Preparation of Antibacterial Silk and Analysis of Interface Formation Mechanism

Xiaoli Chen, Liqiao Wei

Taiyuan University of Technology, Taiyuan, Shanxi CHINA

Correspondence to:
Liqiao Wei email: weiliqiaoty@163.com

ABSTRACT

Nano-Ag-loaded SiO2 antibacterial agent (Ag/SiO2) was prepared by a chemical reduction method and served as a modifier to endow silk fabric with antibacterial activity. Impregnated antibacterial silk (I-silk) and grafted antibacterial silk (G-silk) were obtained by dipping method and grafting with coupling agent KH550, respectively. The morphologies and valence-bond structures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). The washing fastness and antibacterial performance of G-silk were detected by the washing test and oscillation flask method. The results show that the chemical structure of G-silk changed in comparison with that of natural silk. The antibacterial rates of G-silk against E. coli and S. aureus were 96.5% and 92.8%, respectively. And it was still over 80% even after being washed for 30 times, suggesting good wash fastness and long-acting antibacterial activity.

Keywords: Antibacterial silk; Antibacterial performance; Wash fastness; Interface formation.

INTRODUCTION

Bacteria spread through many indirect ways besides direct contact, such as transmission by textiles [1]. Presently, ordinary textiles are endowed with antibacterial activity against bacteria infestation, which greatly raises the added value of products and has received increasing attention in antibacterial technology development and application [2-4]. Antibacterial technology has a wide range of applications in the textile industry, and types of antibacterial functional textiles have been developed and used in many fields to meet the requirements of health, environmental protection, and even medical care.

Natural fiber is a good medium for parasitism of microorganisms as it can provide enough nutrition for their growth. This will cause innumerable problems such as unacceptable odor, loss of strength, stains; and can even affect the health of wearers [5, 6]. Therefore, there has been a growing need to develop of textile materials that can offer improved protection to the users against microbes, bacteria, molds, or fungi [7, 8]. Silk is the lightest, thinnest and softest natural fiber and has a large number of applications in the textile field [9]. Silk possesses especial properties such as luminosity, great air permeability, water vapor transmission, thermo-insulating, and adaptation to skin [10, 11]. So it is widely used in costume, modern industry, and medical science which makes antibacterial silk especially important. However, to the best of our knowledge, few articles focused on antibacterial silk. Thus, methods to improve its antibacterial performance and obtain long-term antibacterial activity are a key problem.

SiO2 has vesicular structure which can release silver ions for a long period of time. This makes Ag/SiO2 antibacterial agent have durable antibacterial property. And for its high chemical durability and no toxicity to human cells, Ag/SiO2 antibacterial agent has potential application in various fields.

In this paper, Ag/SiO2 antibacterial agent was prepared by chemical reduction [12-17]. Antibacterial silk with good wash fastness was obtained by grafting Ag/SiO2 antibacterial agent with coupling agent KH550. Additionally, the interface formation mechanism is discussed.

MATERIALS

The micron-sized SiO2 was purchased from Beijing Shunsida Business Center. All the reagents are analytically pure. Glucose was commercially

obtained from Tianjin No. 3 Chemical Reagent Plant. NaOH was supplied by Tianjin Bodi Chemical Co., Ltd. KH550 was provided by Tianjin University Chemical Reagent Plant. AgNO3 was from Shanghai Shenbo Chemical Co., Ltd. E. coli and S. aureus were provided by Shanxi Dayi hospital.

PREPARATION

2.0 g of SiO2 was dispersed in 20 ml 8.85 mM of AgNO3 solution under vigorous stirring for 20 min. Then 30 ml of alkaline glucose solution was added slowly into the above suspension liquid. The reaction was conducted by a magnetically stirring apparatus and lasted for 10 min at 60°C in sealed condition. Finally the turbid liquid was filtrated, washed, and dried and Ag/SiO2 antibacterial agent with light color was obtained.

The silk fabric being washed and dried in advance was immersed into 40 ml of antibacterial solution containing 0.5 g of Ag/SiO2 antibacterial agent under magnetic stirring for 2 hours at room temperature, and then dried at 40°C. I-silk was obtained.

A functional liquid was obtained by reaction between 0.5 g of Ag/SiO2 antibacterial agent and 0.5 ml of KH550 in 40 ml of deionized water for 30 min at 70°C. Then silk fabric was immersed into the functional liquid and reacted for two hours at 40°C. The G-silk was got. The grafting rate (Rg) was calculated by Eq. (1):

$$Rg = (W1\text{-}W0) / W0 \times 100\ \% \quad (1)$$

Where, W1 is the mass of G-silk (g) and W0 is the mass of natural silk (g).

