Fibers and Polymers 2018, Vol.19, No.11, 2324-2334
DOI 10.1007/s12221-018-8621-1

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Double Protect Copper Nanoparticles Loaded on L-cysteine Modified Cotton Fabric with Durable Antibacterial Properties

Qingbo Xu, Panpan Duan, Yanyan Zhang, Feiya Fu, and Xiangdong Liu*

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China

(Received July 11, 2018; Revised August 19, 2018; Accepted August 26, 2018)

Abstract: In this work, we developed a new method that can achieve immobilization and protection of the Cu NPs coating on the cotton fabrics by a simple two-step impregnation method. Firstly, L-cysteine (Cys) was grafted onto cotton fabric via esterification with the hydroxyl groups of cellulose, then Cu NPs were introduced on the fabric surface in the presence of a protective reagent, citric acid. Due to the doubled stabilization acts of Cys and citric acid, the Cu NPs immobilized on the fabric surface showed an excellent antibacterial effect and outstanding laundering durability. As a result, the mean size of the Cu NPs coating on the cotton fabric is about 62.4 nm, and the modified cotton fabrics showed satisfactory antibacterial ability against both *S. aureus* and *E. coli*, which the bacterial reduction rates are all higher than 98 % even withstand 50 washing cycles. Therefore, this method to prepare antibacterial cotton fabrics showed great potential applications in socks, cosmetic, and medical textiles.

Keywords: Cotton fabric, Copper nanoparticles, L-cysteine, Antimicrobial effect

Introduction

Nature fiber products, especially cotton fabrics, are highly popular with people and widely applied in daily life because of their excellent properties, such as wearing comfortability, flexibility, water absorptivity, and breathability [1]. Recently, a lot of methods for the surface modification of cotton fabrics has been reported to create additional functionalities, including fire retardancy [2], UV protection [3,4], antibacterial activity [5-7], self-cleaning ability [8], hydrophobic properties [9-11], and increase their usages in military and medical devices, technical products, industrial workwear, and household applications. However, these products could be easily damaged by microorganisms on account of its nature feature, which not only cause discoloration, mechanical strengthen loss and foul odor generation of the products but also result in a series of negative healthy effects to human beings [12]. At present, incorporating antimicrobial agents onto cotton fabrics is main methods to solve those problems. In this case, the immobilization of silver [13-17], copper oxide [18,19], gold [20-22], copper [23] nanoparticles on the cotton fabrics can effectively inhibit the growth of bacteria, fungi and algae [24-26].

Copper nanoparticles (Cu NPs) have important applications in many areas, such as catalyst [27], electrical conductors [28], sensors [29]. In addition, due to Cu NPs have low toxicity [30], it has been widely applied as an antimicrobial agents in cotton fabrics [31-34]. However, a number of reports [35-38] have mentioned that there are two drawbacks in the uses of Cu NPs for finishing cotton fabric: the rapid oxidization rate and the weak affinity with cotton fiber surface. To prevent the oxidization of Cu NPs on the cotton fabrics, numerous strategies have been exploited in the last decade [35-38]. For example, Bajpai group [35] used poly acrylic acid grafted cotton fibers to protect the Cu NPs. Sun group [36] applied PMETAC synthesis by ATRP polymerization as a binder to immobilized Cu NPs on the cotton fabrics. As a results, the modified cotton showed effective antimicrobial ability (after 30 washing cycles, the inhibition zone still be observed). Polydopamine [37] has been developed as a binder to improve the durability of the antibacterial cotton fabrics containing Cu NPs, and the value of bacterial reduction rate (BR) were over 88 % even after 50 laundering cycles. Sadanand group [38] reported a new way to generated Cu NPs coating on the cotton fabric surface by using simple hydrothermal method. The obtained cotton fabrics exhibited good antibacterial activity against *E. coli*. However, most of these strategies to avoid oxidation of Cu NPs are unable to permanently immobilize Cu NPs on surface of the cotton fabrics. Therefore, we are attempting to develop a new method that achieve both immobilization and protection from oxidization on the Cu NPs at the same time.

