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Preparation of multi-functional cellulose containing huge conjugated system and its UV-protective and antibacterial property

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ABSTRACT

A novel Schiff base containing huge azo conjugated system and reactive groups, 3,5-bis{2-hydroxyphenyl-5-[(2-sulfate-4-sulfatoethylsulfonyl-azobenzol)methylene amino]}benzoic acid (BHSABA) was applied to modify cellulose. Exhaustion and grafting reactive rate, and grafting quantity of BHSABA on cellulose were calculated. The chemical structure of the modified cellulose was characterized and thermal degradation and morphology were also investigated. The UV protection and antibacterial properties were measured. With increasing the concentration of BHSABA, grafting quantity of BHSABA on cellulose increased from 1.52×10^{-2} mmol/g to 5.08×10^{-2} mmol/g. The multi-functional cellulose fabrics had excellent UV-protective property, which possessed very high UPF value and very low ultraviolet transmittance. The UPF values exceeded 50 and the ultraviolet transmittances were all less than 1%. They also exhibited moderate activity against *Staphylococcus aureus* and after 10 times washing still maintained antibacterial activity. The onsets of degradation slightly decreased. With increasing the grafting quantity of BHSABA on cellulose, mass loss yields of the residues increased. The morphological structure had no noticeable change.

1. Introduction

Cellulose has gained considerable interest as an abundant biocompatible and good biodegradable material. It has potential application in a wide variety of fields from biomaterials to functional materials, such as biosensors, tissue scaffolds, packaging, protective coatings, antimicrobial materials and flexible electronics (Gao, Yan, Dai, & Wan, 2012; Li et al., 2014; Liu, Zhang, & Huang, 2013). In recent years, multi-functional cellulose with UV-protective and antibacterial property, as protection materials and biomaterials, has been paid wide attention (Adamopoulos et al., 2007; Liu, Tai, Ou, & Don, 2012; Sun, Zhao, & Freeman, 2007). A number of attempts have been made to modify cellulose using the compounds containing the certain groups to improve its functional properties (Hou, Yu, & Chen, 2010; Lam, Kan, & Yuen, 2011; Xie, Zhang, & Yu, 2009). The ultraviolet radiation is one of the major causes of degradation of polymer or textile materials due to photo-oxidation. The ultraviolet (UV) protection of biomaterials against photodestruction is of high practical and academic interest (Gouda & Keshk, 2010; Lu, Fei, Xin, Wang, & Li, 2006). Meantime, there is a progressive increase in UV radiation on human skin caused by the depletion of the ozone in the earth's atmosphere. UV radiation can penetrate into the top layer of the skin causing a range of negative health effects, such as acceleration of skin aging, photodermatosis, and even severe skin cancer (Barud et al., 2008; Cakir, Budama, Topel, & Hoda, 2012; Wu, Zhao, Zhang, & Xu, 2012). Although protecting the skin with clothing is a convenient and valid method, common clothing in summer is not effective for UV protection because of the high UV ray transmittance of the fabrics. So, developing textile with protection functionality has been widely researched (Czajkowski, Paluszkiewicz, Stolarski, Kazmierska, & Grzesiak, 2006; Feng, Zhang, Chen, & Zhang, 2007; Maged, Mamdouh, El-Naggar, Fathalla, & Nisreen, 2009).

To date, many approaches have been investigated to improve the UV protection of cellulose fabric (Ibrahim, E-Zairy, & Eid, 2010; Wang & Hauser, 2010). Organic UV absorbers, nanoscale inorganic, such as ZnO and titanium hydrosols and fluorescent brightening agents, have been widely investigated (Cakir et al., 2012; Czajkowski et al., 2006; Radetic, 2013). For example, 2-(2-hydroxyaryl)benzotriazoles and 2-(2-hydroxyaryl)-1,3,5-trizines as UV absorbers have been applied for improving the UV radiation protection of fabrics and achieved good protection property (Sun et al., 2007; Tragoonwichian, O'Rear, & Yanumet, 2008). The important property of these molecules is that they strongly absorb UV

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radiation and rapidly dissipate the energy via some suitable inter or intramolecular rearrangement. However, especially interesting from practical point of view is the absorber containing reactive groups which could form covalent bonds with cellulose. Modified cellulose fabric will be able to maintain its protecting property for long time.