CHARACTERIZATION

Scanning electron microscopy (SEM) was carried out on a JSM-6700F equipped with FEI Nova NanoSEM430 energy dispersive X-ray spectrometer (EDS). High Resolution Transmission electron microscopy (TEM) was performed on a JEM 2010. Fourier transform infrared spectroscopy (FTIR) was recorded on a Tensor 27 (Bruker Optics) spectrometer. The antibacterial performance of the G-silk was measured by oscillation flask method [18-20]. The antibacterial test was carried on a constant-temperature shaker (Guohua Enterprise SHA-B). The antibacterial rates were calculated by Eq. (2):

$$Ra = (A\text{-}B) / A \times 100\ \% \quad (2)$$

Where, A is the number of colonies in blank control sample and B is the number of colonies in antibacterial samples.

RESULTS AND DISCUSSION

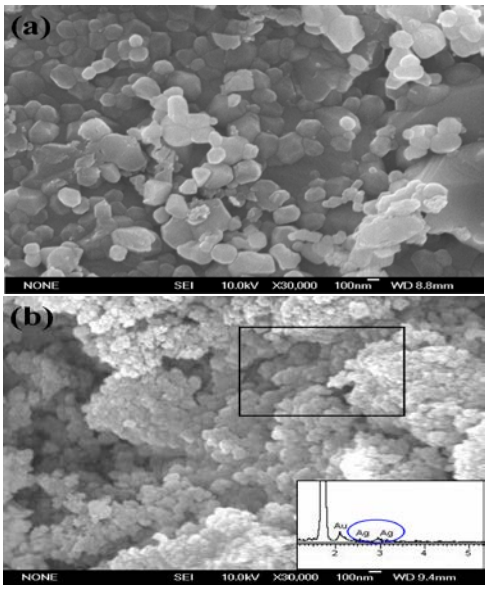

FIGURE 1. SEM images of SiO_2 (a) and Ag/SiO_2 antibacterial agent with EDS spectrum (b).

The morphological contrasts of Ag/SiO2 antibacterial agent and SiO2 are shown in *Figure 1*.The particles of SiO2 are spherical and larger than 100 nm in size *(Figure 1 (a)).* Ag nanoparticles (Ag NPs) distributed in the orifices and on the surface of SiO2 with a mean size of less than 50 nm and the elemental composition [21, 22] was verified as Ag shown in EDS spectrum *(Figure 1 (b)).*

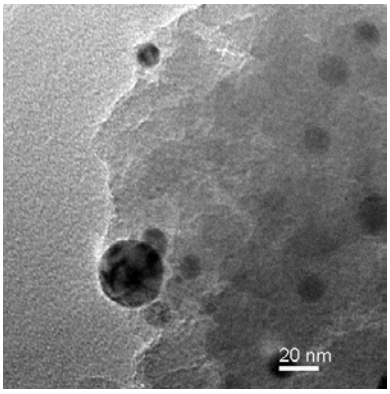

FIGURE 2. TEM image of Ag/SiO_2 antibacterial agent.

The nanostructure of Ag NPs in Ag/SiO2 antibacterial agent can be visualized in *Figure 2*. It can be seen that Ag NPs are spherical and the particle size is mainly in the range 10-30 nm. Ag NPs achieve good nanometer level and disperse well in SiO2.

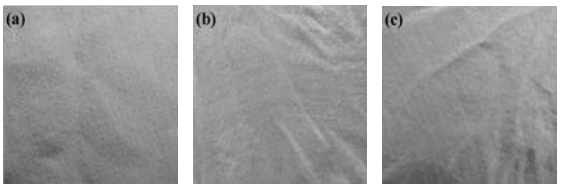

FIGURE 3. Photographs of the natural silk (a), I-silk (b) and G-silk (c).

The color contrasts of natural silk, I-silk, and G-silk are shown in *Figure 3*. It can be seen that there is almost no difference in color between the three photographs.

The color of natural silk is white and after antibacterial treatment, the color changes to be a little yellow.

The surface morphologies of natural silk, G-silk, I-silk, and those after wash testing are shown in *Figure 4*. The surface of natural silk is very smooth, while that of G-silk and I-silk are rough as they are covered by antibacterial agent. The surface of I-silk after being washed for 30 times looks smooth because almost all of the antibacterial agents were washed away. It can be seen that the surface of G-silk is still covered by antibacterial agents even after being washed for 30 times due to the grafting reaction, indicating good washing fastness. The Rg of G-silk was 6.77% calculated by Eq. (1). And there is no doubt that G-silk has long-acting antibacterial activity. The antibacterial performance of G-silk after being washed different times was tested.

