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Preparation and properties of cellulose/silver nanocomposite fibers

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ABSTRACT

We prepared cellulose/silver nanocomposite fibers by soaking the cellulose fibers in $AgNO_3$ aqueous solution, which was heated at 80 °C for 24 h to synthesize Ag nanoparticles in situ. The structure and properties of the composite fibers were characterized by FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmitting electron microscopy (TEM), thermo-gravimetric analysis (TGA) and tensile testing. The content and diameter of the Ag nanoparticles (NPs) increased from 0.15% to 2.40% and from 7.2 nm to 12.5 nm, respectively. In our findings, the pores of the cellulose fiber at wet state were used as a microreactor to synthesize Ag nanopariticles. The cellulose/Ag nanocomposite fibers exhibited good mechanical properties and thermal stability. Antibacterial experiment revealed excellent antibacterial activity of the cellulose nanocomposite fibers against *Staphylococcus aureus*. The cellulose/silver nanocomposite fibers would have great potential in antibacterial textile and wound handling due to easy industrialization.

1. Introduction

Bacteria, as most widely distributed, distresses human life and health, thus antimicrobial materials have been one of the hot topics in scientific research (Ignatova, Stoilova, Manolova, Markova, & Rashkov, 2010; Lu, Jiang, & Chen, 2004; Papageorgiou, Assimopoulou, Couladouros, Hepworth, & Nicolaou, 1999; Shateri Khalil Abad et al., 2009). As early as the Sui and Tang Dynasties, herdsmen in northern China served mare's milk in a silver bowl to keep it for a long time, and thus silver had been known as the "permanent fungicide". Silver nanoparticles have a strong inhibition of dozens of pathogenic microbes with no drug resistance such as *Escherichia coli*, *Neustria gonorrhea* and *Chlamydia trachomatis* etc. (Nadagouda & Varma, 2007). Even using nano-silver thousands of times as the standard dosage, there were no poisoning manifestations appeared on the test animals (Panyala, Peña-Méndez, & Havel, 2008). Silver nanoparticles can also promote repairing the damaged epithelial cells, which exhibited no toxicity and stimulation on skin (Tavares et al., 2012). Thus nano-silver powder is widely used in daily life (Asare et al., 2011), medicine (Jacob, Finub, & Narayanan, 2011; Ramos et al., 2011; Ren, Fang, & Wang, 2011), textiles (El Shishtawy, Asiri, Abdelwahed, & Al Otaibi, 2011; Klemenčič, Simončič, Tomšič, & Orel, 2010; Shateri Khalil Abad et al., 2009) and ceramic (Colomban, 2009) field for human health guaranty.

Antimicrobial fibers can be obtained through the methods of depositing silver nanoparticles on the surface of fabric fiber (Johnston & Nilsson, 2012; Li et al., 2011; Omrani & Taghavinia, 2011; Smiechowicz, Kulpinski, Niekraszewicz, & Bacciarelli, 2011; Song, Birbach, & Hinestroza, 2012). Montazer, Alimohammadi, Shamei, and Rahimi (2011) introduced a new green method for the synthesis of silver nanoparticles on the cotton fabric surface through using Tollens' reagent. In this approach, silver nitrate ($AgNO_3$) has been transformed to Ag_2O followed by an aqueous solution with ammonia. Subsequently, silver nanoparticles are synthesized directly on the cotton fabric. It has also been reported that (Shi et al., 2011) durable antibacterial Ag/polyacrylonitrile (Ag/PAN) hybridnanofibers have been prepared by atmospheric plasma treatment and electrospinning. In their work, atmospheric helium plasma treatment was used to reduce the $AgNO_3$ precursor in pre-electrospinning solutions into metallic silver nanoparticles, followed by electrospinning into continuous and smooth nanofibers with Ag nanoparticles. The Ag/PAN nanofibers exhibited slow and long-lasting silver ion release, which provide robust antibacterial activity against both Gram-positive Bacillus cereus and Gram-negative *E. coli* microorganisms. Bacterial cellulose (BC) nanofibers with silver nanoparticles on the surface have been prepared (Ifuku, Tsuji, Morimoto, Saimoto, & Yano, 2009). Silver nanoparticle-embedded polyrhodanine nanofibers have been synthesized by chemical oxidation polymerization (Kong & Jang, 2008). The synthesized silver/polyrhodanine nanofiber has the excellent antimicrobial activity against Gram-negative *E. coli*, Gram-positive *Staphylococcus aureus*, and *Candida albicans* (Kong & Jang, 2008). Antimicrobial Lyocell fibers by Ag^+ ion sorption

