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In situ Deposition of Silver Nanoparticles on the Cotton Fabrics

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Abstract: A novel method was developed to prepare the antibacterial cotton fabrics through *in situ* deposition of silver nanoparticles on the cotton fabrics by the reduction of Ag^+ without any reductant and dispersant. The data showed that by immersing the cotton fabrics in 160 mM $AgNO_3$ solution at 90 °C, the amount of silver nanoparticles was increased from 0.6890 to 1.3561 mg per gram of fabrics with the increase of reaction time from 10 to 50 min. The obtained cotton fabrics showed excellent antibacterial activity and laundering durability, in which the bacterial reduction was still 98.5 and 94.3 % to *Escherichia coli* and *Staphylococcus aureus*, respectively, even after the fabrics were washed for 20 cycles. Thus, this facile *in stitu* reduction method without any other reducers or stabilizers may bring a promising and green strategy to produce functional cotton fabrics.

Keywords: Cotton fabrics, Silver nanoparticle, *In situ*, Antibacterial activity, Laundering durability

Introduction

The antibacterial textiles containing different types of antibacterial agent have been intensively investigated in the past decades [1-4]. Among these, silver (Ag) and Ag^+ are widely used because of their wide-spectrum antibacterial activity. Especially, Ag exhibits nontoxicity to human cells when it is used in a reasonable amount [5-8].

Nowadays, various kinds of Ag-based antibacterial materials have been developed for curing and preventing diseases in public healthcare and water treatment [9-11]. Among them, Ag-loaded fibers/fabrics were manufactured mainly through dipping the fibers/fabrics in Ag colloids or adding Ag particles into the polymer solutions or melts before spinning [12-14]. However, loading Ag particles simply by physical adsorption often leads to unsatisfied laundering durability, and the mixing polymers with Ag particles usually causes the aggregation of additives, leading to the discontinuity and lower antibacterial activity. Recently, *in situ* synthesis of Ag nanoparticles on fibers/fabrics received a great deal of attention because of the particles' uniform distribution and stability. Vigneshwaran et al. reported *in situ* synthesis of Ag nanoparticles on the cotton fabrics, where the aldehyde terminal of starch reduced the Ag^+ to Ag, simultaneously stabilizing the Ag nanoparticles on the fabrics [15]. Pinto *et al.* obtained the cellulose/Ag nanocomposites with excellent antibacterial activity using sodium borohydride and UV irradiation reduction [16]. However, these methods so far were based on the stabilizers and/or toxic reducers like sodium borohydride, which are harmful to human body and environment. Therefore, it is desirable to develop a more facile and reliable approach to prepare the Ag-based antibacterial fibers/fabrics.

Cellulose is a linear chain polymer having three hydroxyl groups per anhydroglucose unit and presenting in the preferred C_1 conformation. Ribbon shape of cellulose allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. There is a relatively strong interaction between the neighboring cellulose molecules due to the presence of hydroxyl groups forming inter-molecular hydrogen bonds. This molecular structure gives cellulose the characteristics of hydrophilicity and chirality. The chemical reactivity is largely a function of the high donor reactivity of hydroxyl groups [17]. It is well known that the cellulose has heavy metal adsorption capacity as well as physical stability [18,19]. Furthermore, Liu *et al.* developed *in situ* synthesis of Fe_2O_3 nanoparticles on the regenerated cellulose fibers by reducing $FeCl_3$ to Fe_2O_3, indicating that cellulose has a potential ability to reduce various metal ions [20,21].

In this work, a novel and environmentally friendly method was developed to prepare the Ag nanoparticles deposited cotton fabrics possessing desirable level of antibacterial activity without significant color change. The effects of depositing conditions on the fabric color change and the Ag content on the cotton fabrics were investigated. The morphology of Ag nanoparticles on the fabrics was characterized by field-emission scanning electron microscope (FE-SEM), and the laundering durability was tested against gram-negative bacterium *Escherichia coli* (*E. coli*) and gram-positive bacterium *Staphylococcus aureus* (*S. aureus*).

