Research Article

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Fabrication of Ag Np-coated wetlace nonwoven fabric based on amino-terminated hyperbranched polymer

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Abstract: To prepare antibacterial fabrics with simple approach, wood pulp/viscose fibers and amino-capped silver nanoparticles (Ag NPs) solution were utilized to form Ag Nps-coated wetlace nonwove fabric. Characterization of the Ag Nps and prepared wetlace nonwoven fabric was performed in virtue of TEM, UV-vis, XRD, ICP-AES, FESEM, EDS mapping and antibacterial test. FESEM and EDS characterizations demonstrated the hierarchical and uniform coating of high-density Ag NPs on wood pulp fibers, and antibacterial test indicated the excellent antibacterial activity of prepared wetlace nonwoven fabric.

Keywords: Wetlace; fiber technology; silver nanoparticles; antibacterial activity

1 Introduction

The wetlace nonwoven fabric was formed by wet-laid and spunlace reinforcement process [1, 2]. Compared with traditional fabrics, wetlace nonwoven fabric exhibits high generation speed and possess sufficient softness, flexibility and conformability, making it widely applied in moist wipes and biomedical field [3–6]. The traditional wetlace

nonwovens often contain entangled synthetic fibers, leading to difficulty in degradation. The ever-increasing consumer and industrial demand for environmentally friendly products makes natural raw materials popular, such as cotton, viscose, wood pulp, polylactic acid, and chitosan [7–10].

Compared to other metal antibacterial materials, silver nanoparticles (Ag NPs) exhibit an efficient antibacterial activity against a broad spectrum of bacteria including *Escherichia coli* (*E.coli*), *Staphylococcus aureus* (*S.aures*) and *Candida albicans*, thereby enjoying an extensive application in biomedical field. Surface coating of biomedical fibers with Ag NPs has been extensively studied in term of the utility in biomedical field [11–17]. Several methods can be used to make nanoparticle coatings on biomedical fabric, such as chemical deposition, spray pyrolysis, low plasma, and dip coating. Nevertheless, coating Ag NPs on the surface of fabric is challenging as related techniques require sophisticated equipment, large amount of time as well as high cost [18–24].

Recently, hyperbranched polymers and dendrimers have been widely applied to the synthesis of nanoparticles. In our previous study, an amino-terminated hyperbranched polymer (HSDA) was synthesized (Figure 1).

Figure 1: Schematic description of the HSDA molecule structure.

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HSDA was used as template to synthesize and disperse ZnO nanoparticles and also served as a binder to impart and fix the ZnO nanoparticles on the bamboo fabric for generating antimicrobial and anti-ultraviolet activities [25, 26]. In this study, wood pulp/viscose fibers were chosen to produce the wetlace nonwoven fabric. For improving the antibacterial activity of fabric, HSDA was used to prepare Ag NPs to be fixed on the surface of wetlace nonwoven fabric.

2 Experimental

2.1 Materials

Wood pulp (23mm in length) and viscose fibers (38mm, 1.6 Den) were purchased from Well Nonwoven Materials Co., Ltd., Nantong, China, and HSDA was prepared as described in our paper [25]. AgNO_3 was purchased from Guoyao Chemical Reagent, China. *S. aureus* (ATCC 6538) and *E. coli* (ATCC 8099) were obtained from the Shanghai Luwei Technology Co., Ltd. (China).

2.2 Preparation of the Silver Nanoparticles

Equimolar (2mM) aqueous solution of AgNO_3 and 2g/L HSDA were dissolved in deionized water at 40°C using a well-described procedure. The reaction mixture was slowly heated until reduction of Ag^+ to Ag^0 was complete and formed brown silver colloid nanoparticles. The result silver colloidal solution was stored in a brown-glass container.

2.3 Characterization of the Silver Nanoparticles

The morphology and size of Ag NPs were characterized using a JEM-2100F transmission electron microscope (TEM) (JEOL, Japan). The ultraviolet-visible (UV-vis) spectra from 250 to 600nm were recorded on a Hitachi UV-3010 spectrophotometer (Hitachi, Japan). X-ray diffraction (XRD) of silver nano hybrid particles was characterized with an Xpert pro diffractometer (Philips, Holland) utilizing a Cu $K\alpha$ X-ray light source at a voltage of 40 kV and a current of 30 mA.