Schiff base is an important sort of light sensitive and bioactive materials and has got wide application in biological, clinical, analytical and industrial fields (Bibhesh, Hament, Anant, & Narendar, 2010; Chen, Zhang, Peng, Lin, & Sun, 2013; Gupta & Sutar, 2007). Azobenzene Schiff base possesses excellent photochromic or thermochromic property based on intermolecular proton transfer or *cis–trans* isomerization (Hadjoudis, Vitiorakis, & Moustakali, 1987; Shen & Tang, 1995). Moreover, Schiff base and its complexes have been proved that azomethine linkage (—C═N—) provides the opportunity for the stupendous biological activities in loading of oxygen and in mimicking the enzyme activity, such as antitumor, antibacterial, antifungal and herbicidal activities (Fang, Tsai, Luo, Chang, & Chen, 2013; Tumer, Akgun, Toroglu, Kayraldiz, & Donbak, 2008). In recent years, the threat of potentially harmful bacteria and viruses stresses the importance of developing antibacterial cellulose materials to combat human pandemics (Hou et al., 2010; Malek-Ahmadi & Abdolmaleki, 2011). The materials containing Schiff base derivative not only can absorb UV radiation to convert it to less harmful energy, but also possess antimicrobial activity. In our previous research work (Hou, Zhang, & Wang, 2012), *N*,*N*-bis{*p*-[(2′-sulfatoethyl)sulfonyl phenylazo]salicylidene}-1,2-ethylenediamine (BSPEA), was applied to modify cellulose materials. The value of ultraviolet protection factor (UPF) for the obtained functional cellulose can reach 31.7. Because of 1,2-ethylenediamine structure effect, it is difficult to further improve the protection efficiency of cellulose materials. 1,2-ethylenediamine structure of BSPEA only has bridge bond linking two salicylidene units, but does not form huge conjugated system.

In this paper, a novel reactive azo-Schiff base containing azo conjugated system, 3,5-bis{2-hydroxyphenyl-5-[(2-sulfate-4-sulfatoethylsulfonyl-azobenzol)methylene amino]}benzoic acid (BHSABA) was applied to modify cellulose fiber. The chemical and morphological structures of the modified cellulose were characterized by FT-IR spectra, the nitrogen content and SEM. Thermal degradation of the functional cellulose fabric was investigated with thermogravimetric (TG) and derivative thermogravimetry analysis (DTG). UV protective and antibacterial properties were also discussed.

2. Experimental

2.1. Materials

Desized, scoured and bleached cellulose fabric was obtained from Jinqiu Textile and Finishing Company, Shaoxing, China. BHSABA Schiff base was obtained from National Engineering Research Center for Dyeing and Finishing of Textiles, Shanghai, China. The chemical structure of BHSABA is shown in Scheme 1.

Other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Modification of cellulose fabric with BHSABA Schiff base

Modification of cellulose fabric with BHSABA Schiff base was carried out in similar way as described in the previous study (Hou et al., 2012). BHSABA Schiff base was dissolved in distilled water to give various concentration solutions. The cellulose fabric was grafted in PYROTEC-2000 dyeing machine (Roaches International Ltd., UK), with BHSABA Schiff base at a liquor ratio of 1:10. The sodium carbonate (10 g/l) as catalyst was used in the grafting process. Fabric was immersed in the BHSABA solution at room temperature and the temperature was increased to 60 °C. Grafting was carried out at 60 °C for 50 min. The modified samples were rinsed in hot water and soaped in a solution of a nonionic surfactant (OP-10.1 g/l) at 85 °C for 15 min at a liquor ratio 1:15. The samples were removed, rinsed thoroughly in hot tap water, then being dried at ambient condition. Four functional cellulose samples with azobenzene Schiff base were obtained and named as FC-1, FC-2, FC-3, and FC-4 according to grafting concentrations, 1% (w/w, BHSABA Schiff base: fabrics), 2%, 5% and 10%, respectively.