Experimental

Materials

Silver nitrate ($AgNO_3$, analytical grade) was purchased from Hangzhou Mike Chemical Agents Co. Ltd. (Hangzhou, China). Bleached cotton fabrics (183 g/m^2 in density) were kindly supplied by Wensli Co. Ltd. (Hangzhou, China). *E. coli* (ATCC 25922) and *S. aureus* (ATCC 6538) strains were

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provided by College of Life Sciences, Zhejiang Sci-Tech University. Commercial washing powder "Li Bai" was used for laundering durability testing.

In situ Synthesis of Ag Nanoparticles on the Cotton Fabrics

Ag nanoparticles were deposited on the surface of fabrics by direct reduction of Ag^+ on the cotton fabrics. Briefly, the cotton fabrics were pretreated at 90 °C water bath for 30 min to activate the hydroxyl groups of cellulose molecules. The activated fabrics were then immersed in the $AgNO_3$ solution with liquor-to-fabric ratio of 50:1 (v/m), followed by being washed thoroughly with distilled water and then dried at 37 °C in an oven.

To investigate the effect of deposition conditions, including temperature, time and $AgNO_3$ concentration on the Ag content, L9 $(3)^4$ orthogonal test was performed according to the experimental design shown in Table 1. The antibacterial activity against *E. coli* was evaluated as an index after 12 h of culture, which was calculated as the percent of bacterial reduction using the following equation,

$$P\,(\%) = [(C_0 - C)/C_0] \times 100 \quad (1)$$

where P is the percentage of bacterial reduction, C_0 is the number of bacterial colonies on the untreated cotton fabrics, and C is the number of bacterial colonies on the Ag deposited cotton fabrics [22].

Characterization of Ag Deposited Fabrics

UV-vis absorption spectra were examined by Lambda 900 UV-vis spectrophotometer (Perkin Elmer, USA). The morphology of Ag nanoparticles deposited on the cotton fabrics was investigated with JSM-6700F field-emission scanning electron microscope (FE-SEM, JEOL, Japan). The amount of Ag deposited on the cotton fabrics was measured by Solar M6 atomic absorption spectrometer (AAS, Thermo Electron Co., USA). Before the AAS measurements, the fabrics were burned and dissolved in HNO_3.

Table 1. Experimental arrangements of L9 $(3)^4$ orthogonal test for the preparation of Ag deposited cotton fabrics

Test number	Factors			
	(A) Temperature (°C)	(B) $AgNO_3$ concentration (mM)	(C) Time (min)	
1	A_1 70	B_1 160	C_1 10	1
2	A_1 70	B_2 200	C_2 30	2
3	A_1 70	B_3 240	C_3 50	3
4	A_2 80	B_1 160	C_2 30	3
5	A_2 80	B_2 200	C_3 50	1
6	A_2 80	B_3 240	C_1 10	2
7	A_3 90	B_1 160	C_3 50	2
8	A_3 90	B_2 200	C_1 10	3
9	A_3 90	B_3 240	C_2 30	1

Color coordinates of the fabrics (CIE L^*, a^*, b^*) were determined with SF600X spectrophotometer (Datacolor Co., Switzerland) under an illuminant D_{65} using the 10° standard observer. On the basis of measured CIE color coordinates, the color difference (ΔE^*) was calculated using the following equation

$$\Delta E^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (2)$$

where ΔL^* is the color lightness difference between treated and untreated samples; Δa^*, red/green difference between treated and untreated samples; Δb^*, yellow/blue difference between treated and untreated samples.

Antibacterial Activity Testing

The antibacterial activity of cotton fabrics treated for different times was assessed using gram-negative bacterium *E. coli* ATCC 25922 and gram-positive bacterium *S. aureus* ATCC 6538. The bacterial strains were inoculated in the sterilized Luria-Bertani (LB) medium and incubated overnight at 37 °C with shaking. For qualitative measurement of antibacterial activity, the Ag deposited fabrics were cut as the discs with the diameter of 2 cm, and the antibacterial activity was tested using a modified agar diffusion assay (disc test) (ISO 20645: 2004, Textile fabrics-Determination of antibacterial activity-Agar diffusion plate test). The samples were placed on the *E. coil* or *S. aureus* grown LB agar plate and incubated overnight at 37 °C. The inhibition zone was measured as activity against above two microbial species.