In our previous work [39], we used l-cysteine (Cys) as a binder to link Ag NPs, although this method has achieved excellent results in durable antibacterial properties, but due to the Ag NPs have some extent toxicity, so it may be produced harm effect to the environment and humans [6]. In order to further demonstrate the contribution of Cys as a binder in antibacterial cotton fabrics, we choose Cys to link Cu NPs onto cotton fiber surface. It was expected that Cys can covalently graft to cotton fabric via esterification with the hydroxyl groups on the cotton fiber surface, and tightly adhere to surface of the Cu NPs by coordination bonds. Fortunately, the tiol groups not only make Cu NPs immobilized on the cotton surface, but also prevent their oxidization [40].

*Corresponding author: liuxd2007@yeah.net

Herein, we report a new method to prepare antibacterial cotton fabrics using Cu NPs. Sodium borohydride is used as a reducing agent and citric acid is a stabilizer to prevent Cu NPs agglomeration and oxidation [41]. The functionalized cotton fabrics are characterized using methods: fourier transform infrared spectrum instrument (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and field emission scanning electron microscope (FE-SEM). The experimental results show that the modified cotton have excellent and durable antibacterial properties against Gram-positive (*E. coli*) and Gram-negative (*S. aureus*) bacteria.

Experimental

Material

L-cysteine (Cys) was purchased from Shanghai Aladdin Co., Ltd. (China). Cotton fabrics were purchased from Shaoxing Qi Dong Textile Co., Ltd. (60 ends/cm, 30 picks/cm, 0.42 mm thickness, 120 g/m weight, 35.2 m^2/g specific surface area). Before chemical modification, the cotton samples (30 mm×30 mm) were cleaned by ultrasonic washing in a 2 % sodium laurylsulfonate solution for 30 min and then washing in ethanol (50 m*l*, 2 h) and deionized water (50 m*l*, 30 min×3 times). Other reagents were purchased from Shanghai Aladdin Co., Ltd. (China) without further purification.

Preparation of Cys-Cotton

Original cotton fabrics were immersed in Cys solution (100 m*l*, 82.54 mmol/*l*) for 30 min, padded to give a wet pick up of 80±2 %, dried for 3 min at 80 °C, cured at 180 °C for 3 min, rinsed with distilled water (50 m*l*×3 times), and finally dried at 100 °C for 1 h to obtain modified cotton fabrics (Cys-Cotton).

Synthesis of Copper Surface on Cotton Fabric

Copper sulfate solution (100 m*l*, 0.04 mol/*l*) was firstly prepared, the citric acid (4.76 mmol) as a protective agent was added in the solution at 50 °C with stirring. Then the Cys-Cotton fabric sample was immersed into the mixed solution for 30 min, the sodium borohydride solution (10 m*l*, 0.13 mol/*l*) was introduced into the solution with stirring to reduce the copper salt, the temperature was declined to 40 °C, and the treatment was carried out for 1 h. The finished fabric was finally washed with distilled water twice and dried at room temperature approximately 4 h to obtain Cu-Cys-Cotton (Cu-Cys-Cotton).

Characterization

The morphology of Cu NPs was studied by transmission electron microscopy (TEM; TF20, FEI, America). Size distribution of the Cu NPs in the colloid solution was studied by statistically measuring 200 bright points in the TEM image. The other instruments information such as FE-SEM, ATR, XRD, XPS was described in our previous report [5]. Copper content coating on the cotton fabrics were measured by using inductively coupled plasma mass spectrometry (ICP-MS, Aglient 7500a, Australian).