2.4 Preparation and characterization of Ag NPs-coated wetlace nonwoven fabric

The prepared Ag NPs solution was diluted with deionized water to keep the Ag content range from 50 to 200mg/L. To keep the gram weight of wetlace fabric around 60g/m² and the strength of the wetlace fabric around 10N, 7g wood pulp and viscose fibers (70/30 in weight) were immersed in Ag NPs solutions for 30min at a water tank which contained a 0.1m² net curtain with the bath ratio of 1:50 [1, 2]. Beater was used to disperse the mixing fiber in Ag NPs solution. After the water in tank was drained, the homogeneous fiber web was formed in net curtain, which were then bonded at 30 bars water pressure on both sides of the fabric. The Spunlace line used in this experiment was made by Feilong Co., Ltd, Suzhou, China.

The fabric was characterized and analyzed using Energy Dispersive Spectromete (EDS)(Carl Zeiss, EVO15), field emission scanning electron microcopy(FESEM)(scios dual-beam, Czechia). The silver content was measured by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method. (Varian, USA). The antimicrobial activity of silver-treated fabrics was tested against *E. coli* and *S. aureu* by using a shaking flask method according to GB/T 20944.3-2008 (China). 0.75 g sample fabric, cut into small pieces in a size around 0.5×0.5 cm², was dipped into a flask containing 70 ml of 0.3 mM PBS (monopotassium phosphate, pH≈ 7.2) culture solution with a cell concentration of 1×10⁵ cfu/ml-4×10⁵ cfu/ml. The flask was then shaken at 150 rpm on a rotary shaker at 24°C for 18 h. From each incubated sample, 1 ml of solution was taken, diluted and distributed onto an agar plate. All plates were incubated at 37°C for 24 h, and the colonies formed were counted. The percentage reduction was determined as follows:

$$\text{Reduction cfu (\%)} = \frac{C - A}{C} \times 100\%$$

Where, C and A are the bacterial colonies of the original fabrics and the treated fabrics, respectively [27, 28].

3 Results and discussion

Characterization of Ag NP_s

In this work, amino-functionalized Ag NPs were prepared in one-step by mixing AgNO_3 aqueous solution and HSDA aqueous solution under vigorous stirring and heating conditions. With the increase in the stirring strength and heating time, the colorless and transparent solution gradually changed into light-yellow. The formation of silver NPs can

be observed by an UV-vis spectrophotometer, as shown in Figure 2. HSDA has a characteristic peak at 298nm, when the AgNO_3 aqueous solution and HSDA aqueous solution were mixed. However, a new characteristic absorption of spherical silver nanoparticles appeared at 408 nm, corresponding to the characteristic surface plasmon resonance of metallic Ag NPs [29–31].

Figure 2: UV adsorption spectra of the Ag NPs solution.

The Ag NPs further confirmed by the TEM image shown in Figure 3(a) and Figure 3(b) revealed that the monodispersed Ag NPs had an average diameter of about 10nm and a good dispersion. The observed large-scale HSDA capped Ag NPs with a regular spherical structure indicated HSDA has a good control of particle shape.

Figure 3: Characterization of the Ag NPs (a) TEM images of Ag NPs (b)HR TEM of Ag NPs.

To verify that silver nanoparticles were synthesized, the precipitated silver powders in the silver colloid were centrifuged, washed with methanol, and dried in the air for XRD measurement. The result was shown in Figure 4, the peaks at 2θ values are 38, 44, 64, 78, and 82, represent-

Figure 4: XRD spectrum of resulting Ag NPs.

ing the 111, 200, 220, 311, and 222 Bragg reflections of the face centered cubic structure of silver respectively, which are in excellent agreement with the values reported in literature [32–34].

As HSDA has a large number of amino functional groups with reducibility, which can reduce Ag^+ to Ag^0 under a high temperature. HSDA can entrap Ag NPs into the confined inner cavity, preventing them from further aggregation. No noticeable change was found after the result nano-silver colloidal solutions had been stored more than one years.

Preparation of Ag Np-coated wetlace nonwoven fabric

The mechanism of prepare Ag Np-coated wetlace nonwoven fabric was shown in Scheme 1. Wood pulp/viscose fibers were immersed in the HSDA coated Ag NPs solution (Ag content range from 50 to 200mg/L). Ag NPs can be easily combined with cellulose fibers through intermolecular hydrogen bonds between amino end groups and pendent hydroxyl groups on cellulose fiber. Electrostatic bonding interactions between the negatively charged hydroxyl groups on cellulose fiber and positively charged amino end groups contributed to the enhancement of the stability and adhesion of HSDA capped Ag Nps on the surface of wetlace nonwoven [28, 35]. In the reaction, Ag NPs can be coated on the surface of cellulose fiber, with the white cellulose fiber finally turning into yellow, and the light-yellow solution gradually turning into colorless and transparent.