The laundering durability of antibacterial activity was evaluated using a washing color fastness measuring meter (NEWAVE LAB EQUIPMENTS Co., Ltd., Taiwan) at 45 rpm (ISO 105-C06: 2010, Textiles-Tests for colour fastness-Part C06: Colour fastness to domestic and commercial laundering). The Ag deposited cotton fabrics prepared for 30 min were washed in the bath containing 0.4 % "Li Bai" washing powder at liquor-to-fabric ratio of 300:1. After 45 min of washing at 40 °C, the fabrics were rinsed three times (3 min) at ambient temperature and dried at 37 °C. The antibacterial activity after 0, 10, 20, and 30 washing cycles was determined according to the modified standard method (dynamic shake flask method) (ASTM E 2149: 2001, Standard test method for determining the antibacterial activity of immobilized antibacterial agents under dynamic contact conditions). Briefly, 20 mg of fabrics were placed in the sterilized testing tubes and inoculated with 10^5 to 10^6 colony forming units (CFU) of bacterial suspension, which were then incubated at 37 °C with vigorous shaking in order to assure the sufficient contact between the bacteria and the fabrics. At 4 to 12 h contact times, the number of survival colonies was determined by plating serial dilution on plate count agar to obtain the overall number of bacteria. The antibacterial activity was calculated in according with equation (1).

Results and Discussion

Effect of Depositing Conditions

The orthogonal L9 $(3)^4$ test analysis showed that the reaction temperature (R=32.23) was the most significant parameter affecting the antibacterial activity of cotton fabrics, which varied from 23.93 to 99.99 % (Table 2). The highest antibacterial activity was obtained when the cotton fabrics was treated at 90 °C. At the constant time and concentration, the antibacterial activity of cotton fabrics treated at 70 °C was lower than that at 90 °C, revealing that the increase of temperature significantly improved the antibacterial activity. Likewise, the antibacterial activity of cotton fabrics treated for 50 min was significantly higher than that for 10 min. In contrast, the increase of $AgNO_3$ concentration while keeping the temperature and time at constant only slightly increased the antibacterial activity of cotton fabrics.

Characterization of Ag Deposited Fabrics

Based on above investigations while considering the efficiency and color difference, the Ag deposition of cotton fabrics was carried out at $AgNO_3$ concentration of 160 mM at 90 °C, and the reaction time was varied from 10 to 50 min to obtain the cotton fabrics with suitable amount of Ag particles as well as tiny color change. Figure 1(A) shows the FE-SEM image of untreated cotton fabric fiber, which had the smooth morphology. After treatment, the homogeneous Ag nanoparticles with an average size of ca. 40 nm were observed at the surface of cotton fabric fibers when the deposition time was 10 and 30 min (Figure 1(B) and (C)). However, when the deposition time was prolonged to 50 min, the Ag particle size increased to ca. 100 nm. The amount of Ag particles deposited on the cotton fabrics increased owing to the prolonging reaction time. This result was further demonstrated by the UV-vis spectra shown in Figure 2. Compared with the untreated sample, the absorption band at 422 nm in the spectra of Ag deposited fabrics confirmed the presence of Ag nanopartles [23]. The intensity of absorption band became stronger with the increase of deposition time from 10 to 30 min, but this trend disappeared when the time extended to 50 min. This result suggested that the amount of Ag nanoparticles were not further increased, but the size became larger or aggregation occurred.

In this work, the Ag nanoparticles were formed via cellulose molecules as reducer and stabilizer. At 90 °C, the reactive ability of hydroxyl groups and reducing ends of cellulose molecules was largely enhanced, when the fabrics

Table 2. Range analysis of antibacterial activity of Ag deposited fabrics

	A	B	C	Antibacterial activity against *E. coli* (%)
1	A_1	B_1	C_1	23.93
2	A_1	B_2	C_2	84.44
3	A_1	B_3	C_3	94.90
4	A_2	B_1	C_2	93.98
5	A_2	B_2	C_3	95.14
6	A_2	B_3	C_1	93.68
7	A_3	B_1	C_3	99.99
8	A_3	B_2	C_1	99.99
9	A_3	B_3	C_2	99.99
K_1	203.27	217.90	217.60	
K_2	282.80	279.57	278.41	
K_3	299.97	288.57	290.03	
k_1	67.76	72.63	72.53	
k_2	94.27	93.19	92.80	
k_3	99.99	96.19	96.68	
R	32.23	23.56	24.15	

[a]K_i^A: Σ the antibacterial activity at A_i, [b]k_i^A: $K_i^A/3$, and [c]R_i^A: $\max\{k_i^A\} - \min\{k_i^A\}$.

