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The structural analysis of biomacromolecule wool fiber with Ag-loading SiO_2 nano-antibacterial agent by UV radiation

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Abstract

The wool fiber with Ag-loading SiO_2 nano-antibacterial agent was prepared by the method of photografting. The structure of subsequent antibacterial wool fiber was discussed in detail. The morphologies, structures and compositions were characterized by using Scanning Electronic Microscope (SEM), Transmission Electronic Microscope (TEM) and Fourier Transformation Infrared Spectrum (FTIR). The results showed that under ultraviolet irradiation the structure of wool fiber was changed, a lot of active groups were formed and grafting with Ag-loading SiO_2 was realized. Thus an antibacterial layer was formed on the surface of wool fiber by covalent bonding and a lasting antibacterial performance was obtained.

Keywords: Ag-loading SiO_2; Structure; Antibacterial wool; UV radiation; Photografting

1. Introduction

Being lighter, warmer, softer and smoother than other fibers, wool fiber has been known as superior textile material. The antibacterial wool fibers have been studied in recent years [1] and been a focus in the field of materials, but few reports can be found about the grafting of Ag-loading SiO_2 nano-antibacterial agent on wool fiber surface because of possible structural break during the grafting process which needs ultraviolet light irradiation [2]. Therefore the photografting analysis of antibacterial wool fiber has been rarely reported at the present. In this paper, antibacterial wool fiber was prepared by grafting Ag-loading SiO_2 nano-antibacterial agent on wool surface by ultraviolet irradiation. The structure of antibacterial wool fiber was characterized and the grafting mechanism was discussed with emphasis.

2. Experimental

2.1. Materials

Ultrafine wool fiber was got from Shanxi Pinde Wool Co. Ltd. Acetone (A.R), coupling agent (A-1100; Nanjing Shuguang Chemical Industry Co. Ltd., Nanjing, China) and dispersant agent (CH-10S; Shanghai Sanzheng Macromolecule Materials Co. Ltd., Shanghai, China) were obtained commercially. Inorganic Ag-loading SiO_2 nano-antibacterial agent was prepared before use. *Escherichia coli* and *Staphylococcus aureus* were provided by Shanxi Medical University.

2.2. Preparation of antibacterial wool fiber

Twenty grams of SiO_2 nanopowder (average particle size: 20 ± 5 nm)was put into 200 mL of 0.08 mol/L silver nitrate solution. After mixing, the pH value of suspended solution was adjusted to 6–8. Then, the solution was stirred at 75 °C for 4 h in a thermostat water bath to realize the sufficient adsorption of Ag^+ on SiO_2. After the adsorption was finished in water, the

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solution was filtered, the solid sample was washed with distilled water until no Ag^+ was detectable with NaCl solution, and then dried at 110 °C in vacuo [3]. Finally, Ag-loading SiO_2 nano-antibacterial agent was obtained.

Five grams of as-prepared Ag-loading SiO_2 was added into the mixture of 200 mL of deionized water. One milliliter of CH-10S dispersant was added and pH value was adjusted to 6. With stirring at 60 °C for 15 min, 1 mL of A-1100 coupling agent was added into the mixture to give the antibacterial functional solution [4].

About 6 g of original ultrafine wool fiber (Sample A) was treated as follows. First, the wool fiber was washed for several times in acetone and then dried in order to remove the impurities on its surface. Second, the dried wool fiber was exposed to ultraviolet light with wavelength of 280 nm, both upside and backside were irradiated equably for predetermined 30 min (Sample B). Third, Sample B was impregnated in antibacterial functional solution under the UV irradiation on both upside and backside for 30 min, respectively. Then, the treated wool fiber was washed with distilled water for 30 times and dried to give antibacterial wool fiber (Sample C).

2.3. Structures and morphologies of the samples

The morphologies of the samples were observed with scanning electron microscope (JSM-6700F) and elemental analysis was conducted with EDS spectra.

The microstructures of the samples were characterized by transmission electron microscope (HRTEM-2010) and Fourier transformed infrared spectrum (FTIR-1730).

The silver content of Ag-loading SiO_2 nano-antibacterial agent was measured with atomic absorption spectrum (ICPS) (LB-8410).

2.4. Antibacterial performance tests

The antibacterial properties of antibacterial wool fiber were measured by shake flask testing.

E. coli (ATCC 8099) and *S. aureus* (ATCC 6538) were selected as indicators of experimental bacteria. Luria Bertani media (LB) broth was used as growing medium for both the microorganisms *E. coli* and *S. aureus*. Bacteria were cultivated in 10 mL of LB broth (containing 10 g/L peptone, 8 g/L beef extract, 5 g/L sodium chloride, pH value of 7.2–7.4) at 37 °C for 24 h to give cell solution with a cell concentration of $(1–3) \times 10^8$ (CFU)/mL. Then, it was diluted to a cell concentration of $(1–3) \times 10^5$ (CFU)/mL with LB broth.