The maximum absorbance peak (λ_{max}) of BHSABA Schiff base in the visible range occurred at 402 nm. Exhaustion (E) and grafting reactive rate (Gr) of BHSABA Schiff base on cellulose could be calculated by measuring the absorbance of the residual BHSABA Schiff base at 402 nm. E, Gr and grafting quantity (Gq) of BHSABA Schiff base on cellulose fabric were calculated according to Eqs. (1)–(3), respectively.

$$E\ (\%) = \left(\frac{A_0 - A_1}{A_0}\right) \times 100\% \tag{1}$$

$$Gr\ (\%) = \left[\frac{A_0 - A_1 - A_2}{A_0}\right] \times 100\% \tag{2}$$

$$Gq\ (\text{mmol/g}) = \frac{C \times Gr}{MW} \tag{3}$$

where A_0 and A_1 are the absorbance of the Schiff base solution at λ_{max} before and after grafting, respectively; A_2 is the absorbance of the soaped Schiff base solution in the solution of a nonionic surfactant (OP-10.1 g/l). C is the concentration of BHSABA Schiff base. W is the weight of the grafted cellulose. M is the molecular weight of BHSABA (M = 944).

2.3. Characterization of the modified cellulose material

UV–vis spectrum was recorded by U-2910 Spectrophotometer (High-Technologies Co., Tokyo, Japan). FT-IR spectrum was measured by an OMNI Sampler of the Nexus-670 FT-IR-Raman Spectrometer (Nicolet Analytical Instruments, Madison, WI). Element analysis (the nitrogen content) was measured with Vario ELIII, Elmentar, Germany. The samples were dried under vacuum at 50 °C before measuring. The reflectance spectra were measured by Datacolor SP600$^+$ spectrophotometer.

For scanning electron microscopy (SEM) analysis, the samples were sputtered with gold and then examined with a JSM 5600LV Scanning Electron Microscopy (JEOL, Tokyo, Japan), operated at 15 kV. Thermogravimetric analysis (TG) was carried out at a heating rate of 10 °C/min in nitrogen using a Thermalgravimetric Analyzer, TG 209 F1 (NETZSCH-Geraetebau GmbH, Germany).

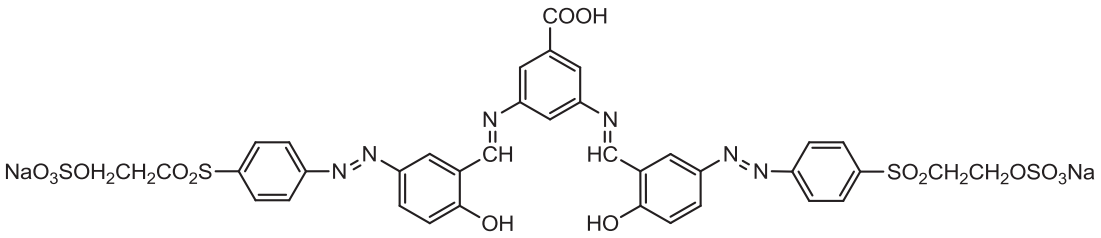
2.4. UV protection and physical property measurements

Transmittance spectrum and the ultraviolet protection factor (UPF), T (UVA), and T (UVB) of the samples were measured by an Ultraviolet Transmittance Fabric Analyzer, UV-1000F (Labsphere Co., USA).

The ultraviolet protection factor (UPF) was calculated according to Eq. (4).

$$\text{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times d\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times d\lambda} \tag{4}$$

where S_λ is erythema action spectrum, E_λ is solar irradiance, $d\lambda$ is wavelength interval in nm, and T_λ is spectral transmittance of the specimen. UPF values were average value at six measurements.



Scheme 1. Chemical structure of BHSABA.

A-range ultraviolet (UVA) transmittance and the B-range ultraviolet (UVB) transmittance can be calculated according to Eqs. (5) and (6), respectively.

$$T\ (UVA) = \frac{\sum_{315}^{400} T_\lambda \times d\lambda}{\sum_{315}^{400} d\lambda} \quad (5)$$

$$T\ (UVB) = \frac{\sum_{280}^{315} T_\lambda \times d\lambda}{\sum_{280}^{315} d\lambda} \quad (6)$$

2.5. Antibacterial activity

Antibacterial activity of the modified functional cellulose against *Staphylococcus aureus* (ATCC 6538) was evaluated by ASTM E2149-01 (American Society for Testing and Materials, 2001). The test method was designed to evaluate the resistance of non-leaching antimicrobial treated specimens to the growth of microbes under dynamic contact conditions. *S. aureus* was used as a test organism. The modified functional cellulose and control (blank cellulose) samples (0.75 g, respectively) were cut into small pieces and transferred to a 250 ml Erlenmeyer flask containing 50 ml of the working bacterial dilution. All flacks were capped loosely, and placed on the incubator, and shaken for 1 h at 37 °C and 120 rpm using an incubator shaker. After a series of dilutions of the bacterial solutions using the buffer solution, 1 ml of the dilution was plated in nutrient agar. The inoculated plates were incubated at 37 °C for 2 days and surviving cells were counted.

