

A Facile Approach Toward Surface Sulfonation of Natural Cotton Fibers Through Epoxy Reaction

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ABSTRACT: This manuscript describes a facile approach to modify the surface of natural cotton fibers with sulfonate groups through epoxy reaction. Sodium 1-chloro-2-hydroxylpropyl sulfonate (SCHPS) was chosen as the sulfonation agent for cotton fibers since it contains a Cl group at one end, a hydroxyl group in the adjacent position, and a sulfonate group at the other end. Epoxy was formed when it was treated with concentrated alkali. Then, the formed epoxy groups reacted with the hydroxyl groups on cellulose backbone. As the consequence, sulfonate groups were introduced over the cellulosic fiber surface. In this investigation, orthogonal experimental design was employed to study the relation-

ships between sulfonate densities on fiber surface and the influencing variables, i.e., concentration of NaOH, molar ratio of NaOH to sulfonation agent, and duration of reaction. Under the optimal condition, up to 4.6 mmol surface sulfonate groups/100 g fiber were achieved. The resulted fibers exhibited a strong affinity to silver ions and therefore were used as the substrate of antibacterial composite of silver nanoparticles and cotton fabric which fabricated via an *in situ* method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1744–1750, 2012

Key words: cellulose; sulfonation; epoxy reaction; silver nanoparticles

INTRODUCTION

As one of the most abundant renewable and biodegradable natural polymer resources, cellulose is traditionally utilized for paper production, textile, and commodity polymers. Recently, it has become a key resource of sustainable biofuels and biomaterials.¹ The chemistry of cellulose and its applications are therefore undergoing extensive research in recent years. Functionalizations of cellulose can broaden its potential applications of this biopolymer in terms of thermal stability, surface chemistry, morphology, crystal structure, and so on.² On the other hand, cellulose is suitable for chemistry functionalization to fit various applications with myriad groups because of its abundant available hydroxyl groups.

Among the functionalizations of cellulose surface, surface charge modification is of great interest since it changes the surface chemistry of cellulose³ and hence enhances its binding ability to metal nanoparticles⁴ and improves its interactions with wet-end additives in papermaking.⁵ Carboxylation is the most studied approach to surface charge modifica-

tion for cellulose fibers and related materials.^{3,6–14} However, carboxylic acid group, with a *pKa* of 3–5, is a weak acidic group. Thus, its binding ability strongly depends to the pH of medium. Sulfonic acid group, with a lower *pKa* of 0–1, is a stronger acidic group than carboxylic acid group. Therefore, sulfonic acid group should behave much more stable when medium pH varies than carboxylic group does. Compared with the extended research on carboxylation of cellulose, the research on sulfonation of cellulose is really limited.

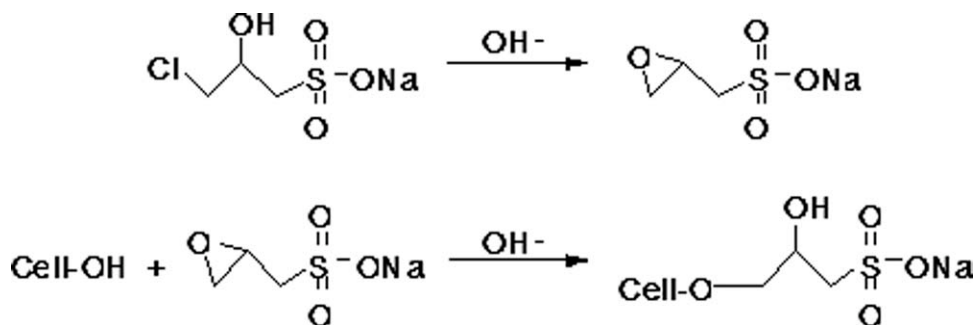
Sulfonated polysaccharides have gained more and more attention recently since its potential applications in wet and dry strength enhancement of paper,⁵ catalysts,¹⁵ health care field as anticoagulant and antiviral agent,^{16,17} and heavy metals adsorbents.¹⁸

