fabric weight). After drying (80 °C, 3 min) the fabric was annealed at 120 °C for 3 min, then washed with a large amount of distilled water and then dried at 80 °C for 3 min in a ventilated oven, and then conditioned at 25 °C and 65% RH for 48 h. The add-on of fabric was calculated from the relation:

$$\text{ADD - on}\% = [(W_2 - W_1)/W_1] \times 100 \quad (1)$$

where W_1 and W_2 were the weights of the controlled and the treated fabrics, respectively.

The silica-treated cotton fabric was impregnated in $AgNO_3$ solution bath with different concentrations for 30 min with occasional stirring. Subsequently, the sample was dried at 80 °C for 3 min in a ventilated oven, washed with distilled water and dried again at 80 °C for 3 min.

2.3 Measurement

The antimicrobial activity of the treated cotton fabrics was determined according to AATCC Test Method 100-1999 [14]. Fabrics specimens (circular swatch 4.8 cm in diameter) were challenged with 1.0 mL of bacterial inoculum in a 250 mL container. The inoculum was a nutrient broth culture containing $1.0\sim2.0 \times 10^5$/mL colony forming units of bacteria. The germs counted on the treated cotton fabric and those on a controlled sample were determined after a 24-h incubation period at 37 °C. The antimicrobial activity was expressed in terms of percentage reduction of the organism after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The results are expressed as percent reduction of bacteria (R) by Eq. (2).

$$\text{Reduction}(\%) = [(C - A)/C] \times 100 \quad (2)$$

where A and C are the numbers of bacteria recovered from the antimicrobial-treated and untreated cotton fabrics in the jar incubated over the desired contact period, respectively.

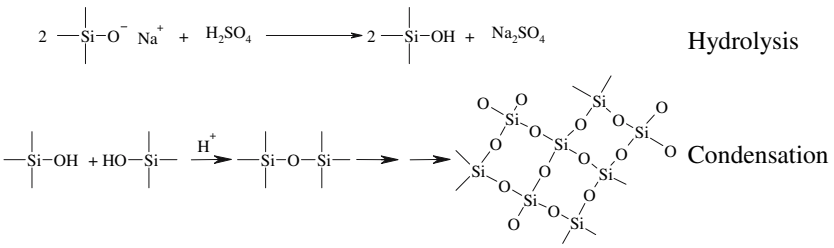
The content of silicon dioxide on antimicrobial textile was measured by photometric method using silicomolybdic blue as the indicator. The content of silver was determined with inductively coupled plasma-atomic emission spectrometry (ICP-AES; Varian Vista AX, Palo Alto, CA). The X-ray diffraction (XRD) was analyzed with a diffractometer (D/max-RA model) employing Cu Kα radiation. The nanoscopic image of the antimicrobial agent on the fiber surface was examined with a scanning electron microscope (SEM, JSM-5600, JEOL, Japan). The chemical composition of the fiber surface was analyzed with a SCALAB MK-II XPS spectrometer (VG, UK). The X-ray source was Mg Kα and the take-off angle was 45°. The pressure in the chamber was 7×10^{-9} mbar. XPS signals were taken with step width 0.05 eV and pass energy 20 eV.

3 Results and discussion

3.1 Treatment of silica sol

When the cotton fabric was impregnated with water glass solution, the precursor molecules entered into fibers and then hydrolyzed within the cotton fabrics in the presence of acid to form silicic acid. During drying, silicic acid molecules condense to form a xerogel, then anneal to form network around the fibers, which is free of solvent and consists of a porous oxide structure [15]. The procedure of water glass to silica network via silicic acid was depicted in Scheme 1.

Scheme 1 The reaction process from water glass to silica network



The coated substrates were annealed at 120 °C for 3 min. The low-temperature annealing process allowed for the preservation of cellulose fibers and the reduction of possible crack formation in the sol–gel coatings due to the difference in thermal expansion coefficients between silicon dioxide and cellulose fibers.

Silicomolybdic blue photometric method was used to analyze the content of silicon dioxide on the fabric, which was carried out by extracting the treated textile with boiling sodium carbonate solution. The result showed that the content of SiO_2 on treated textile has a linear relation with the content of SiO_2 in the padding solution (Fig. 1).