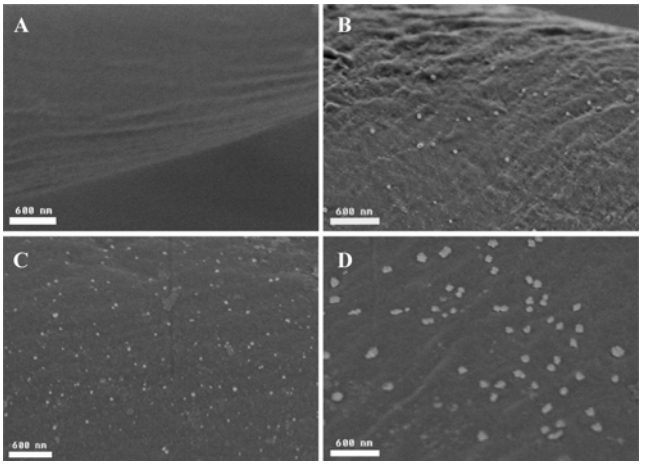

Figure 1. FE-SEM images of Ag deposited cotton fabrics treated for different times; (A) 0, (B) 10, (C) 30, and (D) 50 min.

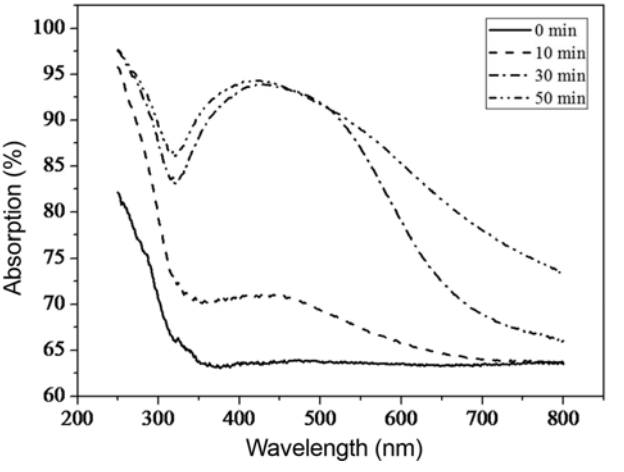

Figure 2. UV-vis spectra of Ag deposited cotton fabrics treated for different times.

were immersed in the $AgNO_3$ solution. The Ag^+ ions were quickly absorbed by the hydroxyl groups, where the Ag^+ ions were finally reduced into the Ag nanoparticles by the reducing ends of cellulose. The important role of cellulose and the reducing ends in forming Ag nanoparticles was also demonstrated by Pinto *et al.* [16], whom found that no Ag nanoparticles could be detected when exposing $AgNO_3$ solution to the UV irradiation without cellulose or with cellulose after removing the reducing ends.

The color change of fabrics from white to yellow due to the plasmon absorption of Ag nanoparticles [24] was observed in Figure 3. The color was maintained even after rinsing in water and drying, suggesting the binding of Ag nanoparticles on the surface of cotton fabric. The color coordinates of fabrics after Ag deposition were quantitatively determined using the CIE L^*, a^*, b^* coordinates (Table 3). While the fabrics reacted for 10 min only presented a slight color change with the color difference values (ΔE^*) of 9.25 when compared with untreated sample. With the increase of reaction time to 30 and 50 min, the color change became more obvious with the ΔE^* of 17.21 and 18.32, respectively,