The antibacterial effect of unwashed and washed antibacterial wool fiber was measured according to the national standard GB1598-1995 for the evaluation of disinfections and antibiosis properties defined by the Public Healthy Department of China. The antibacterial effect was measured by the following testing steps: (1) 0.75 g of sample was put into a 250 mL flask, 5 mL of the cell solution ($(1–3) \times 10^5$ (CFU)/mL) was dropped into the flask and was fully absorbed by the sample inside. Then 70 mL phosphate buffered saline (PBS: 2.83 g/L Na_2HPO_4, 1.36 g/L KH_2PO_4, pH of 7.2–7.4) was added into the flask. (2) The mixed solution in the flask was shook on an agitation shaker with the speed of 300 r/min at 20–25 °C for 0 and 1 h, respectively, so that the cell concentrations before and after shaking could be measured. (3) The antibacterial effect was calculated using the following relationship:

$$R\% = \frac{A - B}{A} \times 100\%$$

where R is antibacterial effect (%), A and B are the mean numbers of bacteria in 0.5 mL of the mixed solutions before and after shaking. The reported data were the average value of three parallel runs.

3. Results and discussion

3.1. The effect of UV irradiation on ultrafine wool fiber's morphologies

UV irradiation influences the morphologies and structures of ultrafine wool fiber greatly. The morphologic changes of wool fiber after UV irradiation can be seen clearly from SEM images. Fig. 1 shows the morphology of original, UV-irradiated and antibacterial wool fibers. Fig. 1(a) is original ultrafine wool fiber (Sample A), Fig. 1(b) is UV-irradiated wool fiber (Sample B) and Fig. 1(c) and (d) are the side-view and cross-sectional view of antibacterial wool fiber (Sample C), respectively. Significant difference can be observed between Fig. 1(a) and (b) that the former is a piece of complete wool with well-defined scales layer covering on the shaft [5], the latter is of smooth edges and corners of scales and lots of deep and coarse grooves on outside surface, with part of scales falling off after UV irradiation. It was shown in Fig. 1(c) and (d) that a compact and smooth antibacterial layer with thickness of 200 nm came into being on the antibacterial wool fiber surface, as will be shown later in Fig. 3. Therefore, two kinds of reactions took place in series during UV irradiation and antibacterial functional solution impregnation. The first kind was the cleavage of surface bonds and the formation of active sites on wool surface during UV irradiation, and the second was the grafting of Ag-loading SiO_2 nano-antibacterial agent on the active sites during irradiation.

3.2. The microstructure characterization of antibacterial wool

Fig. 2 is the cross-sectional TEM images of Sample B. It shows that the layer of scales was partly broken to form a coarse groove with a depth of about 400 nm (Fig. 2b), as shown in Fig. 1(b). No layer outside the scales in Sample B was observed. Fig. 3 is the cross-sectional TEM image of Sample C, in which, a new layer of antibacterial agent was clearly observed. In Fig. 3, Region 1 is grafted functional layer, that is, the antibacterial layer of 200 nm. And Region 2 is the cortical layer of wool fiber. It can be seen that nano-antibacterial agent has infiltrated into cortical layer through scale layer and integrated with ultrafine wool fiber firmly. Fig. 4 is the HRTEM image of antibacterial layer, clearly