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from aqueous silver nitrate solution have been accomplished (Praskalo Milanovic, Kostic, Dimitrijevic Brankovic, & Skundric, 2010). The sorption properties of Lyocell fibers were improved by the selective TEMPO-mediated oxidation (Song et al., 2012). Cellulose/silver nanoparticles composite microspheres (Wu, Zhao, Zhang, & Xu, 2012) and bacterial cellulose/AgNPs composite film (Yang, Xie, Deng, Bian, & Hong, 2012) have also been reported recently.

In our laboratory, a novel solvent system for cellulose has been developed, i.e. NaOH/urea aqueous solution pre-cooled to −12.5 °C, in which the dissolution of cellulose could be achieved rapidly at ambient temperature (below 20 °C) (Cai & Zhang, 2005). Moreover, regenerated cellulose multi-filament fibers, magnetic cellulose fibers and membranes have been prepared successfully from this system (Cai et al., 2007; Qi, Cai, Zhang, Nishiyama, & Rattaz, 2008). The new cellulose fibers from the cellulose solution are bright and had smooth surface and circular section (Cai et al., 2007; Qi et al., 2008; Li et al., 2010). These regenerated cellulose materials displayed good mechanical properties, and could be applied to the textile, fabric, film and filler etc. In this work we attempted to supply a new method to produce cellulose/silver nanocomposite fibers, and evaluated the antibacterial activities to extend the functional application of the new cellulose fibers.

Compared to the reported cellulose/silver nanoparticles composite microspheres (Wu et al., 2012) and bacterial cellulose/AgNPs composite (Yang et al., 2012), our nanocomposite fibers with lower silver content and good antibacterial property would have great potential in special costume and medical dressing due to easy industrialization.

2. Experimental

2.1. Materials

New cellulose fibers were spun from the cellulose solution of 5.2 wt% dissolved in 7 wt% NaOH/12 wt% urea aqueous solution at −12.5 °C (Li et al., 2010) by Jiangsu Longma Green Fiber Co. (Haian, China). The Weight-average molecular weight (M_w) of cellulose fibers was determined to be 5.6×10^4 g mol^{-1}. $AgNO_3$ were of industrial grade, and were used without further purification.

2.2. Produce procedure

After washing by distilled water, 10 g wet cellulose fibers (water content of about 90%) were immersed into 200 ml $AgNO_3$ aqueous solution in a Teflon-sealed glass bottle, and then heated at 80 °C for 24 h for in situ synthesis Ag nanoparticles by reduction. No apparent redox reaction was observed on immersion at room temperature. After cooling to room temperature, the gel was thoroughly washed with distilled water. The concentration of $AgNO_3$ was 1, 5, 25, 125 and 250 mM, and the composite fibers prepared were coded as B1–B5.

2.3. Characterization

FT-IR spectra were recorded on a Nicolet FTIR spectrometer (Nicolet NEXUS 670) by KBr pellet method. The surface and fracture section of the composite fibers were observed by using a SEM (Hitachi, S-570, Japan). Wetted fibers were frozen directly in liquid nitrogen, immediately snapped, and then freeze-dried by using lyophilizer (CHRIST Alpha 1-2, Germany). The surface and the fracture section of fibers were sputtered with gold under vacuum, and then observed and photographed. For observation of TEM, the composite fibers were immersed to a 7:3 (v/v) mixture of methylmethacrylate and butylmethacrylate monomers containing 1.4% (w/v) benzoyl peroxide as initiator to polymerize. After polymerization by curing at 52 °C for 6 h, the embedded specimen was ultrathin-sectioned by a Leica Ultracut-E using a diamond knife. The section approximately 100 nm thick (golden color) was mounted on a grid with carbon support. To observe both of the structures of cellulose and metal nanoparticles, the ultrathin section was disembedded by removing the resin by acetone on the grid, and examined by TEM (JEOL-2000EX, 80 kV tension) without staining (defocus contrast). The X-ray diffractometry of cellulose fibers and cellulose fiber/Ag composite fibers was carried out on an XRD diffract meter (D8-Advance, Bruker). The patterns with CuK_α radiation (λ = 0.15406 nm) at 40 kV and 30 mA were recorded in the