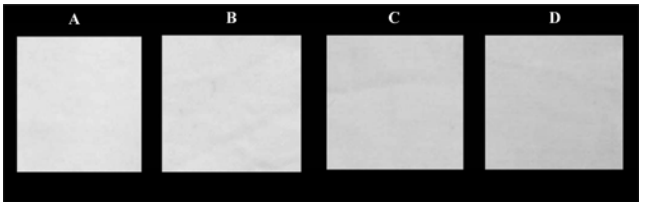

Figure 3. Optical photographs of Ag deposited cotton fabrics treated for different times; (A) 0, (B) 10, (C) 30, and (D) 50 min.

which resulted from the increased amount of Ag nanoparticles deposited on the cotton fabrics. The AAS data showed that the amount of Ag particles deposited on the cotton fabrics was significantly increased from 0.6890 to 1.2136 mg per gram of fabrics when the reaction time increased from 10 to 30 min, but it was 1.3561 mg/g when the time was further prolonged to 50 min, showing an insignificant increase when compared with that of 30 min.

Antibacterial Activity

The inhibition zone test of Ag deposited fabrics with different reaction times was carried out using *E. coli* and *S. aureus*. The results of antibacterial activity were shown in Figure 4. The Petri dish, supplemented with control fabric, showed a dense population of bacterial colonies (Figure 4(A)). However, a clear inhibition zone could be distinctly seen in Petri dish supplemented with the Ag deposited fabrics (Figure 4(B), (C) and (D)). There was no significant difference on the size of inhibition zone when the test was carried out with different Ag deposited fabrics against certain bacterial strain. However, the inhibition zones against *E. coli* (ca. 2.5 cm) were larger than those against *S. aureus* (ca. 2.0 cm), suggesting that the Ag nanoparticles have more effective contact biocidal property against *E. coli*, probably due to the different cell membrane structure between *E. coli* and *S. aureus* [25]. Meanwhile, all the Ag deposited fabrics exhibited strong antibacterial activity against *E. coli* and *S. aureus*, which was more than 99.99 % even the amount of Ag nanoparticles was very low.

The cotton fabrics treated for 30 min were then subjected to the repeated washing for the investigation of laundering

Table 3. Ag content and color difference of cotton fabrics prepared with different reaction times

Reaction time (min)	10	30	50
Ag content (mg per gram of fabrics)	0.6890±0.3149	1.2136±0.2056	1.3561±0.2063
Color difference (ΔE^*)	9.25	17.21	18.32

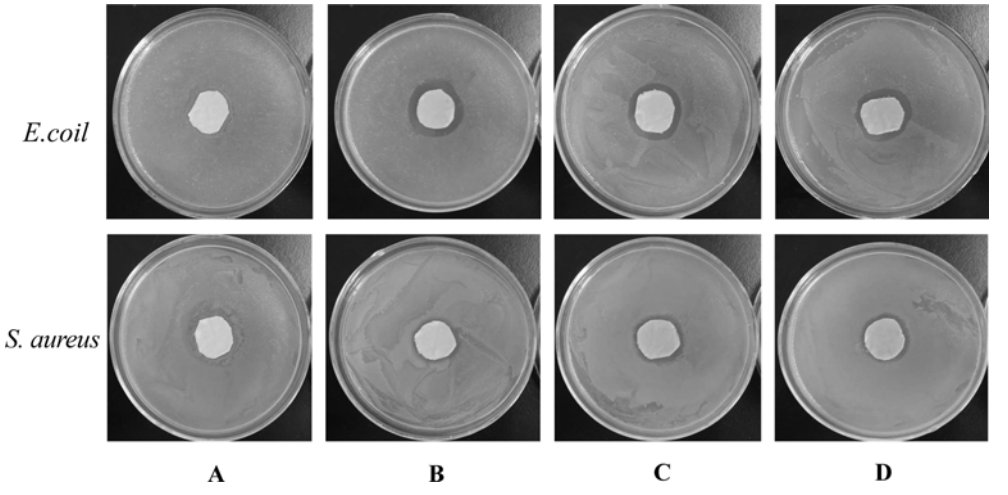

Figure 4. Pictures of inhibition zone test of Ag deposited cotton fabrics treated for different times; (A) 0, (B) 10, (C) 30, and (D) 50 min.