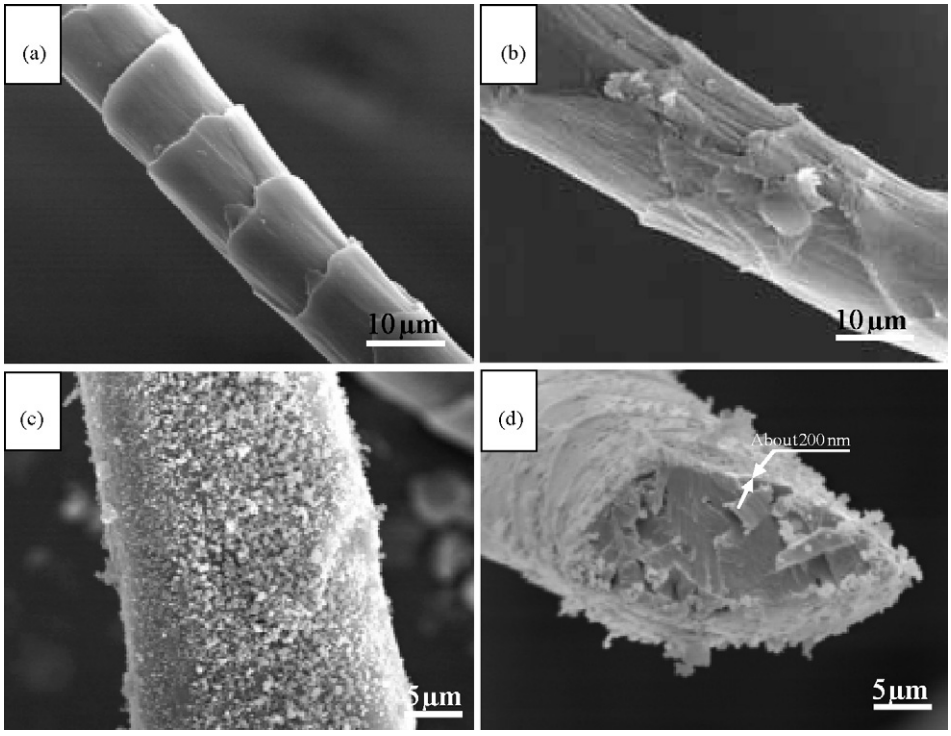


Fig. 1. The SEM images of wool fiber: (a) original, (b) UV-irradiated, (c) antibacterial wool fiber, and (d) the cross-section of antibacterial wool fiber.

showing the particles of Ag-loading SiO_2 nano-antibacterial agent with the size of about 5 nm. The characteristic peaks for different elements in the functional layer are presented in EDS spectra, which was obtained for the surface of antibacterial wool fiber, as shown in Fig. 5. It is important to note silver and its carrier SiO_2 appeared on the ultrafine wool fiber surface. Therefore, it can be suggested that the antibacterial layer was bonded to wool fiber by molecular valence rather than by simple physical adsorption, as will further proved later by FTIR measurement.

3.3. Silver content loaded on the fibers

Silver content of Ag-loading SiO_2 nano-antibacterial agent was measured as 0.69 wt% from atomic absorption spectrum (ICPS) (LB-8410). The initial loading amount of Ag-loading SiO_2 on antibacterial wool fiber was determined by the weight change before and after the impregnation of ultrafine wool fiber into antibacterial functional solution. During washing test, the weight loss after washing was assumed only from the loss of Ag-loading SiO_2 because no detectable loss of ultrafine wool fiber was observed. Therefore, the silver content of antibacterial wool fiber was easily related to the initial silver content on SiO_2. The Ag content loaded on the unwashed and washed antibacterial wool fibers are given in Table 1. It can be seen that the loss of silver loaded on antibacterial wool fiber approached a constant of about 33 wt% after 30 times of washing. Consequently, Ag-loaded SiO_2 nano-antibacterial agent was suggested not physically adsorbed but grafted on the ultrafine wool fiber.

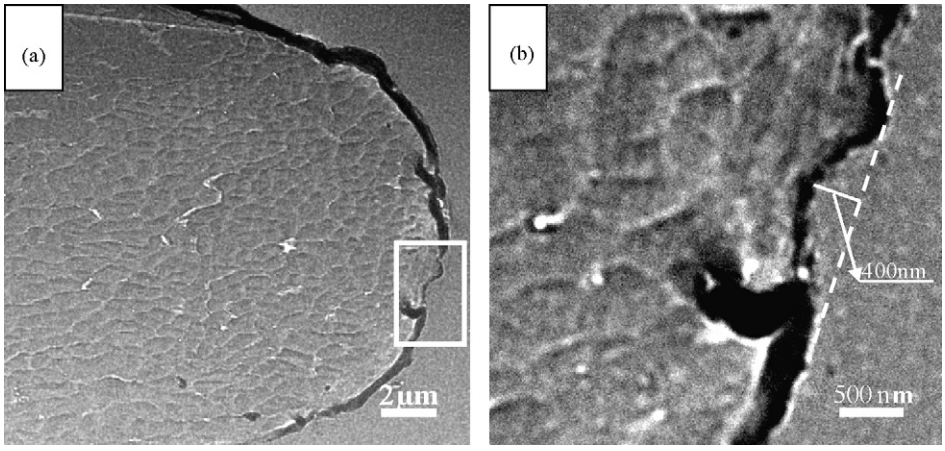


Fig. 2. TEM images of UV-irradiated wool fiber: (a) cross-sectional and (b) zoom in view of entangled part in (a).

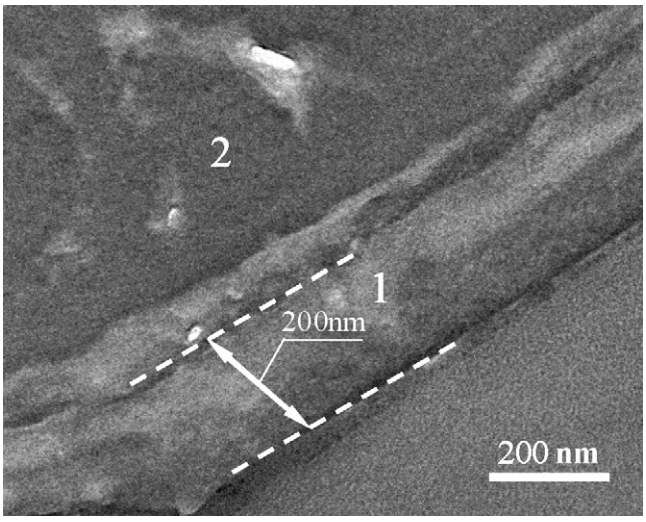


Fig. 3. TEM image of antibacterial wool fiber: (1) antibacterial layer and (2) cortical layer.