One pathway toward sulfonation of cellulose fibers is to oxidatively cleave the C-2,3 hydroxyl groups of the glucose repeating unit of cellulose using sodium periodate initially to yield corresponding dialdehyde. Then the yielded dialdehyde reacts with sodium bisulfite to obtain the resulting sulfonated cellulose product.^{5,19}

In this research, an alternative approach toward sulfonation of natural cotton fibers through epoxy reaction was developed. Cotton fabrics were treated with the mixture of concentrated alkali and a sulfonation agent, Sodium 1-chloro-2-hydroxylpropyl sulfonate (SCHPS) to modify the surface chemistry of cotton fabrics. The sulfonation agent contains a Cl group at one end, a hydroxyl groups in the adjacent position,

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Scheme 1 Sulfonation of cotton fiber with sodium 1-chloro-2-hydroxypropyl sulfonate.

and a sulfonate group on the other end. Therefore, epoxy forms when it is treated with concentrated alkali as illustrated in Scheme 1 (top) and then the formed epoxy groups react immediately with the hydroxyl groups on the cellulose backbone as illustrated in Scheme 1 (bottom). This procedure is similar as that described in positive charged cotton fiber preparation.⁸ In their procedures, positive charged cotton fiber was obtained by reacting (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHTAC) with cotton fiber under concentrated NaOH. The similarity between their reactant and ours is that both contain a Cl group at one end and a hydroxyl groups in the adjacent position. The only difference is the functional groups of reactants which are desired to graft onto the backbone of cellulose. In their case, it is a quaternary ammonia group, whereas in this investigation, it is a sulfonate group. As the consequence of epoxy reaction, sulfonate group will be introduced into the cellulosic fibers. The reaction mechanism is shown in Scheme 1.

Orthogonal array is a fractional factorial design that allows testing multiple independent process variables within a single experiment. It was employed to evaluate the effects of concentration of NaOH, molar ratio of NaOH/SCHPS, and baking time on the sulfonate group density on the fiber surface in this investigation. In the mean time, the experimental condition was optimized to obtain the highest sulfonate group density on the surface of cellulose substrate.

To demonstrate the impact of sulfonation for cellulose, the binding capacity of sulfonated cellulose for heavy metal ions (Ag^+) was compared with the control. The composite of silver nanoparticles on natural cotton fibers was fabricated using an *in situ* method and was examined by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). The results affirmed that the sulfonate groups introduced onto the surface of cellulose fibers improve the binding capability of silver ions on cellulose substrates dramatically and therefore a much denser conformal nanoparticle layer was obtained.

MATERIALS AND METHODS

Materials

Standardized TIC-400 woven cotton fabrics obtained from Textile Innovators, (Rock Hill, SC) were used as cellulose substrates. Sulfonation agent, sodium 1-chloro-2-hydroxypropyl sulfonate (SCHPS) was purchased from Wuhan Bright Chemical Co., (Hubei, China). All other chemicals, including silver nitrate (AgNO_3), sodium borohydride (NaBH_4), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Everbright Chemical (Jiangsu, China). All chemicals were used as received without further purification. All solutions were prepared using distilled/deionized water, which was treated with a Milli-Q system (Millipore Corp., Billerica, MA).

Sulfonation of cotton fabrics

Anionic sulfonated cotton fabrics were prepared by reacting Sodium 1-chloro-2-hydroxypropyl sulfonate (SCHPS) with cotton fiber under concentrated NaOH. Concentrated NaOH solution (50 mL) was prepared initially. After it cooled down, SCHPS powder was put in the NaOH beaker under magnetic stirring. A light yellow transparent solution obtained in several minutes and then fabrics (*ca.* 5 g) were dipped in the solution at room temperature for around 10 min. A padder was used to press the wet fabrics to the wet-pickup at around 100%. Then the fabrics were hang in an oven and warmed at 60°C for 15 min and then baked at 120°C for some time. Orthogonal assay was employed to assign this experiment. The detailed reaction conditions were listed in Table I. After reaction the fabrics were rinsed several times with deionized water to make sure the fibers were in neutral condition and all reactants were removed.