Antimicrobial Test

Escherichia coli (*E. coli*, ATCC 1555) and *Staphylococcus aureus* (*S. aureus*, ATCC 547) were used as the model microorganisms according to an improved AATCC 100-1999 method [5,42-44]. Before each assay, the test bacteria were incubated in letheen broth (LB) fluid nutrient medium (containing 5 g/*l* yeast extract, 10 g/*l* peptone, 10 g/*l* NaCl and adjust pH to 7.4) at 37 °C for 24 h. A standardized density of bacteria was used for the challenge inoculation. The fabric specimens (0.05 g) were cut to about 5 mm piece, sterilized by UV light for 30 min, placed in a sterile container 5.0 μ*l* of activated *E. coli* or *S. aureus* in 4 m*l* fluid nutrient medium (10^8 CFU/m*l*) was added into the sterile tubes containing modified cotton fabrics, shaken at 25 °C for 18 h at 150 rpm. The supernatant was diluted to an appropriate concentration, dispersed onto LB agar plants, and incubated at 37 °C for 24 h. The number of survival microorganism was determined by counting the colonies as a colony forming unit (CFU)/m*l*, and bacteriostatic reduction rate (BR) of microorganisms was calculated as follows:

$$BR = \frac{B-A}{B} \times 100\%$$

where A and B are the (CFU)/m*l* of the surviving microorganisms after 24 h for an agar plate containing the modified sample and control sample, respectively.

Laundering Test

Laundering durability was evaluated by measuring the antimicrobial efficacy of the modified cotton samples after repeated stringent washing cycles. The cotton fabrics (1.5 cm×1.5 cm) were washed by 50 m*l* of aqueous solution of sodium dodecane sulfonate (2.0 %, w/w) in a beaker (diameter, 50 mm) with stirring (300 rpm, magnetic stirrer) at 25 °C for 10 min, rinsed with deionized water (10 m*l*× 4 times), and dried at 60 °C. The antimicrobial function of the laundered samples was evaluated using the antimicrobial test described above.

Nature Properties Tests of Cotton Fabric

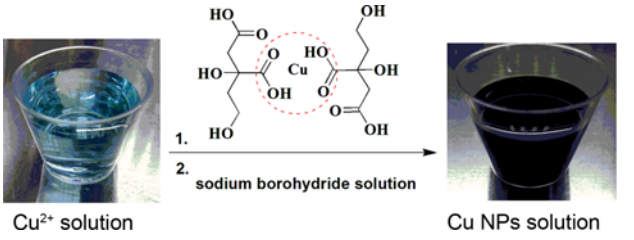
Water absorptivity was measured using the difference in weight of the cotton samples after soaking in plenty of deionized water for 10 min and hanging out for another 10 min. Water vapor permeability was evaluated busing the ASTM E-96 (open cup test) method. The test fabric sample was placed tightly over a shallow dish containing distilled water. The weight loss of the test assembly over 24 h was measured and the vapor transmission rate ($g/m^2/d$) was calculated as water vapor permeability. Tensile strength tests

were carried out on an electronic fabric tensile tester (YG065, China). The fabrics (rectangle shape, 200 mm× 50 mm) were stretched at a constant rate of 20 cm/min. Flexibility was determined by the flat loop method (IS 7016 Part 11). Fabric samples were cut from warp and weft directions (40 mm×160 mm). A loop was made and was placed on a horizontal plane. The height of the loop was measured as an idea of the flexibility of the fabric. The lower the height of the loop, the greater is the flexibility.

Results and Discussion

Characterization of Cu NPs Colloidal Solution

In this study, citric acid played a key role in the synthesis of Cu NPs. When citric acid introduced into the copper sulfate solution, Cu^{2+} ions are surrounded by citric acid molecules, then $NaBH_4$ solution as a reducing agent was added in the mixture solution leads to the generation of Cu^0 [45]. The producing Cu NPs in citric acid solution were effective protected from oxidization. The green color of the solution disappears, becoming reddish brown (Scheme 1). The surface morphology of the particles was examined by



Scheme 1. Solution with a color change before and after reaction.