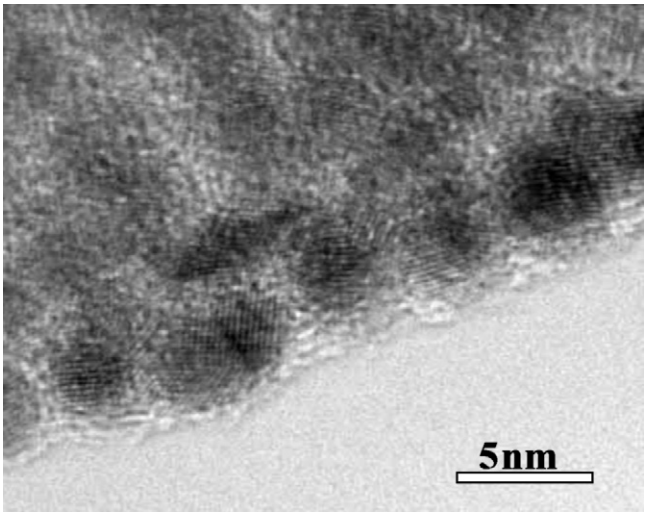


Fig. 4. HRTEM image of antibacterial layer of antibacterial wool fiber.

3.4. The effects of UV irradiation on the structure of ultrafine wool fiber

FTIR spectra of the samples were obtained to investigate the molecular structure changes of ultrafine wool fiber. Fig. 6 is the

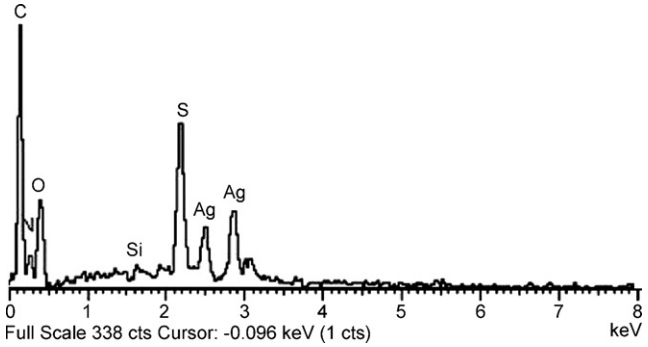


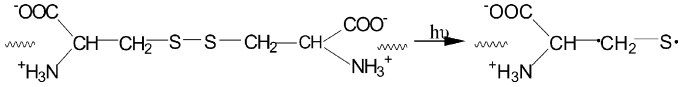
Fig. 5. EDS spectrum of antibacterial wool fiber.

Table 1
Ag content loaded on the unwashed and washed antibacterial wool fibers

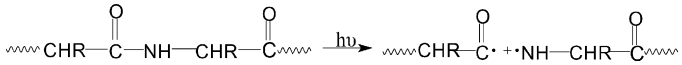
Samples	Ag content (wt%)	Ag loss (wt%)
Unwashed	0.260	0
Washed (10 times)	0.183	29.6
Washed (20 times)	0.174	33.1
Washed (30 times)	0.172	33.5

IR spectrum of the Sample A and Sample B. Fig. 6(1) of the 1750–500 cm^{-1} IR spectra and Fig. 6(2) of 3600–2800 cm^{-1} IR spectra report the differently treated wool fibers. It shows that wool fiber has changed during UV-radiation and in nano-antibacterial agent grafting processes. Fig. 6(1)-a (Sample A) shows that there are three different S–S stretching vibration spectral bands, which are 518.20, 528.07 and 546.75 cm^{-1}. Only S–S stretching vibration band at 528.07 cm^{-1} appears in Fig. 6(1)-b (Sample B). Symmetrical and asymmetrical stretching vibration peaks of SO_2 appear at 1338.89 and 1128.78 cm^{-1}, respectively, which show disulfide bonds are fractured and oxidized to produce sulfonic groups on ultrafine wool fiber surface during UV irradiation. N–H deformation vibration coupled with C–N stretched vibration of Amide II at 1547.58 cm^{-1} and C–NH flexural vibration of amide III at 1254.28 cm^{-1} [6] appear in Fig. 6(1)-a but disappear in Fig. 6(1)-b after UV irradiation, suggesting the breaking of peptide bonds of protein molecules in ultrafine wool fiber. Combined with Fig. 1(b), which shows the desquamation of scales and the formation of deep and coarse grooves during UV irradiation, it can be suggested that the bombardment of UV photons on the long multi-peptide chains caused the change in the primary structure, that is, the composition of amino acids and their arrangement [7]. The high level of disulfide bonds in the cystines and peptide bonds of the ultrafine wool fiber molecules were easily decomposed and broken during UV-irradiation (280 nm) [8–10] to produce a lot of active groups, dangling bonds and molecule holes, which reacted with [O] and $H^{\bullet}$ on the surface of ultrafine wool fiber. The [O] free radicals came from dissociation of oxygen upon the UV irradiation [11,12]. The main chemical reactions are as follows:

(1) S–S bonds breaking:



(2) Peptide bonds breaking:

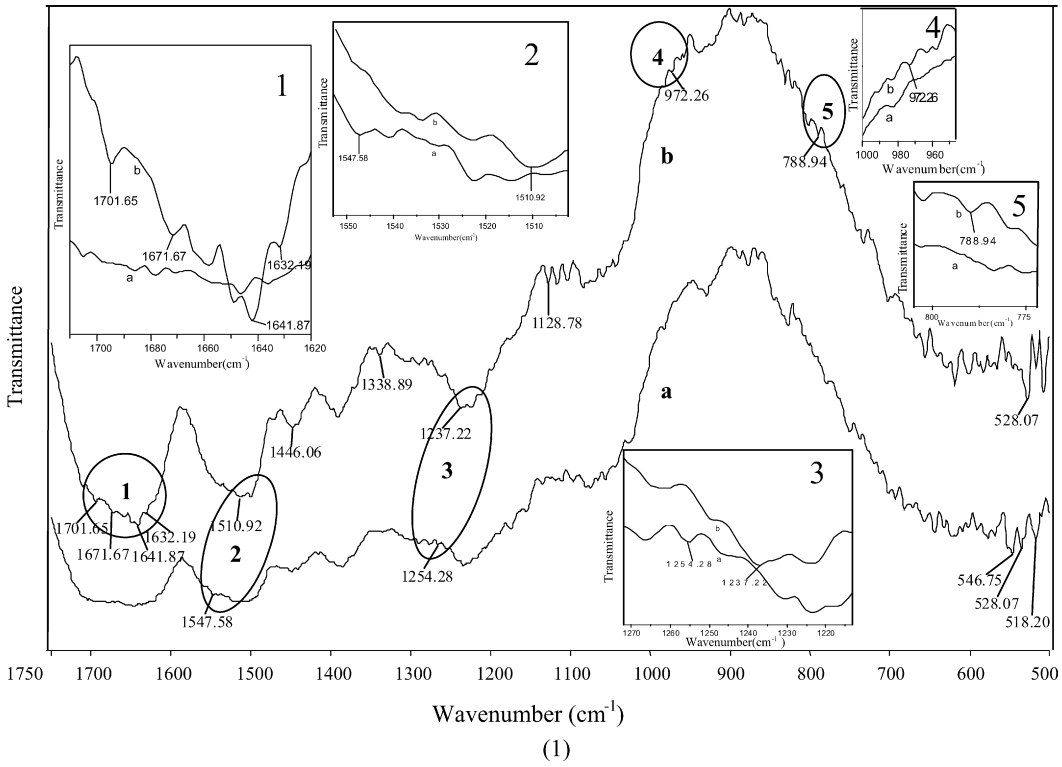


(3) Formation of [O] free radical:

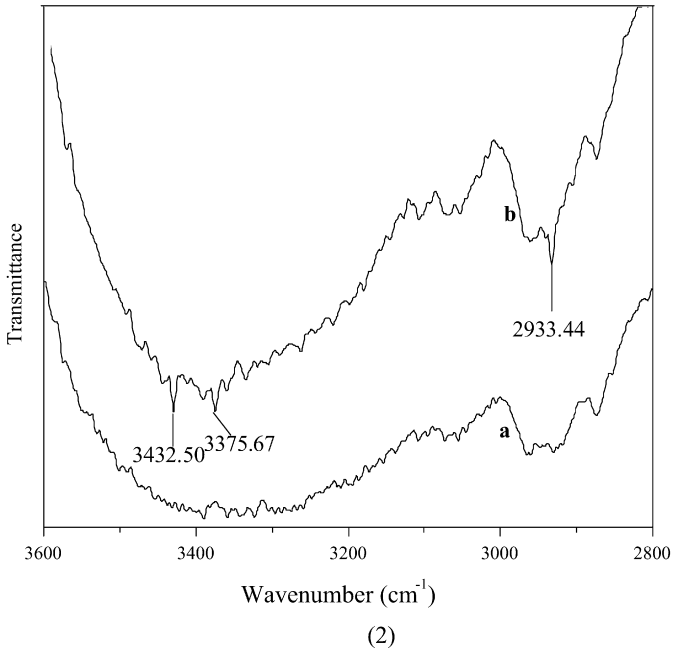
$$O_2 + h\nu \rightarrow [O]$$

$$[O] + O_2 \rightarrow O_3$$

$$O_3 + h\nu \rightarrow [O]$$



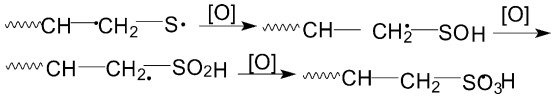
(1)