Sulfonic and carboxylic acids groups determined by conductometric titration

The sulfonic and carboxylic contents of modified cotton fabric samples were quantitatively determined

TABLE I
Results of L₉(3⁴) Experimental Design for the Sulfonation of Cotton Fabrics

Trial no.	C (%)	R	T (min)	Result (mmol sulfonate/100 g fabrics)
1	30	2 : 1	10	1.03
2	30	2.5 : 1	20	3.81
3	30	3 : 1	30	2.43
4	40	2 : 1	20	1.83
5	40	2.5 : 1	30	3.14
6	40	3 : 1	10	2.85
7	50	2 : 1	30	2.23
8	50	2.5 : 1	10	2.74
9	50	3 : 1	20	4.58

by conductometric titration according to the standard method of SCAN-CM 65 : 02. Cotton fabrics were firstly cut into small pieces and suspended in hydrochloric acid at 1% concentration for 15 min. The suspension was then filtrated on a Büchner funnel to remove excess acid by washing repeatedly with deionized water until the conductivity of the washed filtrate was less than 5 $\mu\text{S}/\text{cm}$. Then, ~ 1 g oven-dry cotton fabrics was immersed in a titration beaker and 490 mL of distilled water and 10 mL of sodium chloride solution (0.05 mol/L) were added in. At last, titration was performed by adding sodium hydroxide solution (0.001 mol/L) from a precision burette, with an addition step of about 0.1 mL. The time between each addition was in the range of 10 to 30 s. The conductivity after each addition was recorded and a typical titration curve are present in Figure 1. The titration curve is characterized by three distinct phases. The amount of strong acid, i.e., sulfonic acid and the total amount of acidic groups can be determined from the first and the second intersection points, as illustrated in Figure 1. The amount of weak acid, i.e., carboxyl groups was the difference between the first and the second intersection points. Three replications were run for each sample and the average was taken as the measured amount of sulfonic and carboxylic acid groups for each sample.

In situ synthesis silver nanoparticles on sulfonated cotton fabric substrate

The effect of surface chemistry charge after sulfonation was demonstrated by coating silver nanoparticles on cellulose substrates. In this investigation, only the sulfonated cellulose fabrics with the highest amount surface charge tested by conductometric titration was used as the substrate to adsorb the silver ions in solution and then using an *in situ* method to reduce these ions into silver nanoparticles. For comparison, an untreated cotton fabric was used as the control.

To exchange metal cations from Na^+ of sulfonated cellulose to Ag^+ , 50 mL of AgNO_3 (5 mM) was prepared. Sulfonated and untreated cotton fabrics were then immersed into the solution to allow ion exchange performed in the dark at room temperature overnight, followed by a thorough rinsing with pure water. After removal of the samples from the metal salt solution, they were rinsed with water three times to remove the excess ions. To convert silver ions into silver nanoparticles, the fabrics were then immersed in a 50 mM NaBH_4 solution (50 mL) for 10 min to reduce the metal ions to zero-valence metal. After reduction, the samples were rinsed copiously with water. The obtained specimens were dried in air before characterization.

Characterization by SEM and EDX

Scanning electron microscopy (SEM) was carried out by a LEICA 440 at a voltage of 2 kV and aperture size of 30 μm , with a distance of 5–6 mm to characterize composites of Ag nanoparticles/cellulose substrates. In-lens detector was used. The specimens were sputter coated with an ultra thin layer of Au/Pd before imaging. For untreated and sulfonated specimens, different sputter-coating time was used. For the untreated specimen, it was sputter coated for 20 s as normal. While for the sulfonated sample, it was sputter coated for only 5 s, because it was already covered with a layer of silver particles. EDX was carried out under the condition of primary energy 10 keV, with a distance of *ca.* 7 mm and the aperture size of 60 μm .