The influence of molar ratio of SiO_2 to Na_2O of water glass on the fixation of SiO_2 was also studied (Fig. 2). The results showed that two modules of water glass (molar ratio of SiO_2 to Na_2O were 2.3 and 1.8) with same SiO_2 contents gave the same SiO_2 content on the fabrics, which indicated that the sodium ion in water glass has less influence on the fixation of SiO_2 on cotton fabrics. The further study for the durability to washing was also investigated (Fig. 2). After the first washing circle, the leaching of SiO_2 on the fabric showed a significant increase, which slowed down and kept constant after five washing circles. Moreover, SiO_2 on fabrics prepared from water glass with different modules had practically same durability.

3.2 Treatment of silver salt

After treated with silica sol, the textile was soaked in the solution of silver nitrate, a FDA-approved efficient antimicrobial agent [16]. The silver ion was added and fixed into the SiO_2-fiber matrix by physical absorption during the soaking. The influence of soaking time on the contents of Ag^+ on fabrics was shown in Fig. 3. The result showed the amount of silver ion absorbed on fabrics increased with soaking time, then level off after 40 min. The sample

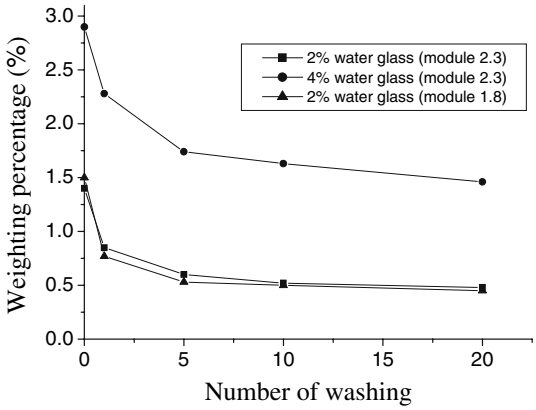


Fig. 2 Influence of concentration and module of water glass on weighting percentage of textile and soaping fastness of SiO_2 on textile

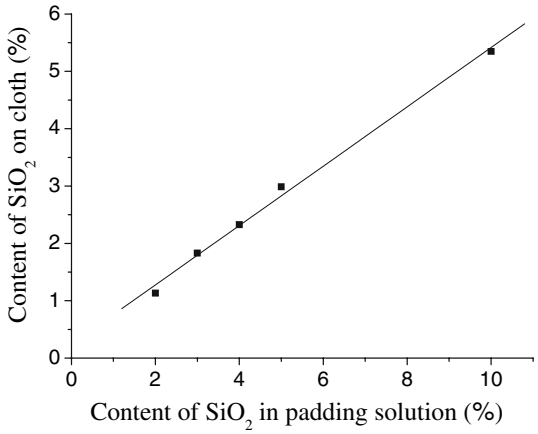


Fig. 1 The relation of content of SiO_2 on textile with the content of SiO_2 in padding solution

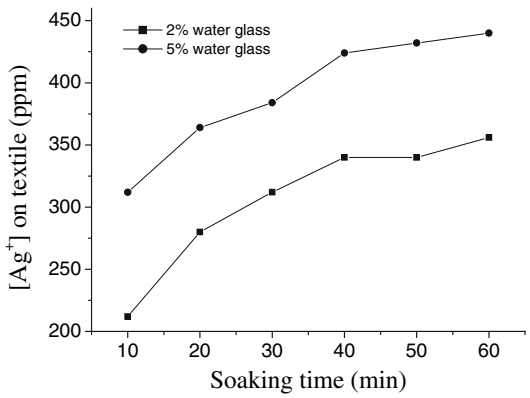


Fig. 3 The absorption of Ag^+ by SiO_2-treated textile on soaking time and concentration of water glass

treated with 5% water glass obtained higher-silver ions than that of the sample treated with 2% water glass.

The antimicrobial activities of finished textiles treated with different concentration of silver solution and water glass were determined (Table 1). It was shown that all the silver-treated textiles had efficient antimicrobial activities, more than 99.99% in all recipes even without water glass treatment, which can be due to the high-antimicrobial activity of silver ion [16].

The durability of antimicrobial activity to washing is one of the major concerns of textile researchers and users because textiles are subjected to frequent laundering. It is shown in Table 1 that the antimicrobial duration of washing increased with the concentration of $AgNO_3$ soaking solution. The higher the concentration of $AgNO_3$ solution, the more antimicrobial duration of washing cycles will be. For textile treated with 0.45×10^{-3} mol/L silver nitrate solution and 2% water glass, the antimicrobial activity still kept an excellent antibacterial effect against *E. coli* (bacterial reduction of 99.97%) even after 50 times washing cycles. For the antimicrobial textile without water glass treatment, the antimicrobial ability decreased from original >99.99% to zero only after 10 times washing, which means a very low laundering durability. Taking all above results into consideration, the laundering durability should be mainly improved by the SiO_2 matrix formed on the fabric by sol–gel technology.

