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Fabrication of High Nano-ZnO Assembled Cotton Fabric with UV Blocking Property

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Abstract: In order to fabricate a novel ZnO/cotton composite, a high proportion of ZnO nanoparticles were assembled in cotton fibers, and the as-obtained cotton fabric can possess better UV blocking property compared with common ZnO/cotton composite. Firstly, the cotton fibers were pre-treated by hydrogen peroxide solution(H_2O_2) and sodium hydroxide(NaOH), urea(CON_2H_4). Secondly, the fabric was fabricated via in situ deposition. The effects of concentration of treatment liquid, ammonia-smoking time and curing temperature on the tensile property of the fabric, UV blocking property and water-washing durability test of as-obtained cotton fabrics were investigated. Thirdly, the as-obtained cotton sample was characterized by X-ray diffraction(XRD) and field emission scanning electron microscopy(FESEM). It was shown that ZnO nanoparticles were assembled between cotton fibers, the surface and inside of the lumen and the mesopores of cotton fibers, while the content of nano-ZnO assembled in fabric can reach 15.63wt%. It is proved that the finished fabric can obtain a very excellent UV blocking property, under the condition of zinc ion in concentration of 15wt%, ammonia-smoking time for 10 min, curing temperature at 150 ℃ for 2 min.

Key words: high-assembled; ZnO; cotton fabric; UV blocking; washing durability

1 Introduction

In recent years, the destruction of the ozone layer in the atmosphere has led to an increased UV radiation due to the rapid development of industry, including skin and skin cancer caused by excessive UV radiation disease[1]. Therefore, fabrication of textile with UV blocking property has become an important subject.

The particle size of nano-ZnO is less than 100 nm,which is far smaller than the wavelength of ultraviolet ray, so nano-ZnO has the ability to absorb ultraviolet light[2]. The index of refractive is 2.03, which has certain ability of scattering UV light, and it can reduce the intensity of UV irradiation in a wider scope of UV containing the strong shielding effect[3-5]. In addition, nano-ZnO has the advantage of heat-resistant, non-toxic, no-stimulation, safe, effective, and stable property, *etc*[6,7].

Cotton fabric is one of the most easily transmitting fabrics of UV light. Because the gel method, which nano-ZnO content assembled on the cotton fabric is low, the cotton fabrics washed repeatedly with UV blocking property declined obviously. This topic aims at adopting a method different from traditional finishing, using pre-treated cotton fabric, zinc acetate and ammonia as raw materials to fabricate high nano-ZnO assembled cotton fabric via a method in situ. This paper mainly studied the preparation process and the related factors on the properties of cotton fabric after finishing, especially the effect of UV blocking property.

2 Experimental

2.1 Materials

All the reagents and solutions including 60 of bleached cotton fabric,whose warp/weft density was 455×265 root/10 cm, 30wt% hydrogen peroxide solution(H_2O_2), sodium hydroxide (NaOH), urea (CON_2H_4), zinci acetas dihydricus ($Zn(CH_3COO)_2\cdot 2H_2O$), ammonia ($NH_3\cdot H_2O$), ice acetic acid (CH_3COOH) were of analytical grade and were used without any further purification, which were purchased from Linfeng Chemical Company of Shanghai. Cotton fibers were gained from commercial market.

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2.2 Treatment process

2.2.1 Preparation of cotton fabric

Under the condition of constant temperature at 40 ℃, the original cotton fabrics were immersed in 30wt% hydrogen peroxide solution for 30 min (bath ratio 1:30). After the treatment, the cotton fabrics were rinsed with clear water up to neutral conditions and dried using a drying oven at 80 ℃.

Compounding the mixed solution of 9wt% sodium hydroxide and 9wt% urea, cotton fabrics will be completely immersed in the mixture under the condition of constant temperature at 5 ℃ with low tension for 12 hours. After the treatment, the cotton fabrics were rinsed with clear water up to neutral conditions (pH = 7) .