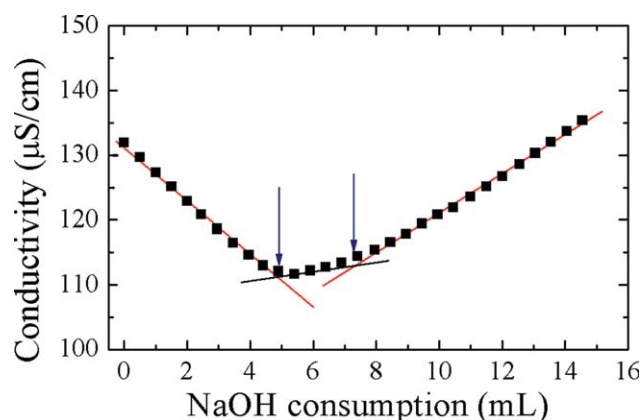


Figure 1 Determination of the sulfonic and total amount of charged groups on fibers by conductometric titration. Determination of the sulfonic and total amount of charged groups on fibers by conductometric titration. The first intersection point represents the volume of NaOH consumed by sulfonic acid and the second intersection represents for the volume consumed by total acids. Hence, the difference between the 1st and 2nd intersection points is the volume of NaOH consumed by carboxyl groups on fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

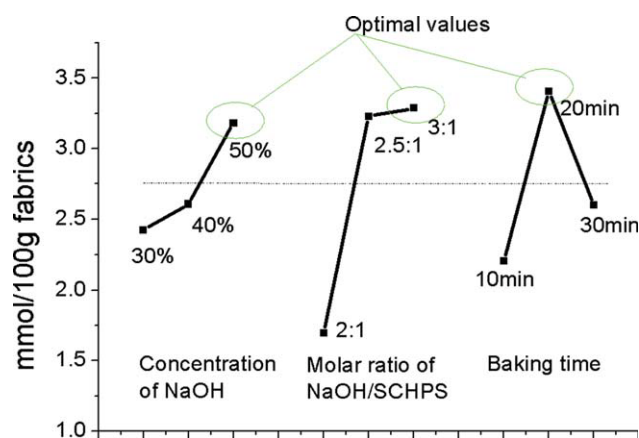


Figure 2 Effects of concentration of NaOH, molar ratio of NaOH/SCHPS, and baking time to the sulfonation efficiency of cellulose fabrics and the optimal reaction condition obtained for sulfonation of cotton fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Experimental design and data analysis

An orthogonal experimental design was employed to study the multiple influencing variables and to reduce the experimental size as well. A three-factor, three-level factorial design was used to evaluate the effects of the following factors, concentration of NaOH (C), molar ratio of NaOH/SCHPS (R), and baking time (T), on the sulfonation efficiency of cellulose fabrics, i.e., sulfate groups density over cotton fibers. To investigate the multiple influencing variables and to pursue the optimal condition to achieve the highest sulfonate density of cellulose fabrics, total nine experiments were performed. The influencing factors and their respective levels are listed in Table I. The results, surface sulfonate group mmol/100 g fabric, based on the conductometric titration, are also reported in Table I. From this Table, it can be observed that the minimum and maximum sulfonate density obtained was 1.03 and 4.58 mmol/100 g fabrics, respectively. They are equivalent to the average degree of substitution (DS) of 0.0016 and 0.007, respectively. These DS values are pretty low. Concentrated NaOH makes cotton fibers swell and sulfonation agent may penetrate into the fibers and to react. Due to the very low DS values, it can be safely concluded that sulfonation reaction mainly occurs on the surface of fibers. In other word, since only the surface of fibers is modified with charged group, a low DS of surface charge modification is acceptable. From Figure 1, it can be seen that substantial carboxyl groups also present in fibers. It can be explained that under thick alkali and elevated temperature conditions, peeling, stopping, and oxidation reactions occur for cellulose. However, slight variation of carboxyl group density on the surface of cotton fibers (in the range of 1.5–1.8 mmol/100 g fabric)

for different reaction conditions was observed. Therefore, in this investigation, we only focus on the sulfonation efficiency. It has to admit that these carboxyl groups over cotton fiber also affect the surface chemistry of cotton fiber to some extent.

Effect of NaOH concentration on sulfonation efficiency

Concentration of NaOH is very important for the reaction of sulfonation of cellulose due to the following reasons (1): under alkali condition, SCHPS forms epoxy which reacts with the hydroxyl group of cellulose. Hence, the concentration of NaOH affects the balance of epoxy formation (2); concentrated NaOH can also activate the hydroxyl group of cellulose (3); concentrateder concentration of NaOH can reduce the side reaction of SCHPS, i.e., to hydrolyze into alcohol. Therefore, if sulfonate density is plotted against the concentration of NaOH, there is an obvious trend that sulfonate density raises with NaOH concentration increase, as illustrated in Figure 2. It is worthy to mention that the increase of surface sulfonate density when NaOH concentration changing from 40 to 50% is more noticeable than that from 30 to 40%, implying that a higher concentration of NaOH is favored in the reaction of cellulose sulfonation.