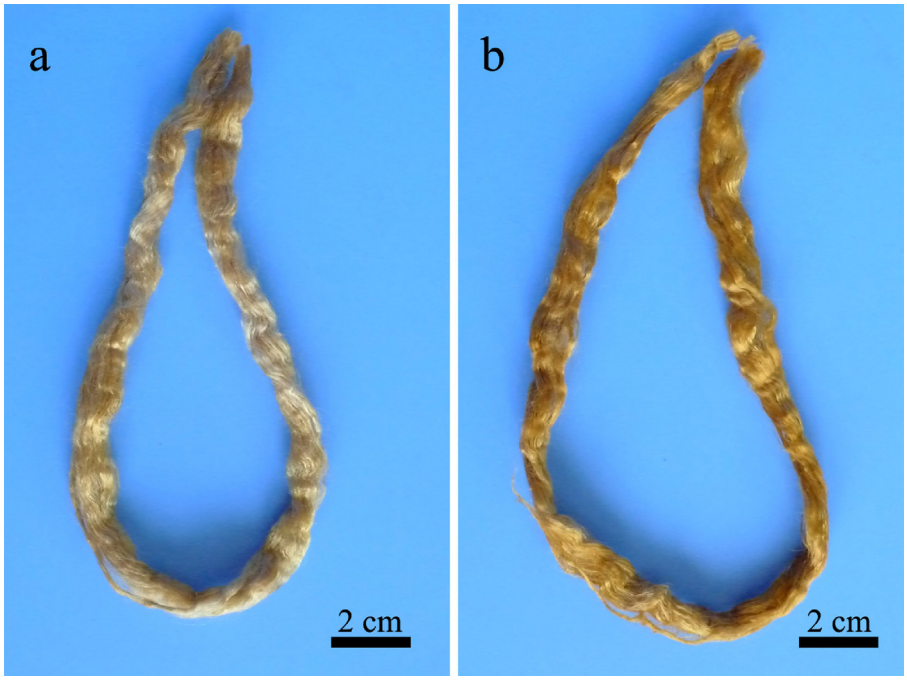

Fig. 1. Photographs of the composite fibers (a—B1 and b—B4).

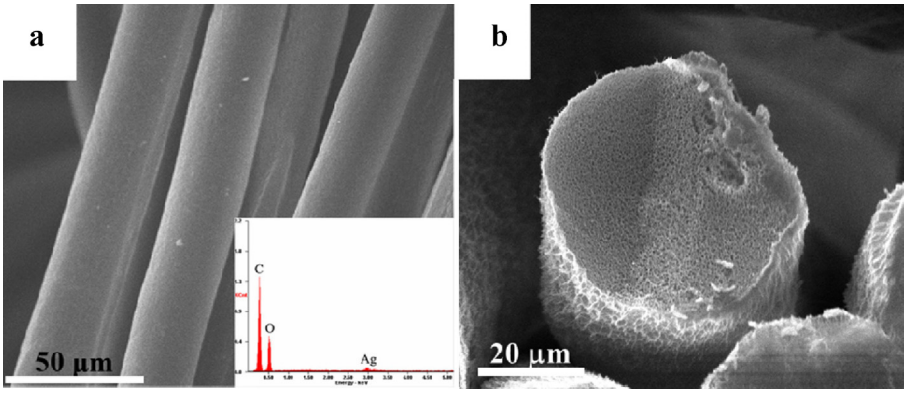

Fig. 2. SEM images of the composite fibers (a—surface of B5 and b—cross section of B5). Insert is the EDS of B5.

region of 2θ from 5° to 45°. Samples were ground into powders and dried in a vacuum oven at 60 °C for 48 h. The spherical size of crystalline (D) was estimated by Scherrer's formula (Cai, Kimura, Wada, & Kuga, 2008):

$$D = K\lambda/B\cos\theta \quad (1)$$

where K is a constant (0.94), B is the full-width half-maximum of respective diffraction peak (rad), and 2θ is the peak angle in radian.