2.2.2 Process of nano-ZnO assembled cotton fabrics

The process of ZnO-assembled cotton fabrics was carried out as the following procedure. Firstly, the zinci acetas dihydricus was dissolved into distilled water to compound the zinc ion concentration of 5wt%, 10wt%, 15wt%, and 20wt%, respectively, and then alkali-treated cotton fabrics were completely immersed in zinc acetate solution for 10 min. When the concentration of zinc ion was higher than 15wt%, the solution concentration was increased gradually to soak. Secondly, putting the fabrics into a sheng, having strong aqua with cover in the beaker after taking out the cotton fabrics. There was a bracket used to support the cotton fabric, which was placed in the beaker at appropriating temperature to accelerate volatilization of concentrated ammonia. Thirdly, the ammonia-smoking cotton fabrics will be taken out after 5 to 15 min, and then put fabrics in ventilated place for 30 min. Finally, the cotton fabrics were dried at 80 ℃ for 5 min, curing for 2 min at 150 ℃, and then washed with hot water,and dried at 80 ℃.

2.3 Measurement and characterization

2.3.1 Water quantity

Take a sample of 10 cm×10 cm size cotton fabric in a dry container to balance for 24 h before weighing G_0, then put it into a certain amount of distilled water (bath ratio 1:100) for 1 h before taking out, and then weighing the G_1 after the excess liquid dropped, and according to the formula to calculate the water mass per unit fabric (g water/g fabric), which was represented by A.

$$A=(G_1-G_0)/G_0 \tag{1}$$

2.3.2 XRD anlysis

The as-obtained samples were characterized using X-ray diffraction (XRD), which was carried out on a D/max-2550VB+PC X-ray diffractometer equipped with a CuKα radiation tube operating at 40 kV and 30 mA at room temperature. The speed of scanning was 5.0 (°)/min and the range of scanning angle 2θ was from 10° to 80°.

2.3.3 FESEM analysis

The morphologies of samples were observed by field emission scanning electron microscopy (FESEM). The samples were gold sputtered to give the samples electronic conductivity under a vacuum prior to the observation.

2.3.4 UV blocking property

The UV blocking properties of the nano-ZnO assembled cotton fabrics were investigated by UV2000F type fabric SPF analyzer to determine the ultraviolet prevention performance of sample, which was taken under AATCC text method 183-2010[8], the effect with ultraviolet protection factor (UPF) said. If the numerical of UPF is higher, UV blocking property will be better.

2.3.5 After finishing the fabric handle performance evaluation

The performance of cotton fabric handle was assessed by using sensory method. The finished fabric, which was handled in the process of the experiment was divided into 1, 2, 3, 4, 5 (five grades); and the worst is level 1, and level 5 is the best; unfinished fabric was level 5.

2.3.6 Determination of nano-ZnO assembled in cotton fabrics and water-washing durability test

The content of zinc assembled in cotton fabric was in terms of nano-ZnO, which was measured by weighing method. Using electronic balance according to 10 cm×10 cm size of the mass of the unassembled and assembled cotton fabrics G and G', respectively. According to the formula to calculate the content, which is represented by C:

$$C = (G'-G)/G'\times 100\% \tag{2}$$

The water-washing durability test was taken under GB/T 3921.3 1997 with 5 g/L neutral detergent solution (bath ratio 1:50), and washing for 10 min at 40 ℃, then rinsing off with clear water, washing a certain number of times repeatly, and then dried at 80 ℃[9].

3 Results and discussion

3.1 Influence of swelling pretreatment of cotton fiber with water quantity

When cotton fabric were immersed in distilled water, water molecules come into the pore inside cotton fibers and between the fibers. When the internal porosity of cotton fibers became larger, the amount of water molecules came into the pore became more and more, so the water mass of cotton fabrics can be reflected from the size of the pore capacity of cotton fibers after swelling. Fibers can hold more nano-ZnO particles if the internal porosity of fibers is larger, and the amount of nano-ZnO, which was assembled in cotton fabrics became larger. Cotton fabrics, which were unswelled and swelled measured in the experiment through the test to measure the water mass (g water/g fabric) were 2.87 g water/g fabric and 4.55 g water/g fabric. It can be seen that water absorbption capacity of cotton fibers increased obviously after the swelling treatment. This is because the swelling after alkali treatment occurred and oxidation of cellulose fiber led to its internal lateral connections between the macromolecular chain weakened, the structure of the cellulose fibers in the amorphous region growing. Amorphous region was increased in the number of positions available for adsorption, resulting in water absorbing capacity increased significantly, indicating that the fibers of pore volume increased obviously in aqueous solution, and internal porosity of fibers increased obviously, which held the space of nano-ZnO particles.