The antibacterial activity was expressed in terms of % reduction of the organism after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The bacteria reduction percentage was calculated according to Eq. (7).

$$R(\%) = \frac{B - A}{B} \times 100 \quad (7)$$

where A and B are the surviving cells (colony forming unit CFU/ml) for the flasks containing test samples (modified functional cellulose fabric) and the control (blank cellulose fabric), respectively, after 1 h contact time. R (%) is the bacteria reduction percentage.

2.6. Washing cycle

The modified fabrics were washed using a domestic washing machine in warm water (40 °C) for 15 min, then in cold water for 15 min. They were dried at ambient condition.

3. Results and discussion

3.1. Preparation of multi-functional cellulose with azobenzene Schiff base

Modification of cellulose surface is an important method for making functional materials to enhance the performance in some specific areas. BHSABA Schiff base contains huge π–π conjugated system by —N=N— and —C=N— linkage based on 3,5-di-aminobenzoic acid. UV–vis spectrum of BHSABA Schiff base was measured and shown in Fig. 1. Its UV–vis spectrum shows that the compound has three strong absorbance bands in 230–280 nm, 300–350 nm and 360–410 nm. This should be attributed to π–π* and n–π* transition of Schiff base containing azo conjugated system. This absorbance spectrum is corresponding to the UV radiation the sun emits.

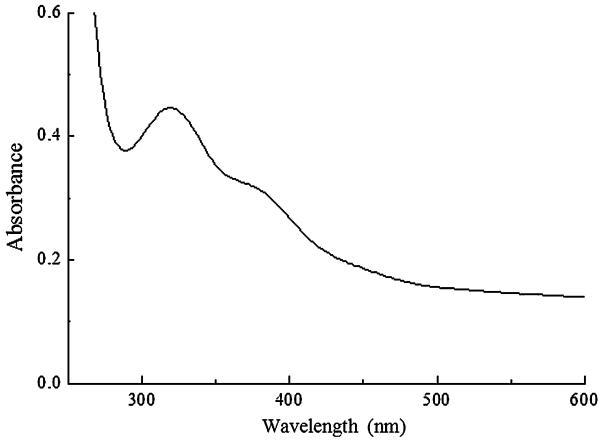


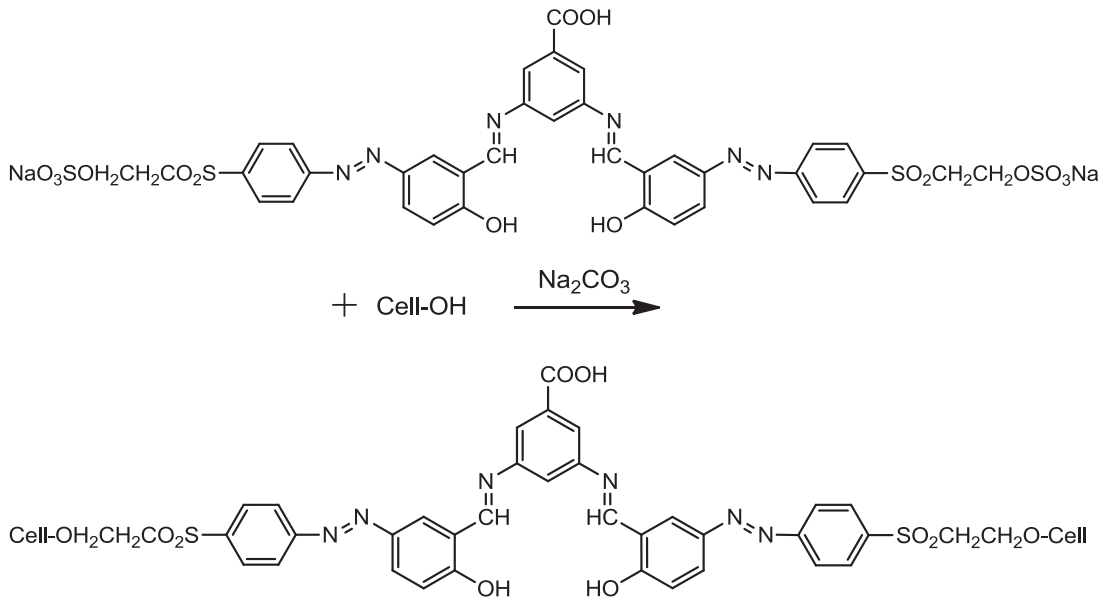
Fig. 1. UV–vis spectrum of BHSABA.