To investigate the adsorption ability and content of Ag NPs on the fiber, the treated fabric was measured quantitatively with ICP-AES. As shown in Figure 5, the content

Scheme 1: Schematic illustration of Ag NPS on the surface of wetlace nonwoven fabric.

Figure 5: Silver content of Ag NPs coated fabric.

of Ag NPs were confirmed to be highly dependent on Ag NPs concentration. With increasing the concentration of Ag NPs from 50 to 200 mg/L, the silver content of fibers increased proportionally from 2.5 to 7.5 mg/g. This result revealed that the adsorption ability of Ag NPs on fibers was very strong. The maximum silver content of coated fibers can reach up to 7.5 mg/g.

SEM morphology and EDS Mapping of the AgNP-calcium alginate fibers

The morphologies and distribution of Ag NPs coated on the surface of wood pulp fiber can be seen in Figure 6. Pure wood pulp fiber displayed a flat, dense and smooth surface, as shown in Figures 6(a). By contrast, the surface of Ag NPs-coated wood pulp fiber saw a uniform distribution of high-density white spots, as shown Figures 6(b), revealing a stronger adhesion of Ag NPs on the wood pulp fiber.

The chemical characteristics of the nano coating were further confirmed by the EDS mapping. Figure 7(a) showed additional Ag elements in the Ag NPs coated fabric, Cellulose fiber have O and C elements showed in Figure 7(b) and (c), Figure 7(d) showed the even distribution of Ag NPs on the fabric surfaces, which was in good agreement with FE-SEM measurements. This effect was mainly attributed to the strong adsorption between the wood pulp fiber and the amino groups capped on Ag NPs.

Figure 6: FESEM of (a) blank and (b) Ag NPs-coated wood pulp fiber (Ag content: 7.5 mg/g).

Figure 7: EDS mapping of (a) elements on wetlace nonwoven fabric and (b) C on fabric (c) O on fabric (d) Ag on fabric (Ag content: 7.5 mg/g).

Table 1: Antibacterial activity of wetlace nonwoven fabrics

Sample	Silver content (mg/g)	<i>S. aureus</i>		<i>E. coli</i>	
		Surviving cells (CFU/mL)	Reduction (%)	Surviving cells (CFU/mL)	Reduction (%)
Wetlace fabric	0	1.58×10^6	-	2.5×10^5	-
HSDA treated fabric	0	1.05×10^6	50.4	1.4×10^5	44
Ag NPs fabric	2.5	1.2×10^4	99.24	1.5×10^3	99.4
	5	2.3×10^2	99.98	2.1×10^2	99.91
	7.5	3	100	2	100
	7.52	0	100	0	100

Antibacterial activity of Ag NPs coated wetlace nonwoven fabrics

The antibacterial activity of wetlace nonwoven fabric was qualitatively evaluated by the shake-flask method using gram-negative *E. coli* and gram-positive *S. aureus* bacteria cells. Blank and HSDA treated fabric as contrast sample, the results of which were presented in Table 1. Cellulose fibers did not show antibacterial activities against *S. aureus* or *E. coli*, indicating the fiber itself was insufficient to inhibit the bacterial growth. As the Cationic group in HSDA, HSDA treated fibers showed antibacterial activities, the reduction rates of *S. aureus* and *E. coli* can reach about 50%. By contrast, Ag NP-coated fibers exhibited excellent antibacterial activities. The bacterial reduction rates of both *S. aureus* and *E. coli* can reach above 99%, even at the minimum silver content (2.5 mg/g) [25, 36].

4 Conclusions

HSDA-capped Ag NPs were prepared in one-step by mixing AgNO_3 and HSDA aqueous solutions under heating condition. HSDA-capped AgNPs were endowed with positive charges and high binding affinity towards wood pulp fiber. The Ag NPs-coated wetlace nonwoven fabric was formed by wet-laid and spunlace process. Both SEM and EDS analysis showed that high-density Ag NPs were well distributed on the surface of wetlace nonwoven. Also, Ag NPs-coated fabric showed excellent antibacterial activity against both *S. aureus* and *E. coli*.

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