Effect of molar ratio of NaOH/SCHPS on sulfonation efficiency

The effect of molar ratio of NaOH/SCHPS on sulfonation of cellulose is present in Figure 2. When the ratio was 2 : 1, the average sulfonate group on fiber surface was pretty low. When the ratio increased to 2.5 : 1 and 3 : 1, the sulfonate group soared abruptly, indicating that a higher molar ratio of NaOH/SCHPS is favored in the reaction of cellulose sulfonation. However, compared with the sulfonate density of the ratio of 2.5 : 1 and that of 3 : 1, the latter is only slight higher than the former. It indicates that there is little margin can be gained even reacting at a higher molar ratio.

Effect of baking time on sulfonation efficiency

The effect of baking time on sulfonation of cellulose can be seen in Figure 2 as well. It showed that the

TABLE II
ANOVA of the Sulfonation of Cellulose Fabrics

Source of variance	Sum of square	Degree of freedom	F value	Significance
C	0.944	(2)	Pooled	
R	4.882	2	5.802	*
T	2.245	2	2.668	
Pooled error	1.68	4		
Total	9.751	8		

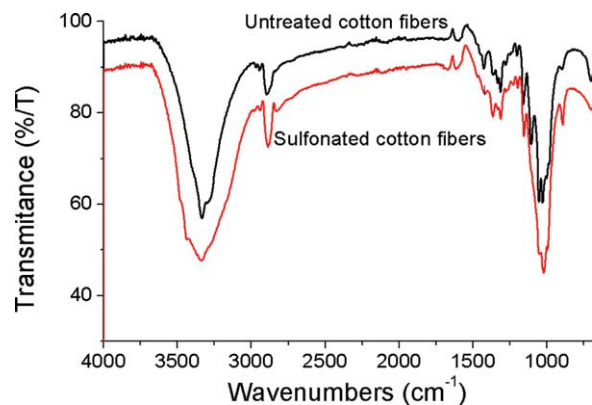


Figure 3 FTIR spectra of untreated and sulfonated cellulose fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfonation efficiency baked at 120°C for 20 min was much higher than that for 10 min. However, the sulfonation efficiency baked for more than 20 min at that temperature seems start to deteriorate. It can be explained by that cellulose starts to decompose under concentrated alkali at 120°C for more than 20 min.

The optimal condition for cotton sulfonation

Through the analysis above, the optimal condition of surface charge sulfonation obtained so far is as

follows: the concentration of NaOH 50%, the molar ratio of NaOH/SCHPS 3 : 1, and the baking time at 120°C for 20 min. This is illustrated in Figure 2. Since 50% NaOH is close to saturate, it's hard to prepare a higher concentration of NaOH solution. It can be regard that the optimal NaOH concentration is 50%. For molar ratio of NaOH/SCHPS, it can be seen that when the ratio of NaOH/SCHPS increased from 2.5 to 3, there is no significant increase of sulfonation efficiency when compared with that increased from 2 to 2.5. That means the ratio of 3 : 1 is high enough. In term of the baking time, it is easy to notice that 20 min is the optimal value. Therefore, the optimal condition obtained in this experiment, i.e., experiment 9 can be regarded as the optimal condition for cotton sulfonation.