BHSABA Schiff base with azo conjugated system contains two symmetrical reactive groups, *p*-[(2′-sulfatoethyl)sulfonyl]benzol groups, having high reactivity. It is able to form covalent bonds with cellulose under the alkaline condition by crossing reaction. The chemical reaction of BHSABA Schiff base and cellulose is shown in Scheme 2.

E, *Gr* and *Gq*, calculated according to Eqs. (2)–(4) are summarized in Table 1. With increasing the concentration of BHSABA, exhaustion and grafting reactive rate of BHSABA Schiff base on cellulose gradually decreased. However, grafting quantity (*Gq*) of BHSABA Schiff base on cellulose fabric increased from 1.52×10^{-2} mmol/g to 5.08×10^{-2} mmol/g. The nitrogen contents of the FC-4 and control sample were 0.035% and 0%, respectively. Compared with the control sample, the nitrogen content of FC-4 noticeably increased. The calculated nitrogen content of FC-4 according to grafting quantity of BHSABA Schiff base on cellulose fabric (5.08×10^{-2} mmol/g) is 0.042%. The measured nitrogen content of FC-4 was slightly less than that of the calculated value. It demonstrates that the

Table 1
Exhaustion, grafting reactive rate and grafting quantity of BHSABA Schiff base on cellulose fabric.

Samples	Weight ratio (w/w, %)	*E* (%)	*Gr* (%)	*Gq* (mmol/g × 10^{-2})
FC-1	1	80	72	1.52
FC-2	2	78	68	2.88
FC-3	5	69	47	4.97
FC-4	10	49	24	5.08



Scheme 2. Reaction of BHSABA Schiff base and cellulose.

crosslinking reaction between BHSABA Schiff base and cellulose was successful.

FT-IR spectra of FC-4 and control sample (non-grafted cellulose) were also measured (shown in Fig. 2). The infrared band of —COOH showed at 1651 cm^{-1}. FT-IR spectrum assured the presence of —N=N— at 1583 cm^{-1} and —N=C— at 1514 cm^{-1}. This further confirms that the Schiff base compound was able to form covalent bonds with cellulose.

Reflectance spectra of the grafted cellulose and control samples were measured and shown in Fig. 3. It indicates that the control cellulose had high reflectance and had no absorbance in 350–700 nm. Four grafted cellulose samples had strong absorbance in 350–500 nm being attributed to π–π^* and n–π^* transition of carbonyl and azomethine groups and the π–π^* transition of C=C bonds available in aromatic rings. It can be seen that BHSABA Schiff base was crosslinked to cellulose macromolecules by the covalently grafted way and obtained functional cellulose.

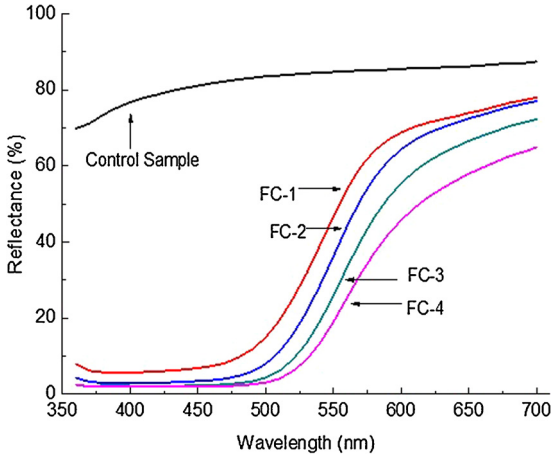


Fig. 3. Reflectance spectra of control and functional cellulose samples.