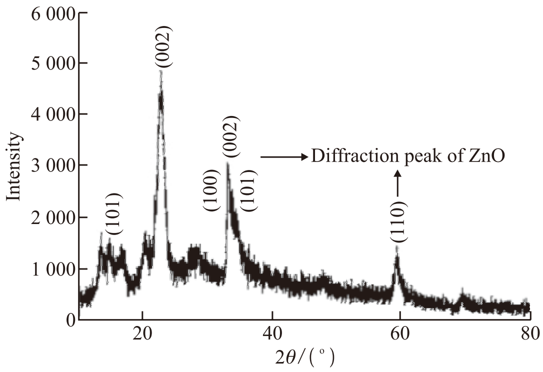

Fig.1 XRD patterns of high nano-ZnO assembled cotton fabric

3.2 XRD analysis

The crystallinity and crystal phase of the treated cotton fibers assembled with ZnO nanoparticles were examined by the X-ray diffraction (XRD) patterns with Cu-Kα radiation and are depicted in Fig.1. For the sample of 15.63wt% nano-ZnO assembled in cotton fabric, the peaks at (101), (002) are the diffraction peaks of cotton fiber(cellulose I). This indicates that the cotton fibers exhibited cellulose I structure. In addition to the diffraction peaks of the cotton fiber(cellulose I), there are also strong diffraction peaks at 2θ values of 33.18°, 33.74°, 34.32°, and 59.24° corresponding to the (100), (002), (101), and (110) planes respectively,and can readily be indexed to the phase of ZnO. In the low ZnO content of the cotton fabrics (ZnO content of 0-1.50%) XRD pattern[10], these peaks corresponding to the nanometer zinc oxide (100), (002), (101), and (110) planes are not distinct. It can be proven that much amount of nano-ZnO deposition generated in cotton fabrics, which have high ZnO content of the fabrics.

3.3 FESEM analysis

In order to observe the distribution of the in situ deposition of ZnO on the cotton fibers, SEM was used to observe the surface morphology of assembled cotton fibers and fibers after washing 30 times, and Figs.2(a) and 2(b) show the images of the treated cotton fibers.

It could be seen from Fig.2(a) that there was a large number of particles on the surface of the cotton fibers after the assembled distribution. As shown in Fig.2(b), the surface of the cotton fiber is smooth, with no attachments, and it shows that ZnO on the surface of the cotton fiber has been washed away after washing 30 times, and it is also revealed that the adhesion of ZnO deposition on the surface of fibers is not enough. The existence of the ZnO and its content in the fabrics will be discussed in the following water-washing durability test as a result of the SEM observation is just surface morphology of fibers.

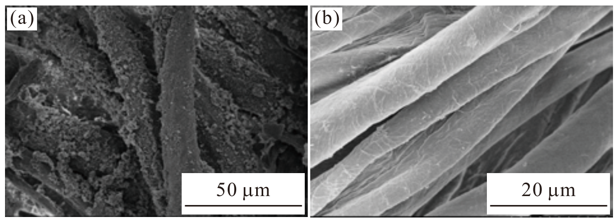

Fig.2 SEM images of cotton fibers: (a)ZnO-Assembled cotton fibers; (b) ZnO-assembled fibers after washing 30 times

3.4 UV blocking property influence factor analysis

3.4.1 Effect of processed liquid zinc ion concentration on the property of fabrics UV blocking

The relationship between treated liquid zinc ion concentration and the property of UV blocking is shown in Table 1.