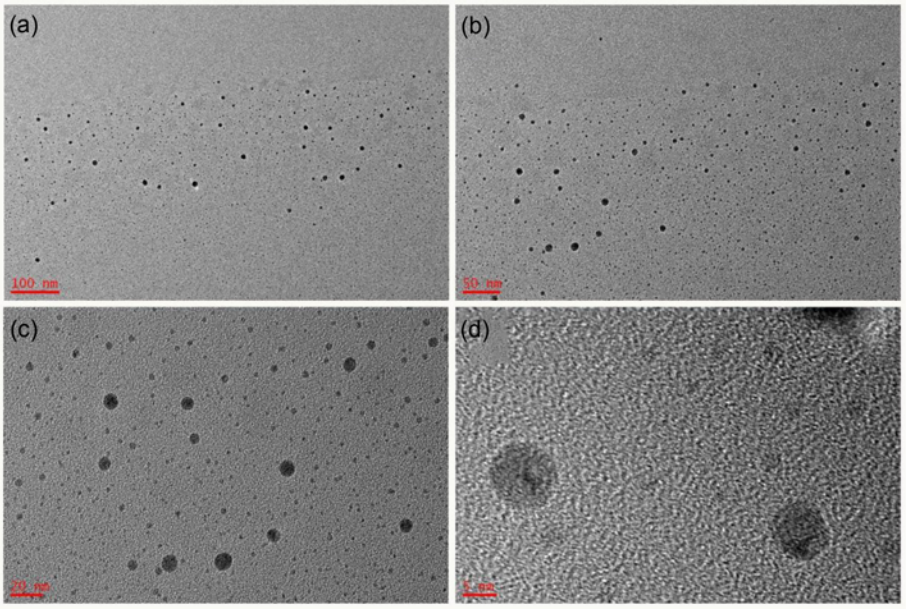


Figure 1. TEM images of the particles in the mixture solution.