Thermogravimetric analysis was carried out by STA 449C (NETZSCH Co., Germany) for Ag content determination and analysis. The sample was placed in a platinum pan and heated from 25 to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. Set C_0 (%) as the residual weight of B0, C_x (%, x = 1, 2, 3, 4 and 5) as the residual weight of B_x (x = 1, 2, 3, 4 and 5) and C_{Ag} (%) as Ag content in cellulose fibers, then an equation is obtained as shown below.

$$(1 - C_{Ag})C_0 + C_{Ag} = C_x \quad (2)$$

And then we can get Ag content in cellulose fibers.

$$C_{Ag} = (C_x - C_0)/(1 - C_0) \quad (3)$$

The tensile strength (σ_b) and the elongation at break (ε_b) of the dried fibers were measured on a universal tensile tester (XQ-1, Shanghai Textile University, China) according to GB/T 19975-2005. The σ_b and ε_b values represented averages of 10 measurements.

2.4. Antibacterial test

Culture medium, inoculating loop, Petri dish, normal saline, 10 ml centrifuge tube (used to dilute the bacteria) and others were sterilized in high-pressure steam for 20 min. Put specimen, spirit lamp, test tube rack into the Clean Bench, and ultraviolet (UV) sterilized for 30 min. The culture medium in the high-pressure steam sterilization (to avoid the culture liquid cooling and solidification) was dumped into a Petri dish (about 20 ml). UV sterilized for 30 min during culture medium solidified. Three milliliter of normal saline solution was taken into a centrifuge tube. *S. aureus* colonies were scraped with inoculating loop, and then transferred to saline, vortexing to disperse bacteria evenly. Sixty microliter of broths were added to the medium and then scratched. Sample was tiled on the culture medium and placed at 60 °C in incubator and cultured for 48 h. The treatment process was the same for *E. coli*.

3. Result and discussions

3.1. Structure of the cellulose/Ag composite fibers

Hydrothermal method was used to convert Ag^+ in the composite cellulose fiber to Ag at 80 °C according to the references (Cai et al., 2008; Jiang, Liu, & Yao, 2011; Shin, Bae, Arey, & Exarhos, 2008). Photographs of the cellulose/Ag composite fibers coded as B1 and B4 are shown in Fig. 1. With an increase of the concentration of Ag^+, the color of the cellulose/Ag composite fibers changed from yellowish to brown, indicating an increase of Ag content. There was homogeneous porous structure at the wet fibers, which can be used as micro-reactor (Liu, Zhang, Zhou, & Wu, 2008; Liu, Zhang, Zhou, Xiang, et al., 2008). Thus, cellulose/silver nanocomposite fibers were prepared from the cellulose fibers by soaking them in $AgNO_3$ aqueous and then heating at 80 °C for 24 h (reduction) for in situ synthesis Ag nanoparticles. After redox reaction, Ag^+ could be fixed in the cellulose porous structure to construct the inorganic-organic hybrid materials. Fig. 2 shows SEM images of the composite fiber of B5. The insert is the EDS of B5. The backbone of the cellulose fibers was not devastated. EDS pattern revealed that little Ag existed in the composite fibers. TEM images of the composite fibers and particle size histograms of Ag nanoparticles from TEM images are shown in Fig. 3. The Ag nanoparticles were dispersed well in the cellulose fibers. From B1, B3 to B5, the average diameter of the Ag nanoparticles, calculated from the TEM images, were 7.2 ± 2.6 nm, 10.0 ± 2.4 nm, 11.3 ± 3.3 nm, and 12.5 ± 2.7 nm respectively. The diameter of the Ag nanoparticles grew with an increase of the concentration of $AgNO_3$ in the reaction solution. Generally, the porous size of the wet fibers was about 100–200 nm (Li et al., 2010), which could be changed to about 10–20 nm after drying. So the size of Ag NPs should be less than 20 nm, because they were synthesized by in situ synthesis in the pores of the cellulose fibers. In our findings, the pores of the cellulose fibers provided the space for the nanoparticles production and restricted their sizes at the same time.