3.2. Thermal degradation and morphological structure of the functional cellulose

In order to investigate thermal stability of the functional cellulose fabrics, TG and DTG of them were measured and shown in Figs. 4 and 5, respectively. Comparison with that of control cellulose, the onsets of degradation of the functional cellulose samples slightly decreased. It is assigned to the typical thermal degradation of cellulose. With increasing the grafting quantity of BHSABA Schiff

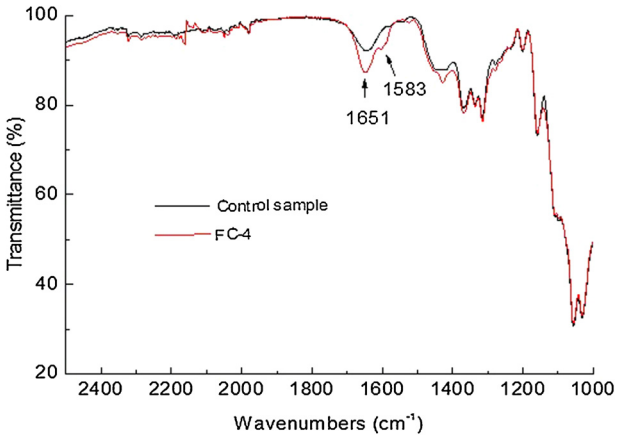


Fig. 2. FT-IR spectrum of control sample and FC-4.

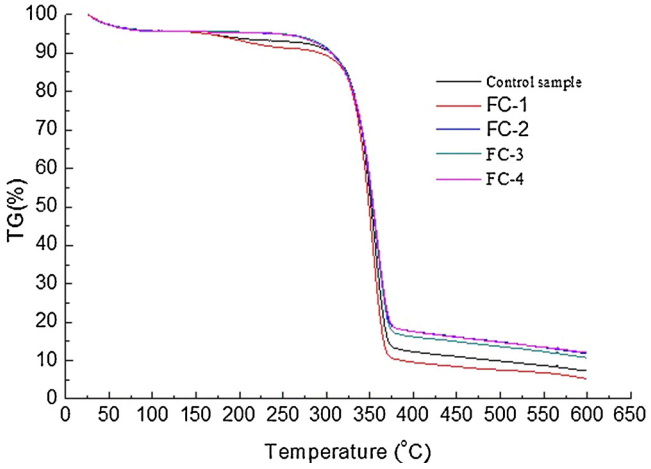


Fig. 4. TG of the functional and control cellulose samples.

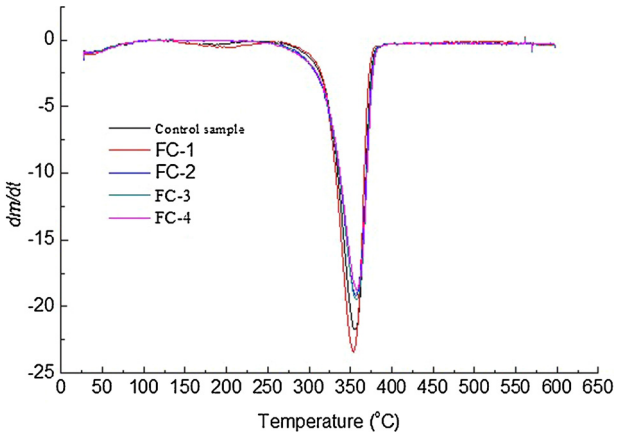


Fig. 5. DTG of the functional and control cellulose samples.

base on cellulose fabric, for FC-2, FC-3, and FC-4, mass loss yields of the residues increased. The maximum temperature of mass loss for the functional cellulose slightly increased. The maximum rates of mass loss for the functional cellulose samples, except of FC-1, obviously decreased (Fig. 5). It might be attributed to the increase of nitrogen content of the functional cellulose.

SEM analysis was used to characterize the surface morphological change of the functional cellulose. Fig. 6(a–c) is the SEM images of control cellulose fiber, FC-2, and FC-4, respectively. The morphological structure of the functional cellulose had no noticeable change. The surfaces of FC-2 and FC-4 were smoother than that of control sample. The functional cellulose fiber was slightly swelled during crosslinking process.

3.3. UV-protection property of the functional cellulose fabric

Ultraviolet transmittance spectra represent the UV-protection ability of the functional materials. Ultraviolet transmittance spectra of four functional cellulose fabrics were measured and shown in Fig. 7. The control sample had very high ultraviolet transmittance. This indicates that the resistance of the control cellulose fabric to ultraviolet ray was very poor. Four functional cellulose fabrics had very low ultraviolet transmittance (less than 2%). Generally, the UV-protective property of fabric would be evaluated as excellent when the ultraviolet transmittance was less than 5%. It can be attributed to BHSABA having three strong absorbance bands in 230–280 nm, 300–350 nm and 360–410 nm.