It can be seen from Table 1 that with the increase of liquid contained zinc ions, the properties of cotton fabrics UV-blocking had been improved significantly. With processed liquid of zinc ions concentration treated on cotton fabric higher, the amount of nano-ZnO will be more in the end. When handled liquid zinc ion concentration in cotton fabrics from 0 to 10wt%, the handle level of cotton fabrics did not change, and properties of UV-blocking increased significantly. When zinc ion concentration increased from 10wt% to 20wt%, the improvement of high nano-ZnO assembled cotton fabrics UV blocking performance was not obvious. However, when zinc ion concentration reached 20wt%, the fabric comfortable level dropped down by two levels, and the strength loss was higher, so deal with zinc ion concentration in liquid should not be too high, and it is advisable to choose 15wt% zinc ion treated fluid concentration.

3.4.2 Effect of ammonia-smoking time on the property of UV blocking

The relationship between ammonia-smoking time and UV blocking property is shown in Table 2.

Table 2 shows that with the increase of ammonia-smoking time, cotton fabric UV blocking performance was also improved. Because ammonia-smoking

Table 1 Relationship between treated liquid zinc ion concentration and the property of UV blocking

Processed liquid zinc ion concentration /%	Contents of ZnO/%	UVA/%	UVB/%	UPF	Handle level
0	0	19.51	11.10	7.51	5
5	6.54	0.26	0.24	286.78	5
10	9.96	0.15	0.15	421.42	5
15	15.63	0.09	0.11	647.78	4
20	18.44	0.06	0.10	747.84	3

Note: Ammonia-smoking time is 10 min, baking temperature at 150 ℃

Table 2 Relationship between ammonia-smoking time and UV blocking property

Ammonia-smoking time /min	Contents of ZnO /%	UVA/%	UVB/%	UPF	Handle level
5	13.62	0.07	0.13	567.15	4
10	15.63	0.09	0.11	647.78	4
15	15.88	0.09	0.11	656.12	4

Note:Concentration of processed liquid zinc ion was 15wt%, curing temperature at 150 ℃

Table 3 Relationship between baking temperature and property of UV blocking

Baking temperature/℃	Contents of ZnO/%	UVA/%	UVB/%	UPF	Handle level
120	15.63	0.09	0.11	637.13	4
135	15.63	0.09	0.11	640.62	4
150	15.63	0.09	0.11	647.78	4
165	15.63	0.09	0.11	639.56	3

Note:Concentration of processed liquid zinc ion was 15wt%, ammonia-smoking time for 10 min

time became longer, the strong aqua ammonia, which volatiled into contact with the treatment fluid on the cotton fabrics produced by the reaction of hydroxyl ions and zinc ions more completely, particles of nano-ZnO generated more at the time of curing. When the ammonia-smoking time was more than 10 min, cotton fabrics contained zinc ions on the processed liquid zinc ions have almost reaction finished completely, if continue to ammonia-smoking, the content of nano-ZnO in cotton fabrics was nearly unchanged. From factors of saving raw materials and experimental time, it is advisable to choose 10 min as ammonia-smoking time.

3.4.3 Effect of curing temperature on the property of UV blocking

The relationship between baking temperature and property of UV blocking is shown in Table 3.

It can be seen from Table 3 that with the improvement of baking temperature, UV blocking property of cotton fabrics was nearly unchanged. Within certain limits of temperature, elevated temperature was advantageous to the nano-ZnO particles crosslinking with the reactive group of cotton fabric,so the cotton fabric finished with a certain amount of UV blocking performance.When the curing time was 2 min, with the increase of curing temperature, nanometer zinc oxide and cotton fabrics were crosslinked, but after finishing of cotton fabrics UVA, UVB, UPF almost unchanged. When the temperature was higher than 150 ℃, the finishing of cotton fabrics became yellow, feel is hardening phenomenon, and the fracture strength loss rate increases, fabric damaged length also increases. When the temperature is below 150 ℃, the degree of crosslinking reaction is reduced, and then the ZnO-assembled on the cotton fabrics are easy to be washed away. Above all, it is advisable to choose baking temperature at 150 ℃.