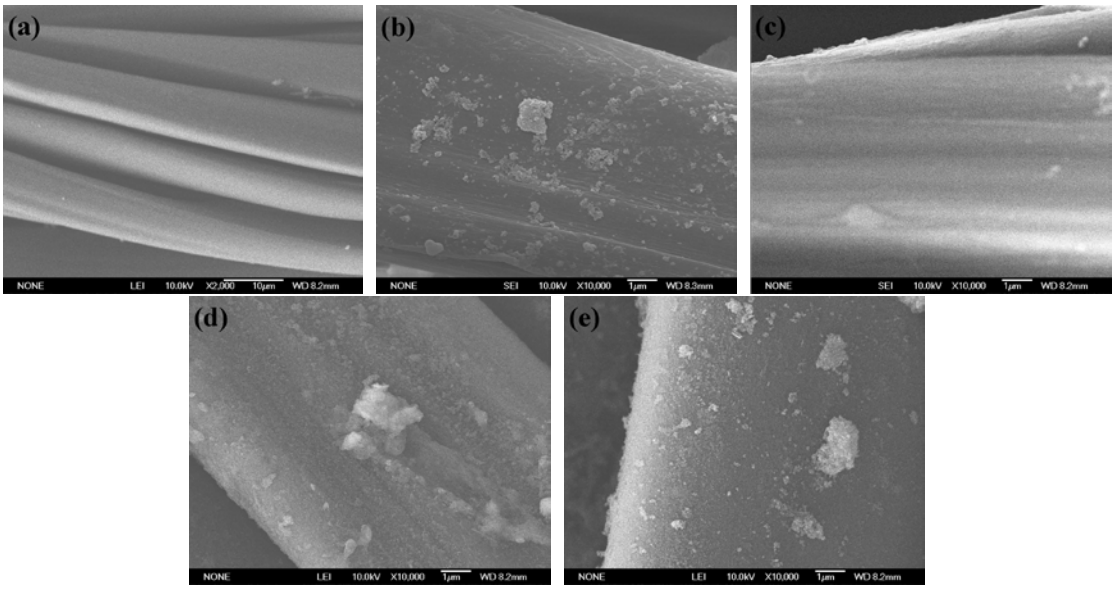

FIGURE 4. SEM images of natural silk (a), I-silk (b), I-silk after being washed for 30 times (c), G-silk (d) and G-silk after being washed for 30 times (e).

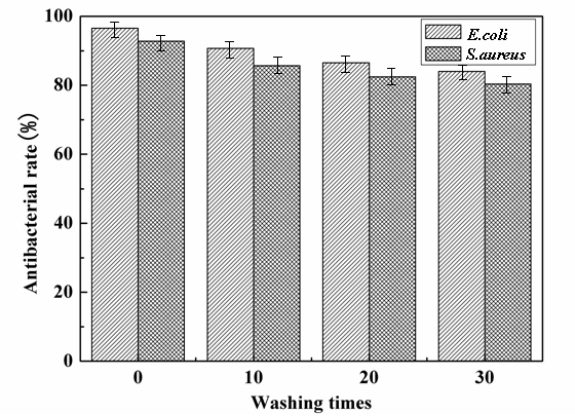

FIGURE 5. Antibacterial rates of grafted antibacterial silk against *E. coli* and *S. aureus* after different washing times.

TABLE I. Antibacterial rate index of antibacterial knitwear [23].

Antibacterial level	Washing times	Antibacterial rate(%)	
		S. aureus	*E. coli*
A	10	≥99	--
AA	20	≥80	≥70
AAA	50	≥80	≥70

The antibacterial rates of G-silk before and after was testing are shown in *Figure 5*. The antibacterial rates of unwashed G-silk against E. coli, and S. aureus in the concentration of about 5×104 cfu/ml were 96.5% and 92.8%, respectively. With the increase of washing time, even though the antibacterial rates reduced gradually, they were still over 80%, indicating G-silk guarantees AA level of antibacterial knitwear according to the standard of FZ/T73023-200623 shown in *Table I.*

The FTIR spectra of G-silk before (*Figure 6c*) and after washing (*Figure 6d*) are obviously different from that of natural silk (*Figure 6a*) at 1600-500 cm-1, while the whole spectrum of I-silk (*Figure 6b*) is similar. And partial absorption peaks of G-silk occurred blue shifting [24] from 3443 cm-1 to 3422 cm-1 and red shifting from 1630 cm-1 to 1636 cm-1. This indicates that G-silk has a chemical structural change and the antibacterial layer is strong enough against washing.