Generally, the sun emits UV radiation across a broad spectrum from the high energy UVC band (wavelength below 280 nm) to the UVB band (wavelength 280–315 nm) and UVA band (wavelength 315–400 nm). Due to absorption of ozone layer in the upper atmosphere, UVC was filtered. UV radiation reaching the earth's surface is mainly UVB and UVA. Therefore, UPF, T (UVA), T (UVB) for the functional cellulose fabric and the washed samples were measured. The results are listed in Table 2. It demonstrates that control sample had low UPF value (4.54). The modified functional

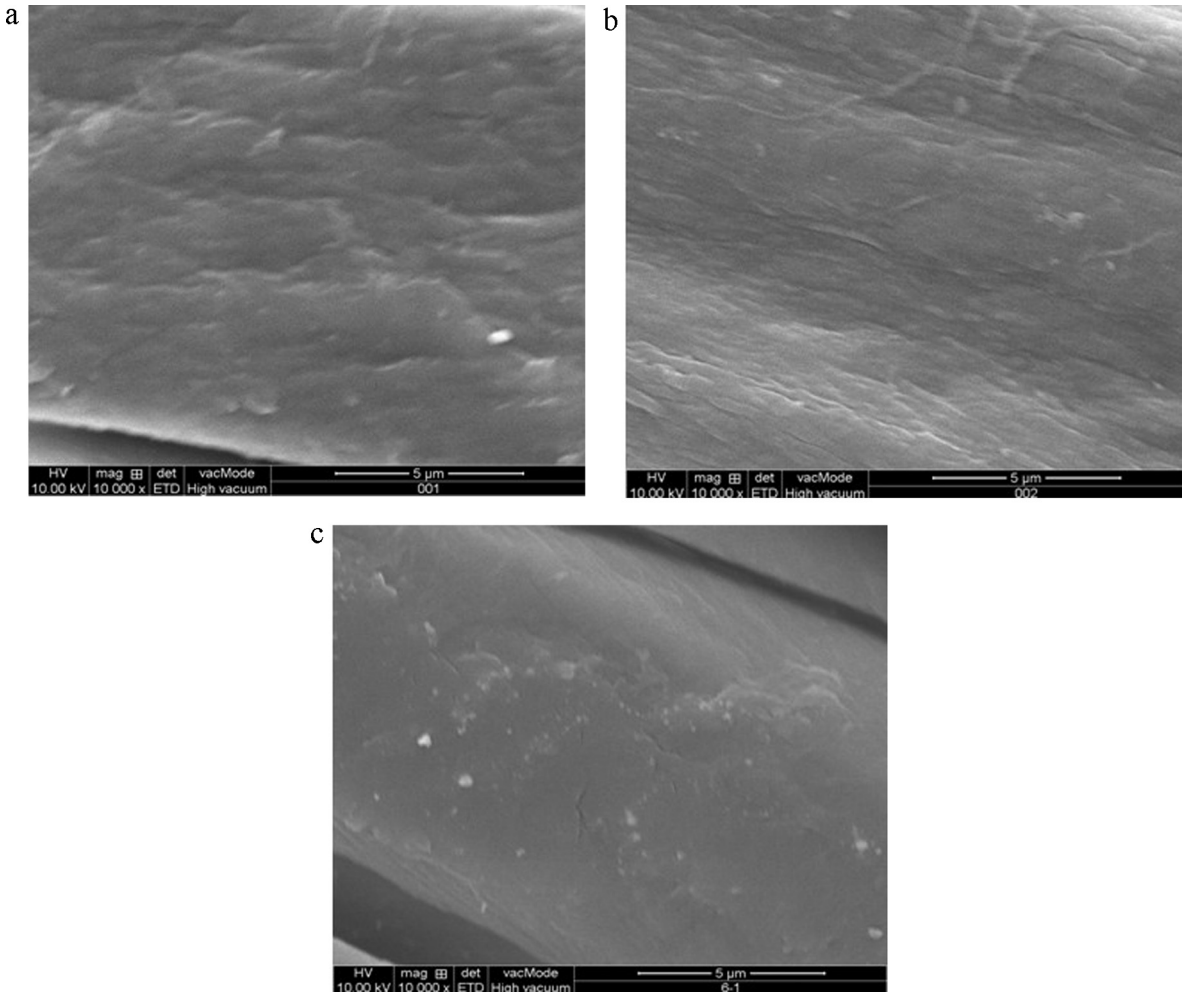


Fig. 6. SEM of control cellulose (a), FC-2 (b), and FC-4 (c).