ANOVA analysis

The ANOVA results for calculated models are shown in Table II. The orthogonal design table used in this investigation is an $L(3^4)$ table but only three factors were considered in. Therefore, the residual error (0.729) was calculated from the blank column at first. Since the variance from concentration of NaOH was less than two times of the residual error, it was put together with residual error to calculate as pooled error and therefore the degree of freedom of pooled error

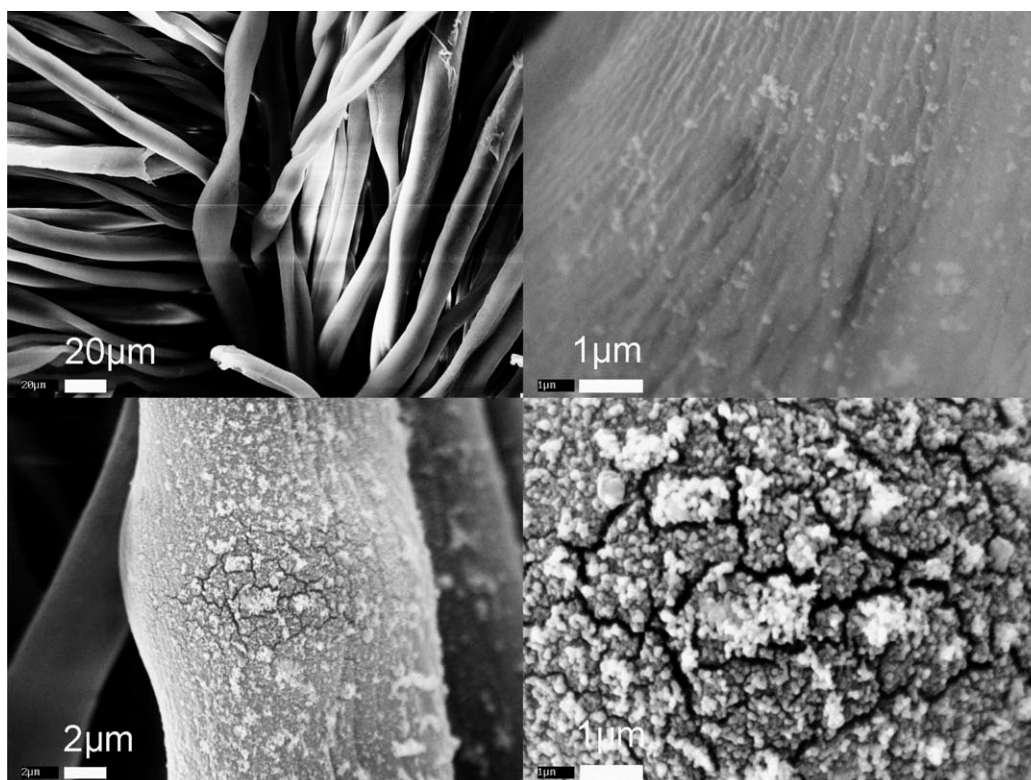


Figure 4 Adsorption of silver ions on untreated (top) and sulfonated cellulose fibers (bottom) and *in situ* reduced into silver nanoparticles and imaged by SEM. *In situ* synthesis silver nanoparticles on untreated (top) and sulfonated cellulose fibers (bottom) and imaged by SEM.