3.5 Cotton fabrics nano-ZnO after water-washing durability test

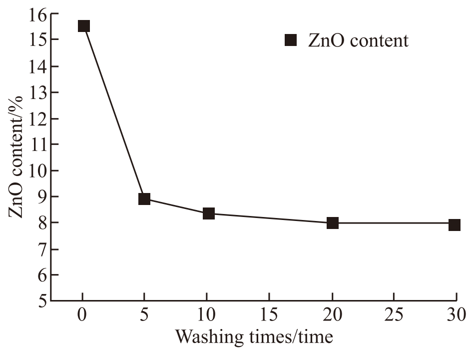

Fig.3 The curve of washing times and ZnO content

To select the best process conditions of cotton fabric finishing, the effect of washing times on the property of ZnO-assembled on cotton fabric with UV blocking was analyzed. Washing frequency relations with ZnO-assembled curve are shown in Fig.3. It can be seen from Fig.3 that with the increase of washing times, nano-ZnO content in cotton fabrics was reduced gradually.The loss rates of 5, 10, 20, and 30 times were 43.38wt%, 48.42wt%, 52.87wt%, and 48.42wt%, respectively. This indicates that after washing 30 times,

Table 4 Relationship of Washing times with UV blocking property

Washing times / time	Contents of ZnO/%	UVA/%	UVB/%	UPF	Handle level
0	15.63	0.09	0.11	647.78	4
5	8.85	0.17	0.18	380.49	5
10	8.42	0.18	0.19	335.57	5
20	8.03	0.19	0.20	315.03	5
30	7.97	0.19	0.20	313.62	5

Note: Concentration of processed liquid zinc ion was 15wt%, ammonia-smoking time for 10 min,baking temperature at 150 ℃

Table 5 Comparison between high ZnO-assembled cotton fabric and low ZnO-assembled cotton fabric with UV blocking property

ZnO-assembled cotton fabric	Contents of ZnO/%	UVA/%	UVB/%	UPF
High-assembled	15.63	0.09	0.11	647.78
High-assembled after washing 30 times	7.97	0.19	0.20	313.62
Low-assembled	＜2	5.00	1.45	45.35
Low-assembled after washing 30 times	＜1	5.77	2.78	35.14

the content of ZnO in cotton fabrics remains the same basically, and it means that 15.63wt% ZnO exists almost half in cotton fiber internal pore and lumen,and the content of ZnO is still high after washing 30 times.

Washing times and the performance of UV blocking relations are shown in Table 4.

Table 4 shows that high nanometer zinc oxide content of cotton fabrics has a very excellent UV blocking property. Along with the increase of washing times, cotton fabrics UV blocking performance is not obvious, when washing times come up to 30 times, UV blocking performance of cotton fabric remains unchanged basically.

3.6 With comparison of the high ZnO-assembled cotton fabric and low ZnO-assembled cotton fabric with UV blocking property

The comparison of the high ZnO-assembled cotton fabric and low ZnO-assembled cotton fabric with UV blocking property is shown in Table 5.

According to the 2002 release of textile industry standardization institute responsible for drafting the GB/T18830-2002 standard for textile UV blocking property evaluation, UPF with UVA transmittance as evaluation index of UV-blocking fabric, regulation UPF > 30, $T\ (\text{UVA})_{\text{AV}} < 5\%$ is UV blocking products.It can be seen from Table 5 that high nano-ZnO assembled cotton fabric with UV blocking property is far better than the standards stipulated even after washing 30 times, and UV blocking property is still better than low ZnO-assembled cotton fabrics, and low ZnO-assembled cotton fabrics cannot meet the UV blocking property metrics after washing 30 times.

4 Conclusions

It is concluded that the optimal assembled for process through experiment is: zinc ion processed liquid concentration is 15wt%, ammonia-smoking time is 10 min, curing temperature is 150 ℃, and the content can reach 15.63wt% of nano-ZnO in cotton fabrics, cotton fabric belongs to high nano-ZnO assembled fabric. High nano-ZnO assembled cotton fabrics possess excellent UV blocking property, and they are harmless to environment and human body, belonging to green environmental protection fabric.According to GB/T 18830-18830 standard for textile UV blocking property evaluation, high nano-ZnO assembled cotton fabric with UV blocking property rises obviously, after washing 30 times, the content of ZnO remains around 8wt%, still belongs to the high nano-ZnO assembled cotton fabric, and UV blocking property is better than that of low nano-ZnO assembled cotton fabric.

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