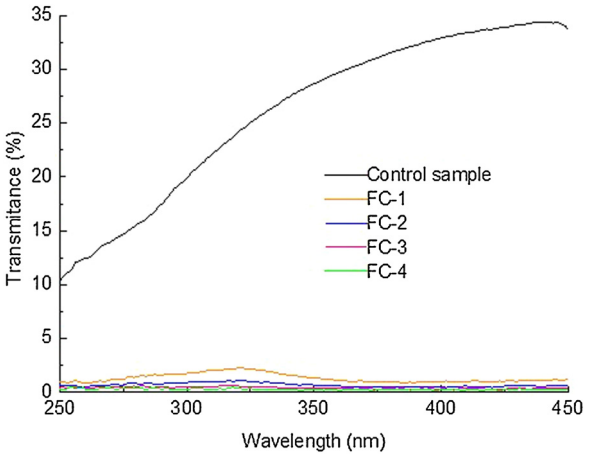


Fig. 7. Ultraviolet transmittance spectra of the functional and control cellulose fabrics.

Table 2
UPF, T (UVA), T (UVB) of the functional and control cellulose samples.

Samples	UPF	T (UVA) (%)	T (UVB) (%)	UPF After washing
Control	4.54	28.64	20.31	4.51
FC-1	66.75	1.08	1.46	65.93
FC-2	122.93	0.58	0.81	122.14
FC-3	176.23	0.46	0.58	175.87
FC-4	230.38	0.38	0.45	229.79

cellulose samples had higher UPF values. After washing, the modified functional cellulose samples still had higher UPF values. This showed that they had excellent washing ability. With increasing the concentration of BHSABA, UPF value sharply increased from 66.75 for FC-1 to 230.38 for FC-4. The ultraviolet transmittance (UVA and UVB) for FC-2, FC-3, and FC-4 were less than 1%. Generally, the UV protection property of fabrics would be evaluated as good when the ultraviolet transmittance was less than 5% and UPF reached 10–30. Because they reached very high UPF values and very low ultraviolet transmittance, four modified functional cellulose samples with the azobenzene Schiff base had excellent UV protection property. It should be attributed to π–π^* and n–π^* transition of huge conjugated system, which caused the change of the molecular structure based on its *cis–trans* isomerization and intermolecular proton transfer. It can be seen that the azobenzene Schiff base compounds containing huge conjugated system could be used to improve the fabric performance of ultraviolet resistance. The results were agreement with their reflectance spectra. The grafted cellulose samples had strong absorbance in 250–450 nm.

3.4. Antibacterial property of the functional cellulose fabrics

Antibacterial activity of four functional cellulose samples against *S. aureus* was evaluated by ASTM E2149-01. Washing cycles were tested according to domestic machine standard. The antibacterial activities of four functional cellulose fabrics are summarized in Table 3. It can be seen that the functional cellulose samples exhibited moderate activity against *S. aureus*. With increasing of the concentration of BHSABA, the antibacterial activity of the functional cellulose sample was improved. After washed 10 times, the functional cellulose samples still maintained antimicrobial activity. It demonstrates that the cellulose crosslinked with BHSABA improved the antibacterial activity. The multi-functional cellulose will have potential application in biomaterials and textile fields.

Table 3
Antibacterial property of the functional cellulose samples.

Samples	*R* (%)	
	Without washing	Washing
FC-1	53.27	48.56
FC-2	68.39	61.89
FC-3	73.23	69.16
FC-4	76.26	71.45

4. Conclusions

The multi-functional cellulose materials were prepared by crosslinking between cellulose and reactive azo-Schiff base containing azo conjugated system, BHSABA. The prepared multi-functional cellulose fabrics had very high UPF value and very low ultraviolet transmittance. They had excellent UV protection property. With increasing the concentration of BHSABA, grafting quantity (*Gq*) of BHSABA Schiff base on cellulose increased from 1.52×10^{-2} mmol/g to 5.08×10^{-2} mmol/g. The functional cellulose samples exhibited moderate activity against *S. aureus*. After washed 10 times, they still maintained antimicrobial activity. Compared with control cellulose, the onset of degradation of the functional cellulose slightly decreased. With increasing grafting quantity of BHSABA Schiff base on cellulose fabric, mass loss yields of the residues increased. The morphological structure of the functional cellulose fiber had no noticeable change. The multi-functional cellulose will have potential application in biomaterials and hi-tech textile fields.

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