Table 1 Influence of concentration of Ag^+ and water glass on antimicrobial durability[a]

$[Ag^+]$ in soaking solution (mol/L)	Content of water glass (%)	Bacterial Reduction[b] (%)			
		0 cycle	10 cycles	20 cycles	50 cycles
0.15×10^{-3}	2.0	>99.99	99.86	0	0
0.30×10^{-3}	0	>99.99	0	0	0
	2.0	>99.99	>99.99	>99.0	98.13
	5.0	>99.99	>99.99	>99.99	>99.0
0.45×10^{-3}	2.0	>99.99	>99.99	>99.99	99.97

[a] Treatment condition: 20 °C, 2.0% water glass, soaking time 30 min, liquor ratio 1:40

[b] Percent bacterial reduction as measured against an untreated control sample

3.3 Characterization of treated fabrics

SEM microscopy was used to evaluate the surface morphology of both the untreated (Fig. 4a) and the SiO_2-treated cotton textile (Fig. 4b). It was shown that the surface of treated textile was coarser than that of the untreated textile, indicating the existence of SiO_2 matrix.

The content of silver in antimicrobial textile before or after washing was measured quantitatively with ICP-MS (Table 2). It can be seen that the silver was leached rapidly during first 20 washing cycles and still remained 5 ppm after 50 times washing cycles. This is the reason that the antimicrobial textile treated with $\geq 0.30 \times 10^{-3}$ mol/L $AgNO_3$ still had good antimicrobial ability after 50 times washing cycles and also implied that even only small quantity of silver existed on fabrics would offer a good inhibition to *E. coli*.

It was understood that the form of silver fixed in the network of SiO_2 determined the antimicrobial activities of treated cotton fabrics [17]. X-ray diffraction method was used first to characterize the state of silver in the textile. XRD of controlled sample was compared to the SiO_2-treated textile and the antimicrobial textile. However, no significant peak of silver was detected in the XRD spectra of the antimicrobial textile (Fig. 5). This could be due to the small quantity of silver remained on fabrics. The peaks of silica for all treated samples were overlapped by the big and broad peak of cellulose.

In order to further elucidate the mechanism of antimicrobial finishing, the elemental composition of fabric surface was determined by XPS (Table 3 and Figs. 6–8). It is shown that silver, carbon, oxygen and silicon element were detected on the treated fabric.

A doublet peak of Ag on the surface of antimicrobial cotton textiles was presented in the XPS spectra of silver (Fig. 6). The binding energies for these two peaks were 368.4 ($3d_{5/2}$) and 374.2 eV ($3d_{3/2}$), respectively, which were all higher than that of Ag_2O (367.7 and 373.7 eV)

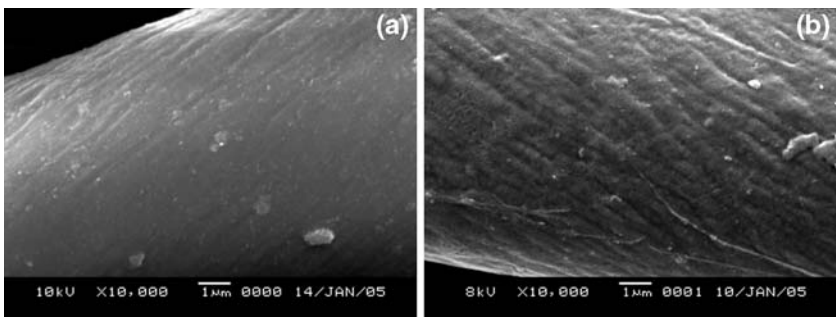


Fig. 4 SEM images of surface of cotton before (**a**) and after (**b**) SiO_2 treatment

Table 2 Content of Ag on laundered antimicrobial textile[a]

Number of washing cycles	0	20	50
[Ag] within textile (ppm)	210	16	5

[a] Treatment condition: 20°C, 2.0% water glass, $[Ag^+] = 0.30 \times 10^{-3}$mol/L, soaking time 30 min, liquor ratio 1:40