Fig. 4 shows powder X-ray diffraction patterns of the regenerated cellulose fibers (a) and the B5 composite fibers (b). The cellulose composite fibers exhibited not only three peaks at 2θ = 12.4°, 20.2° and 22.2°, assigned to the (1 1 0), (1 $\bar{1}$ 0) and (2 0 0) planes of crystalline cellulose II (Isogai, Usuda, Kato, Uryu, & Atalla, 1989), but also four peaks at 2θ = 38.1°, 44.4°, 64.8° and 78.5°, assigned to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of Ag crystalline (Bernabo, Ciardelli, Pucci, & Ruggeri, 2008). It was indicated that the cellulose composite fibers were still the structure of crystalline cellulose II. There was only physical interaction existed between Ag NPs and cellulose matrix. From analysis by the Scherrer equation, the average particle size was 13.9 nm for silver. The size value was in good agreement with those determined from TEM images (12.5 ± 2.7 nm).

As we know, there are a lot of —OH group and end group in the cellulose fiber, which can be used to reduce Ag^+ into Ag. After cellulose fibers were immersed into $AgNO_3$ solution, Ag^+ penetrated into the micro pores of the cellulose fibers, and then was reduced by —OH groups of cellulose at 80 °C, and simultaneously

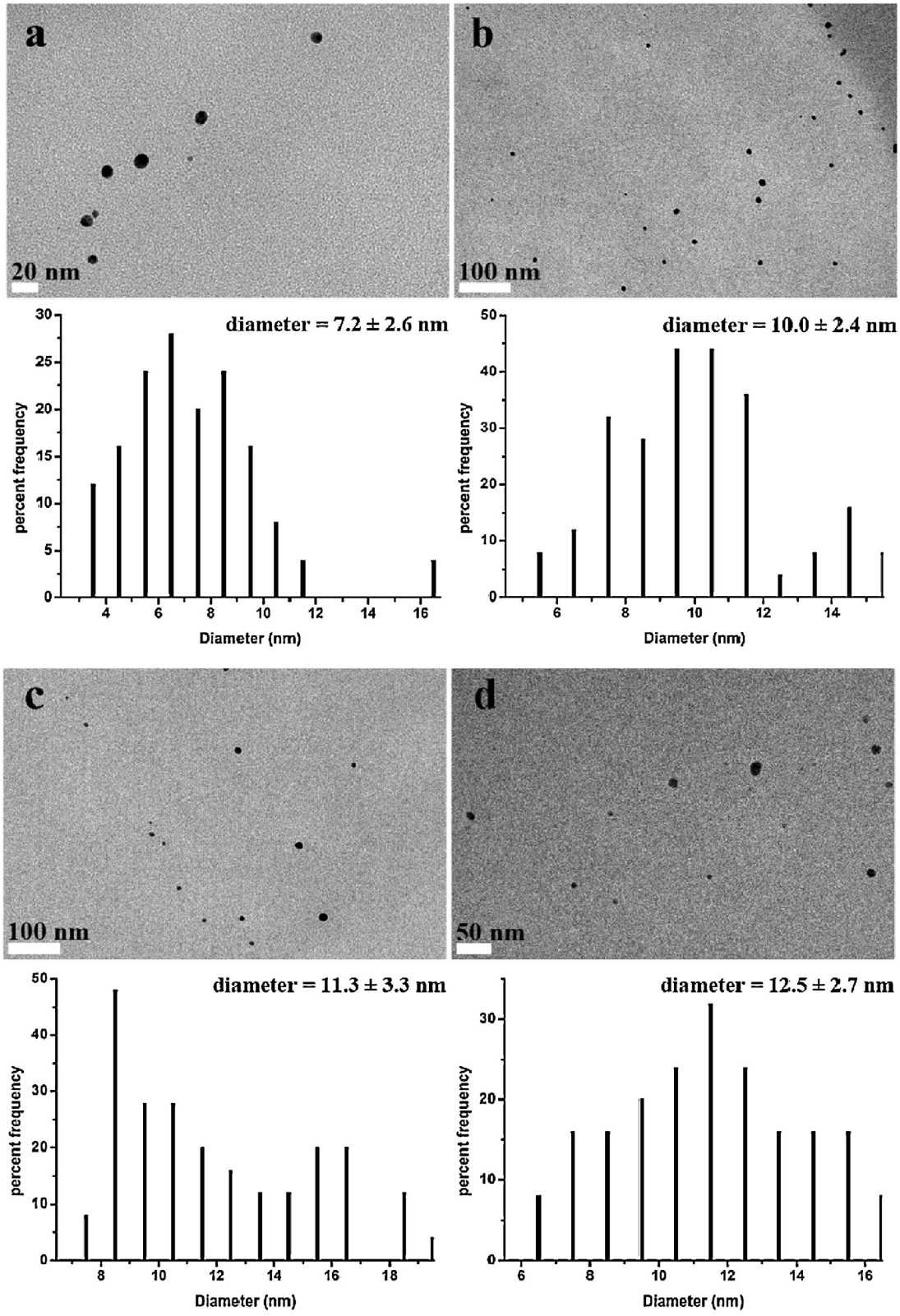

Fig. 3. TEM images of the composite fibers (a, b, c and d represent B1, B3, B4 and B5 respectively) and particle size histograms of Ag nanoparticles from TEM images.

cellulose was oxidized. In this work, the $AgNO_3$ concentration was very low, so just little cellulose was oxidized, and the cellulose structure were mostly maintained. Thus FT-IR spectra of the cellulose fiber and composite fibers were almost the same, as shown in Fig. 5. However, the intensity of the peaks at the wave number of 1710 cm^{-1} and vibration peak of C=O changed slightly. It was revealed that some end aldehydes may have been oxidized to carboxyls.

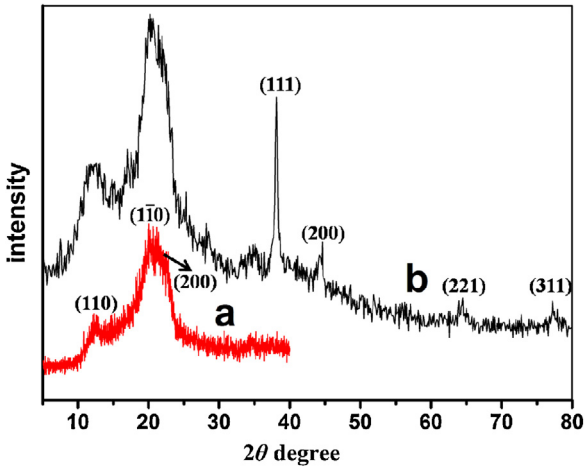

Fig. 4. Powder X-ray diffraction patterns of the regenerated cellulose fibers (a) and the composite fibers of B5 (b).

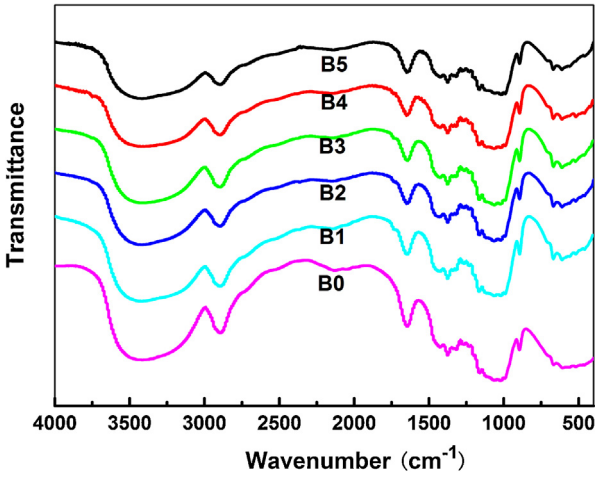

Fig. 5. FT-IR spectrum of the cellulose fiber and composite fibers.