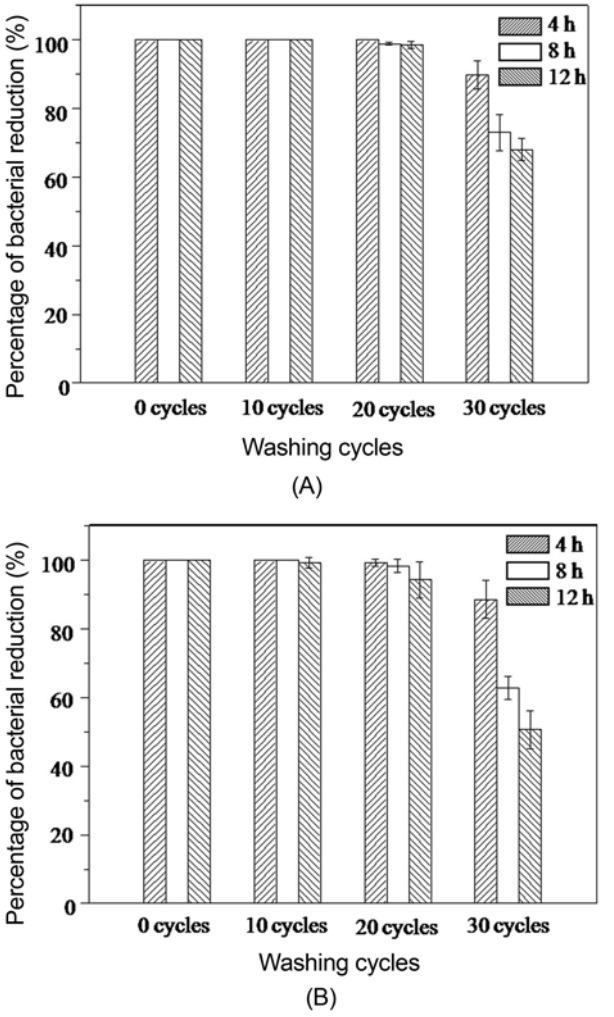

Figure 5. Laundering durability of antibacterial activity of Ag deposited cotton fabrics treated for 30 min against (A) *E. coli* and (B) *S. aureus*.

durability of antibacterial property by cultivating the *E. coli* and *S. aureus* strains in LB medium for 4 to 12 h. Figure 5 shows that, regardless of the cultivation time, the antibacterial activity of cotton fabrics after 10 washing cycles was similar to the unwashed fabrics. After 20 washing cycles, the antibacterial activity was more than 94 %, indicating the excellent laundering durability of Ag deposited fabrics. After 30 washing cycles, although the antibacterial activity decreased and dropped significantly with increase of contact time compared with the cases washed for 10 and 20 cycles, the fabrics still exhibited bacterial reduction values of 73 and 63 % for *E. coli* and *S. aureus*, respectively, for 8 h cultivation. Under LB broth cultivation, the Ag nanoparticles could only delay the growth of bacterial due to the aggregation between the particles and the destroyed cells, which resulted in their being removed from the liquid system [26]. So that, with the longer cultivation time, the Ag nanoparticles were coagulated with the dead bacterial and intracellular substances, leading to the growth of resumed bacteria.

Conclusion

The antibacterial cotton fabrics deposited with Ag nanoparticles were fabricated by *in situ* direct reduction of $AgNO_3$ with cellulose molecules without any additional stabilizers or reducers. Orthogonal test showed that the strong antibacterial activity of fabrics could be obtained by adjusting the depositing conditions including the reaction temperature, time and $AgNO_3$ concentration. A serial of antibacterial cotton fabrics deposited with different amounts of Ag nanoparticles were prepared. The obtained fabrics exhibited a slightly color change after being immersed in 160 mM of $AgNO_3$ solution at 90 °C for 30 min. Moreover, after 20 washing cycles, the fabrics still exhibited bacterial reduction values of 98.5 and 94.3 % for *E. coli* and *S. aureus*, respectively, showing excellent laundering durability. Thus, this novel and facile method may bring a promising and green strategy to produce a range of cellulose-based functional textile.

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