Silk is 97.34% composed of protein, whose functional groups mainly include amino acid (R-CH (NH2)-COOH), amino (-NH2), carboxyl (-COOH) and peptide bond (-CONH-).

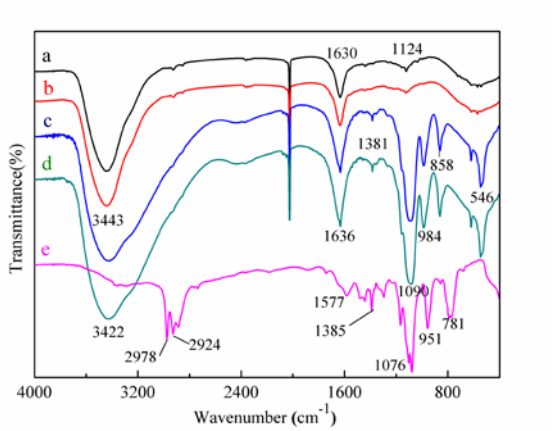

FIGURE 6. FT-IR spectra of natural silk (a), I-silk(b), G-silk(c), G-silk being washed for 30 times (d) and KH550 (e).

The absorption peaks around 1380.95 cm-1, 1089.72 cm-1, 990~800 cm-1 and 546 cm-1 in *Figure 4c* and *4d* correspond to stretching vibration of (-CONH-), (-C-O-), (-C-H) and (-C-C-) which were greatly enhanced in comparison with those in *Figure 6a* and *6b*. This indicates that the chemical structure of G-silk changed due to the reaction between silk fiber and coupling agent KH550.

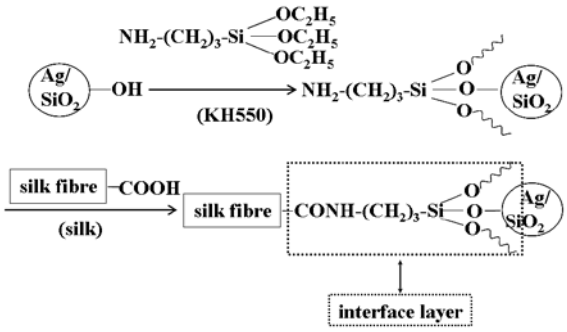

FIGURE 7. Schematic of antibacterial function layer formation mechanism of G-silk.

FIGURE 8. Diagrammatic drawing of G-silk's formation.

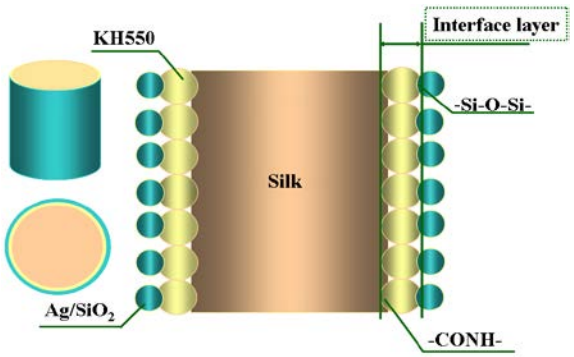

FIGURE 9. Diagrammatic section drawing of interface layer of G-silk.

The reaction principle and diagrammatic drawings are shown in *Figure 7* and *Figure 8*. First, Ag/SiO_2 antibacterial agent reacted with KH550 and connected through -Si-O-Si- bond. Then $-NH_2$ in the other side of KH550 reacted with -COOH of silk fiber to form -CONH-. After that, Ag/SiO_2 was grafted on the surface of silk fiber by aid of KH550. And G-silk was obtained with good washing fastness and long-acting antibacterial activity. The simulated section of G-silk and the connection between silk fiber and Ag/SiO_2 antibacterial agent can be seen in *Figure 9*, which shows that the antibacterial interface layer formed due to the bonding of -Si-O-Si- and -CONH-.

CONCLUSION

Ag/SiO_2 antibacterial agent with light color was prepared and served as a modifier to endow silk fabric with antibacterial performance by grafting with KH550. The chemical structure of G-silk changed in comparison with natural silk. It could be demonstrated that Ag/SiO_2 antibacterial agent was covalently bonded with silk fiber. The antibacterial rates of G-silk against *E. coli* and *S. aureus* were 96.5% and 92.8%, respectively and still over 80% after being washed 30 times, suggesting good wash fastness and long-acting antibacterial performance. Analysis of interface formation mechanism indicates that the interaction between silk fiber and antibacterial agent was strong due to the chemical bonding of -Si-O-Si- and -CONH-.

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AUTHORS' ADDRESSES

Xiaoli Chen
Liqiao Wei
Taiyuan University of Technology
Yingze Street 79#
Taiyuan, Shanxi 030024
CHINA