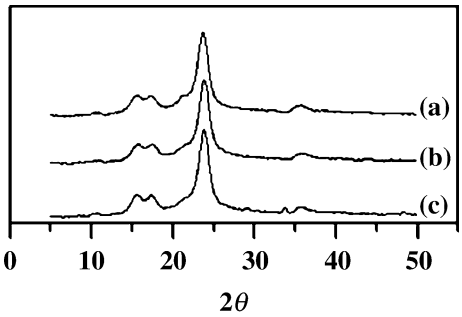


Fig. 5 XRD patterns of untreated cotton (**a**), SiO_2-treated cotton (**b**), antimicrobial cotton (**c**)

Table 3 XPS Data of surface of antimicrobial textile

Element	Untreated	Treated
C	71.74	33.03
O	28.26	56.09
Si	0	10.63
Ag	0	0.25
O/C	0.39	1.70

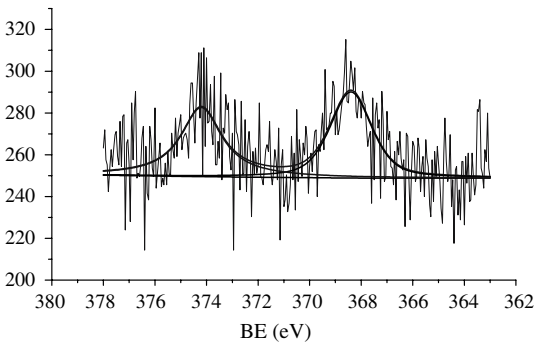


Fig. 6 XPS spectra of Ag3d in surface of antimicrobial textile

[18] and AgO (367.3 and 373.2 eV) [19]. But the difference of binding energies between these two peaks (5.8 eV) lied between that of Ag_2O (6.2 eV) [18] and AgO (5.6 eV) [19]. This suggested that there existed two different states of silver on the surface of fabrics. The overall high-antimicrobial ability of treated textiles should be contributed by both two silver states [17, 20, 21].

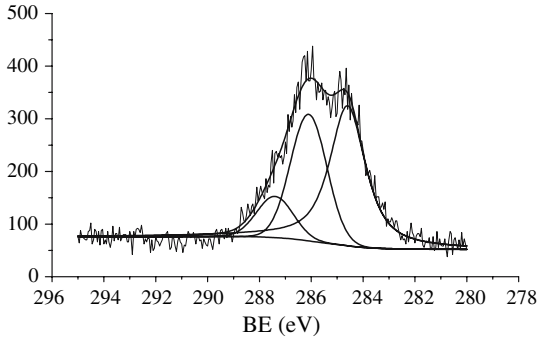


Fig. 7 XPS spectra of C1s in surface of antimicrobial textile

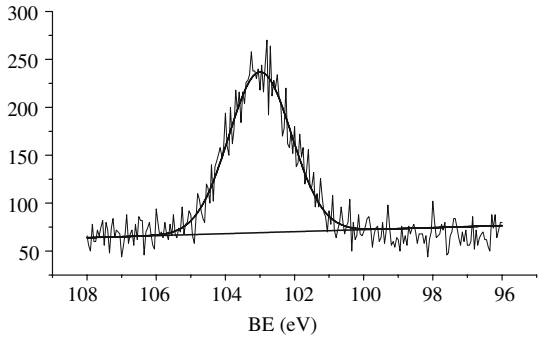


Fig. 8 XPS spectra of Si2p in surface of antimicrobial textile

The C1s spectra showed three peaks at 284.6 eV for C–C and C–H bonds, 286.1 eV for C–O bond, and 287.4 eV for O–C–O bond (Fig. 7), which was similar with the XPS data of the controlled standard cotton [22]. The XPS peak of Si2p at 103.0 eV (Fig. 8) was coincident with the reported Si peak of SiO_2 [23], indicating that there only existed physical interaction between silica network and cellulose fibers. Moreover, there was no any peak for sodium found in the XPS spectrum [24]. All these results indicated that silicate ion in water glass has been transferred to SiO_2 and sodium ion has been washed off after antimicrobial finishing.

4 Conclusions

An antimicrobial cotton textile was prepared by the sol–gel method using water glass and $AgNO_3$ solution. Some conclusions were obtained as following:

(1) The SiO_2 network was easily and cost-effectively prepared from water glass by padding process and used as good matrix for the absorption of silver ions.
(2) Antimicrobial cotton textile was achieved with water glass treated cotton textile using silver nitrate solution by soaking process.

(3) The antimicrobial textile showed an excellent antimicrobial effect against *E. coli* and could withstand 50 washing cycles.
(4) XPS confirmed that silver presented on the surface of the antimicrobial textile was in two different states, i.e. Ag^{+} and Ag^{2+}. Both two silver states have contribution to the overall antimicrobial activity.

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