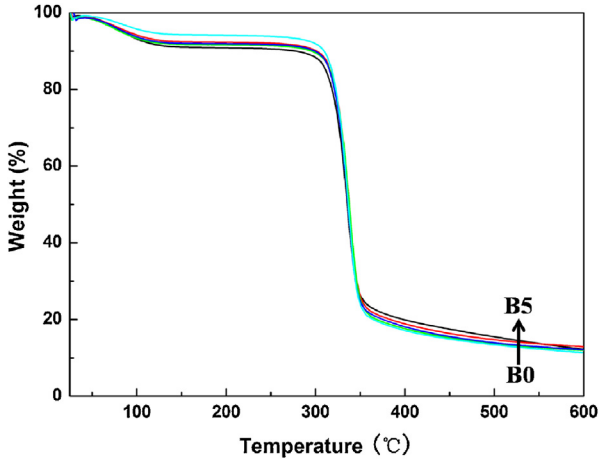

Fig. 6. TGA curves of the cellulose fibers and composite fibers.

Table 1
The diameter, content of Ag NPs, mechanical properties in the composite fibers and the diameter of inhibition zone in antibacterial test.

	Diameter of Ag NPs (nm)	Content of Ag NPs (%) from Eq. (3)	Mechanical properties		Diameter of inhibition zone (mm)	
			σ_b (cN/dtex)	ε_b (%)	*Staphyoccocus aureus*	*Echerichia coli*
B0	–	–	*1.80*	*19*	–	–
B1	7.2 ± 2.6	0.15	1.72	19	15	–
B2	8.3 ± 2.4	0.55	1.68	19	22.0	–
B3	10.0 ± 2.4	0.83	1.67	18	17.9	–
B4	11.3 ± 3.3	1.54	1.65	16	18.3	–
B5	12.5 ± 2.7	2.40	1.62	15	28.5	21.0

B0—regenerated cellulose fibers.

3.2. Properties of the composite fibers

The tensile strength (σ_b) and elongation at break (ε_b) of the cellulose fibers and composite fibers are summarized in Table 1. As the concentration of $AgNO_3$ increased, the σ_b and ε_b values of the composite fibers changed hardly. The results indicated that