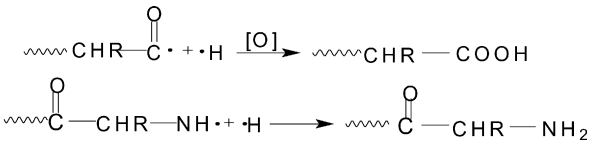
(2)

Fig. 6. FTIR spectra of (a) original and (b) UV-irradiated wool fibers. (1) 1750–500 cm^{-1} IR spectra and (2) 3600–2800 cm^{-1} IR spectra.

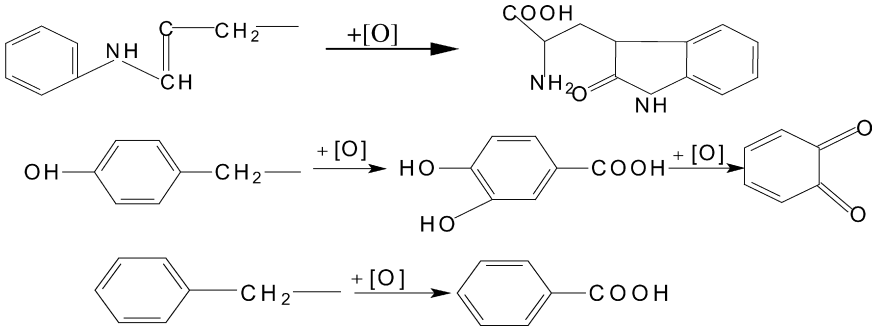
(4) Sulfonation reactions:



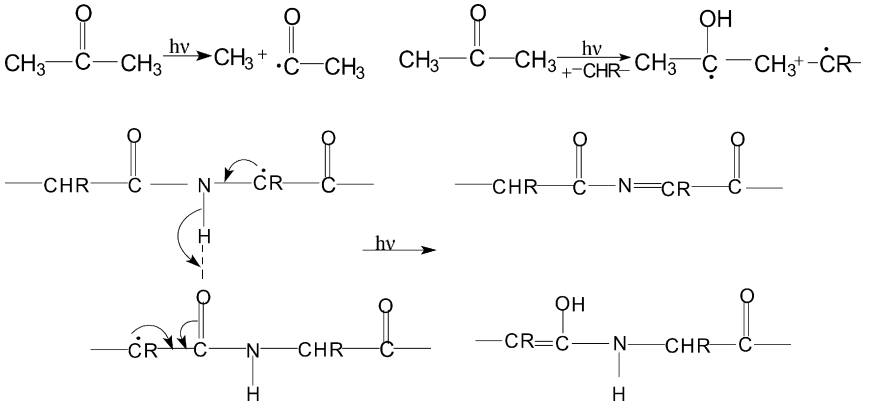
(5) Reactions of the broken bonds of peptide:



There are new characteristic occurring peaks in the IR spectra of Sample B from Fig. 6-b compared with Fig. 6-a. It illustrates that new functional groups were introduced into Sample A. The first of this kind is carboxylic acid, showing an absorption peak of carbonyl group at 1701.65 cm^{-1}. And the other characteristic peaks, such as O–H stretching vibration bands at 3375.67 cm^{-1}, C–H stretching vibration bands at 2933.44 cm^{-1}, C–O stretching vibration bands at 1237.22 cm^{-1}, O–H bending vibration absorption peak at 972.26 cm^{-1} with wider FWHM and medium intensity, and O–H deformation vibration band at 1446.06 cm^{-1} [13]. The second is indole molecule, giving N–H stretching vibration band at 3432.50 cm^{-1}. The wide FWHM suggests the presence of amino groups in indole molecule. Finally, the band at 1671.67 cm^{-1} can be attributed to the carbonyl group in 1,2-benzoquinone [14]. C–H bending vibration peak (788.94 cm^{-1}) belonging to 1,2-substituted benzene and C=C absorption peaks (1510.92 and 1632.19 cm^{-1}) belonging to aromatic compounds are inferred that *ortho*-benzoquinone was formed after UV irradiation. Therefore, from the analysis of IR spectra, carboxylic acid, benzoquinone and indole molecules were formed during UV irradiation. In his research on the keratin of wool fiber photodegradation, Gerald J. Smith pointed that three kinds of amino acids, that is, tryptophan, tyrosine, and phenylalanine, are easy to degrade after absorbing photons irradiated energies when radiation wavelength is in the range of 250–310 nm [15]. Their unsaturated bonds and active groups react with [O] on the ultrafine wool fiber surface and finally produce oxindolylalanine, *ortho*-benzoquinone and benzoic acid, respectively, so that a large number of oxygenic groups are introduced. Their reactions are as follows:

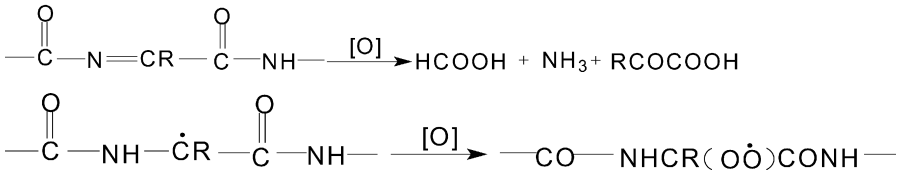


In Fig. 6(1)-b the band at 1641.87 cm^{-1} was attributed to the stretching vibration of C=N in R–C=N– structure, indicating the introduction of new group –C=N– into Sample B. The cause may be that the acetone free radical can capture one hydrogen atom from peptide chain. Acetone molecules physically adsorbed on the ultrafine wool fiber surface during washing could be excited to three-level state upon absorbing the energy of UV photons, which then transferred to free radicals by Norrich cracking and thus induced grafting reaction by capturing H from –CRH group in peptide chain [16]. Once free radical were formed in peptide chain by loss of H to acetone, they could be stabilized in different ways: (1) they reacted with each other and then got stabilized by oxygen free radical; (2) they combined with oxygen free radicals to produce new unstable active groups [17] which formed grafting chains in protein molecular chains; (3) they acted as active sites for the grafting of nano-antibacterial agent. The main reactions include:



(1)

(2)



(3)

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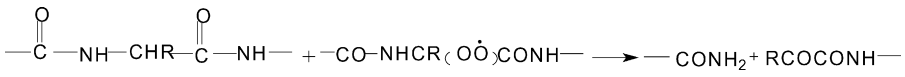


(5)

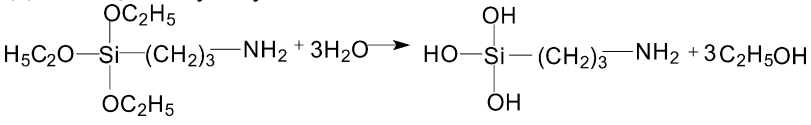
In summary, new groups were introduced onto the surface of Sample B to graft a lot of branch chains [18] on the macromolecules of ultrafine wool fiber. There branch chains were readily to lose the most active atoms upon the attack of free radicals to become active radicals which could be grafted with inorganic nano-antibacterial agent. When Sample B was immersed into the inorganic nano-antibacterial agent solution and irradiated by UV again, grafting reaction took place with nano-antibacterial agent molecules to give Sample C.

Compared with Samples A and B, Sample C is quite different in the IR spectra (Fig. 7). Two new characteristic peaks appeared at wave number 1152.08 cm^{-1} belonging to Si–O–Si stretching vibration band and at 1098.50 cm^{-1} belonging to Si–O–C symmetrical stretching vibration band [19]. This proved the presence of valence antibacterial layer formed by the grafting reaction between UV-induced active radicals with inorganic Ag-loading SiO_2 nano-antibacterial agent on the surface of ultrafine wool fiber.

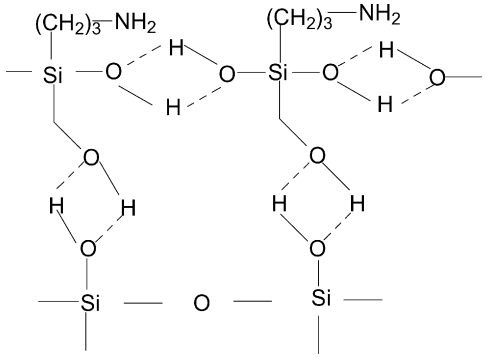
3.5. The formation mechanism of antibacterial layer

FTIR analysis showed that the groups of Si–O–Si and Si–O–C were grafted on the surface of Sample C. And EDS analysis (Fig. 5) showed the existence of silver element on the surface of Sample C. Thus the satisfying integration of inorganic Ag-loading SiO_2 nano-antibacterial agent with macromolecular polymer of ultrafine wool fiber can be concluded. On the other hand, the coupling agent of A-1100 took an important role of bridging in the process [20]. The molecular formula of A-1100 is $H_2N(CH_2)_3Si(OC_2H_5)_3$, of which $–OC_2H_5$ groups are readily hydrolyzable to form silanol. Hydrogen bonds could be formed among the hydroxyl groups of silanol or between the hydroxyl groups and Ag-loading SiO_2 nano-antibacterial agent. Si–O–Si chemical bonds could be further produced by dehydration reactions. The hydrophobic $–(CH_2)_3–NH_2$ group could graft with the dangling bonds or active groups $P^•$ produced on the surface of wool fiber, just as follows:

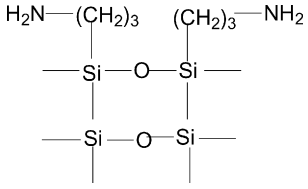
(1) OC_2H_5 was hydrolyzed to form silanol:



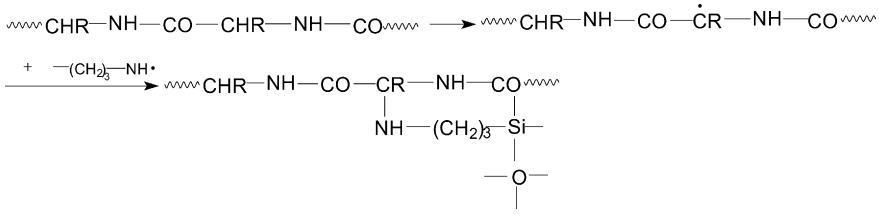
(2) Hydrogen bonds were formed among the hydroxyl groups of silanol or between the hydroxyl groups and Ag-loading SiO_2 nano-antibacterial agent:



(3) Si–O–Si chemical bonds were produced by dehydration reactions:



(4) $–(CH_2)_3–NH_2$ could graft with the dangling bonds or active groups $P^•$:



As mentioned above, when Sample B was immersed into in the inorganic nano-antibacterial agent solution, the UV-induced active radicals from its branch chains easily grafted organic aminopropyl on the surface of carrier SiO_2 [21]. So a valence antibacterial layer formed on the surface of ultrafine wool fiber.

4. Antibacterial property

The antibacterial efficiency against *E. coli* and *S. aureus* was higher than 96% for unwashed antibacterial wool fibers. Because no standard washing procedures are given in GB1598-1995, the

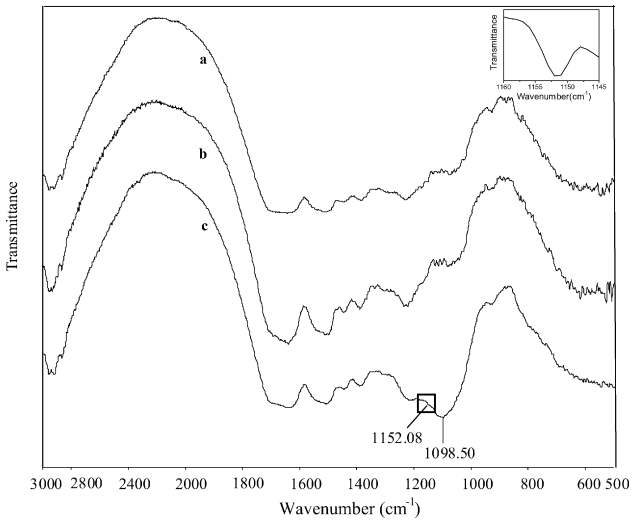


Fig. 7. 3000–500 cm^{-1} FTIR spectra of (a) original, (b) UV-irradiated and (c) antibacterial wool fibers.

Table 2
The tests of antibacterial and washable properties

Washing times	Antibacterial effect (%)	
	Escherichia coli (ATCC8099)	*Staphylococcus aureus* (ATCC6538)
0	98.5 ± 0.1	96.7 ± 0.1
10	96.9 ± 0.1	95.5 ± 0.1
20	95.0 ± 0.1	93.4 ± 0.1
30	92.0 ± 0.1	90.4 ± 0.1

washing was done according to the standard of Japan JISL0217-130, that is, the temperature of water was 30 ± 1 °C and the washing rate was five times per minute by hand-stirring. As can be seen in Table 2, the antibacterial efficiency was ever 90% after repeated washing.

5. Conclusion

1. The structures of scale layers were broke and the primary structures of protein macromolecule were changed during UV irradiation, thus introducing a great deal of active free radicals and unsaturated bonds onto the surface of ultrafine wool fiber.
2. With the help of coupling agent, these radicals reacted with [O] and $H^{\bullet}$ active groups to produce a lot of branch chains on the surface of ultrafine wool fiber. These branch chains grafted inorganic Ag-loading SiO_2 nano-antibacterial agent upon UV irradiation. Due to the dense and uniform antibacterial layer with thickness of 200 nm on the antibacterial wool fiber surface, permanence of antibacterial function was realized.
3. The antibacterial wool fibers were found good in antibacterial effect against *E. coli* and *S. aureus* and even after 30 washing times, thus indicating good washability.

Acknowledgements

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