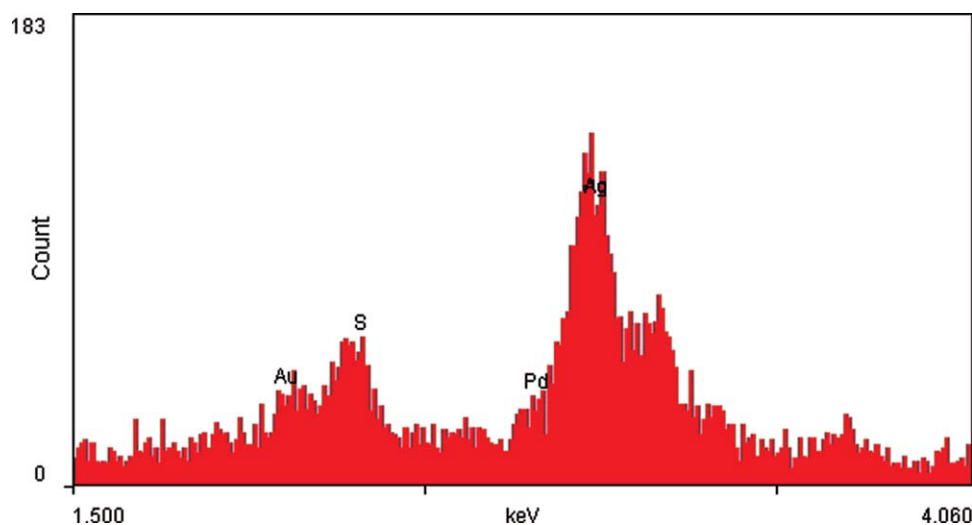


Figure 5 EDX spectrum of the composite of silver nanoparticles on sulfonated cellulose substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was increased to 4. The ANOVA analysis indicates that the molar ratio of NaOH/SCHPS plays the most important role in cellulose sulfonation than other variables since it possesses the greatest F value. Its F value is 5.802, greater than $F_{\text{critical}} 4.32$ ($P < 0.1$) but lower than $F_{\text{critical}} 6.94$ ($P < 0.05$). So it affects the sulfonation efficiency statistically significant. Nevertheless as for other parameters, including concentration of NaOH and baking time, do not have statistical significant effects on the sulfonation efficiency.

FTIR study on sulfonated cotton fabrics

The FTIR spectra of untreated and sulfonated cotton fabrics are present in Figure 3. Both curves show much similarity and no noticeable difference can be observed. S=O band, with the location ranging between 1000 and 1400 cm^{-1} , is not pronounced to be observed. It may be caused by the weak strength of S=O band due to its small amount of sulfonate groups over fibers since they only present on the surface of fibers ($DS = 0.007$).

Fabrication of composite of silver nanoparticles on sulfonated cotton fabrics

In general, there are two ways to incorporate silver nanoparticles onto substrates. One is by direct deposition; the other is by *in situ* synthesis. In this investigation, since silver ions carry positive charges, whereas sulfonate group bears negative charge in aqueous solution. Therefore, it is convenience to coat the surface of cotton fibers with a uniform layer of silver nanoparticles using *in situ* method.

The composites of silver nanoparticles and cellulose substrate were imaged using SEM, as illustrated in Figure 4, to assess the surface packing of the

nanoparticles on the cotton fabrics. Well-dispersed nanoparticles were found to pack with high surface coverage on the surface of sulfonated cellulose fibers, whereas there were only few nanoparticles found on the surface of the control sample. There were some cracks appearing on the surface of cotton fibers due to the short (10 s) sputter coating time. As a consequence, the heat generated by the electron beam could not be transfer out efficiently and therefore the heat accumulated made the fiber surface crack. Energy-dispersive X-ray spectroscopy (EDX) spectrum is presented in Figure 5, which was collected from the sample imaged by SEM. It clearly showed the presence of a Ag signal peak, indicating the effectiveness of the electrostatic assembly of the particles on the surface of the cotton fibers. Another peak of sulfur was also appeared in the EDX, which indicating the sulfonate groups were successfully introduced over the surface of substrate. While the two weak peaks of Au and Pd confirmed the arguments that the sputter-coating layer was not concentrated enough to transfer the heat generated when imaging. Compared with the control, the coating layer of silver nanoparticles on sulfonated cotton fabric is much denser. It provides some evidences that sulfonated cotton fabrics have a higher binding capability to silver ions due to the introduction of negatively charged sulfonate groups into the cotton fibers. Negatively charged sulfonate groups on cotton fibers lead to a higher binding ability to positively charged metal ions by electrostatic forces. Therefore, sulfonated cellulose fabrics are potential in application of heavy metals absorbent for waste treatment. What's more, since the incorporation of silver nanoparticles in cellulosic substrates, the composite of silver nanoparticles on sulfonated cotton fabrics should have superior antibacterial ability and

can be potentially used in health care and other applications.

CONCLUSIONS

In this article, a facile and easy operational sulfonation method was developed to modify the surface of cellulose. An orthogonal experimental design was employed to investigate the effects of NaOH concentration, molar ratio of NaOH/SCHPS, and baking time on the sulfonation efficiency of cotton fibers and the optimal reaction condition was obtained. Sulfonated cotton fabrics are found to have enhanced binding ability to positive silver ions and, therefore, it is promising to be used as a candidate of substrate of composite of silver nanoparticles and as an absorbent for heavy metals removal in the waste treatment.

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