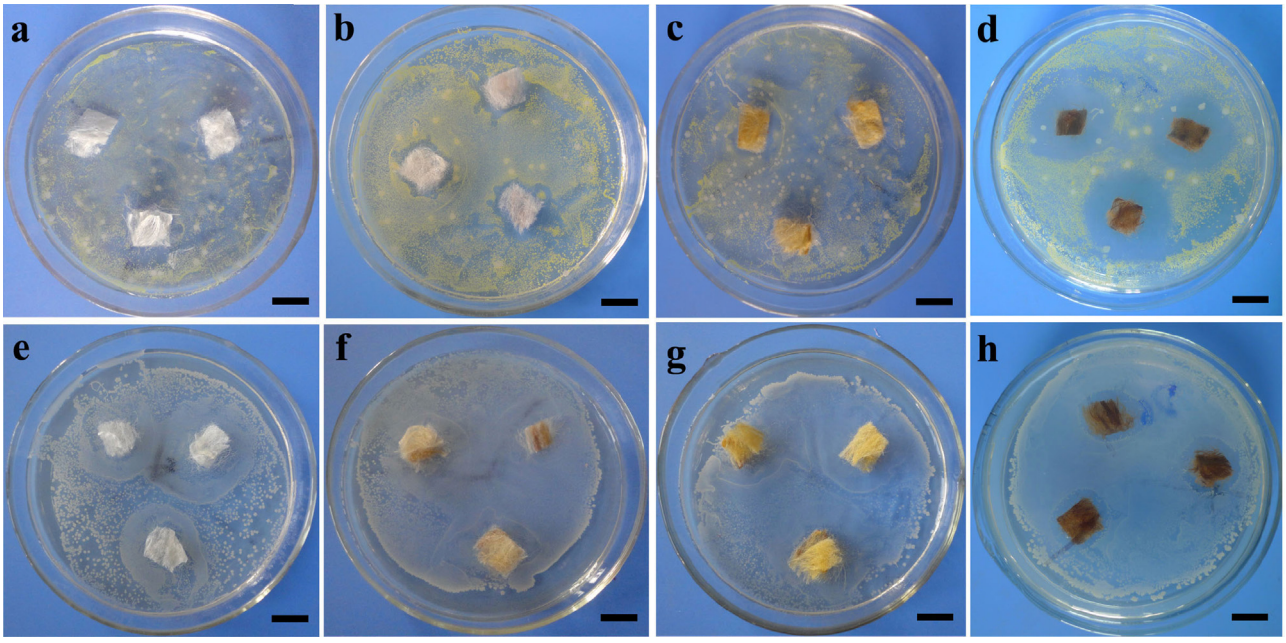

Fig. 7. Antibacterial test of cellulose/silver composite fibers. a,e—B1, b,f—B3, c,g—B4, d,h—B5. a–d: *Staphyoccocus aureus*; e–h: *Echerichia coli*. The scale bar is 1 cm.

the cellulose nanocomposite fibers exhibited good mechanical properties, which were almost the same as pure cellulose fiber.

Fig. 6 shows TGA curves of the cellulose fibers and composite fibers in N_2. The main weight loss of the cellulose fibers and composite fibers was in the range of 300–350 °C, indicating that the addition of silver did not reduce the thermal stability of the materials. From the percentage of the solid part, the silver content in the composite fibers was calculated and listed in Table 1. The silver content was 0.2%, 0.6%, 0.8%, 1.5% and 2.4% for cellulose/Ag nanocomposite fibers, respectively. In view of these results, the composite fibers exhibited good mechanical properties and thermal stability.

3.3. Antibacterial activites

Usually, most of the Ag antibacterial fibers deposited colloidal silver on the fiber surface, and then blended into the fabric in order to achieve antibacterial properties (El Shishtawy et al., 2011; Klemenčič et al., 2010; Shateri Khalil Abad et al., 2009). In our findings, a mild hydrothermal reaction, using cellulose as the reducing agent, restored Ag^+ to Ag nanoparticles, and the silver nanoparticles were fixed in the cellulose fibers. So, this method for the preparation of Ag antibacterial fibers was simple and easy. To test the anti-bacterial activities, implanted *S. aureus* and *E. coli* strains were placed in a Petri dish, a bunch of fibers was cut and spread to $1 \times 1\,cm^2$, and then stuck on the Petri dish to culture for 48 h. The inhibition zone diameter and took photos were measured. The results of the inhibition zone diameter are listed in Table 1, and their photos are shown in Fig. 7. With an increase of the silver nanoparticles content and particle size in the composite fibers, the antibacterial capacity enhanced. Especially, B5 exhibited very strong antimicrobial activity, where the inhibition zone diameter of *S. aureus* and *E. coli* was 28.5 and 21.0 mm, respectively. From Fig. 7(f–h), there was no zone of inhibition of *E. coli*, but *E. coli* did not grow on to the surface of composite fibers. According to deduction of the previous work (Feng et al., 2000), silver achieved antibacterial through the destruction of the bacterial cell wall. The cell wall structure of these two bacteria was quite different. The *S. aureus* cell wall is thicker with less protein content than *E. coli* cell wall, so *Staphylococcus aureus* is more easily destroyed (Feng et al., 2000). Therefore, the inhabitation ability of the composite fiber on *S. aureus* was significantly higher than *E. coli*.

4. Conclusion

Cellulose/Ag nanocomposite fibers were successfully constructed by soaking the cellulose fibers in $AgNO_3$ aqueous solution and then heating the solution at 80 °C for 24 h to reduce Ag^+, which was very facile. The Ag nanoparticles with size from 7.2 nm to 12.5 nm were in situ synthesized in the pores of cellulose matrix. With an increase of the concentration of $AgNO_3$, the diameter of Ag nanoparticles and Ag nanoparticles content both increased. The cellulose/Ag nanocomposite fibers exhibited good mechanical properties and thermal stability. Antibacterial test revealed that the composite fibers containing silver nanoparticles displayed excellent antimicrobial activities on *S. aureus*. This work provided new application prospects of the cellulose fibers in antimicrobial textiles.

Acknowledgments

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