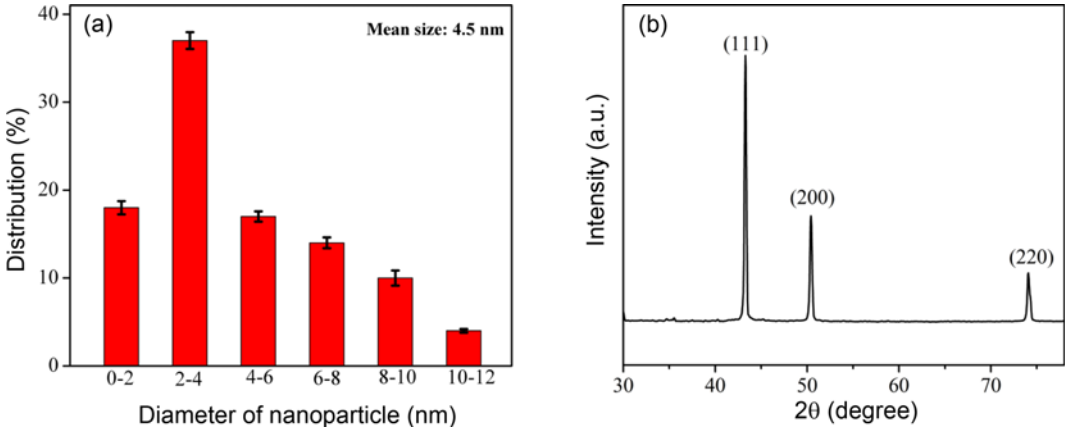
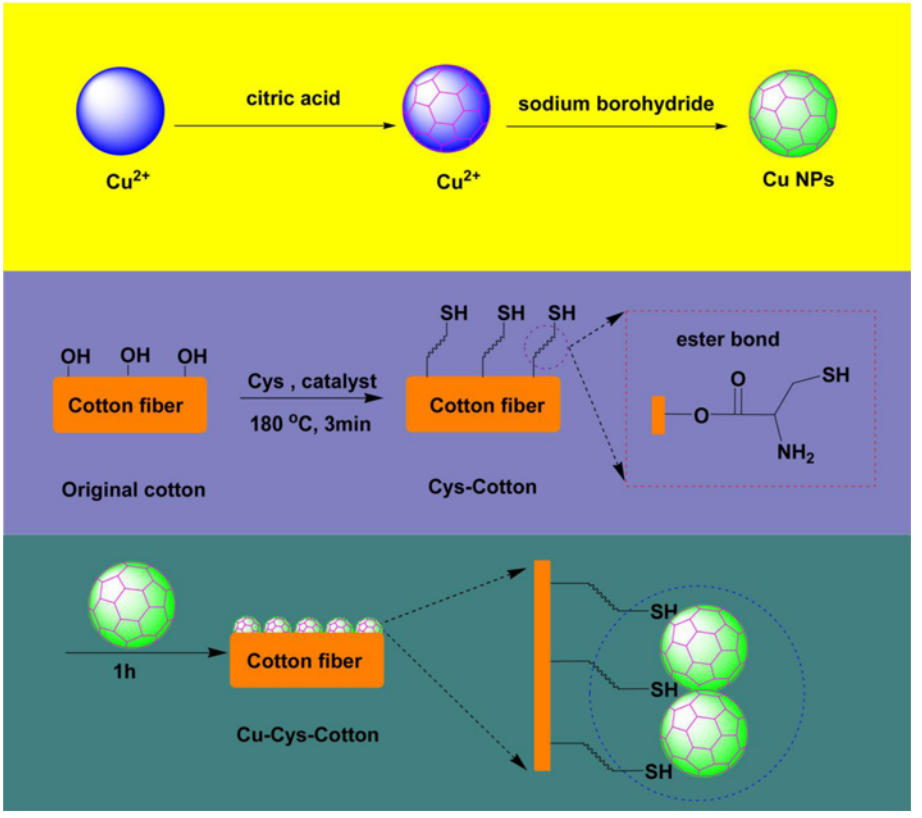


Figure 2. Size distribution (a) and XRD pattern (b) of the particles in the mixture solution.



Scheme 2. The surface modification on the cotton fabric using Cu NPs with double protection.

TEM analysis (Figure 1). The low (Figure 1(a) and 1(c)) and high (Figure 1(d)) magnification TEM images showed a good dispersion with spherical morphology of the particles. The size distribution of the particles (Figure 2(a)) was measured from TEM images, and the mean size is 4.5 nm [46]. Figure 2(b) shows the XRD pattern of the particles in the mixture solution, the sharp diffraction peak appeared at 2θ values of 43.7 °, 50.9 ° and 74.5 ° for the index (111), (200) and (220) planes of Cu particles [47], respectively. These results support that the produced particles are Cu NPs.

Modification and Characterization of the Cotton Fabric Surface

Figure 3 shows ATR-IR spectra of the cotton fabrics. The cotton fabrics show the peak at 3337 cm^{-1} can be assigned to the -OH group [3,4,48-50]. Compare with the original cotton fabric, Cu-Cys-Cotton and Cys-Cotton fabric samples have a new peak at 1730 cm^{-1} which attributable to the C=O (in ester group) group, it suggested that esterification occurs between the Cys molecules and the cotton fabrics. Due to the Cu-Cys-Cotton fabric surface was covered by Cu NPs, it will affect the ATR peaks intensity, so the Cu-Cys-Cotton fabric has a low intensity peaks compare with the Cys-Cotton fabric.

The XRD image of the cotton fabrics are shown in Figure 4. The typical peaks of cellulose at 2θ=12, 20, and 22 ° were displayed on the cotton fabrics. Compare with original cotton and Cys-Cotton fabric, the Cu-Cys-Cotton fabric show the new peaks appeared at 2θ values of 43.7 °, 50.9 °

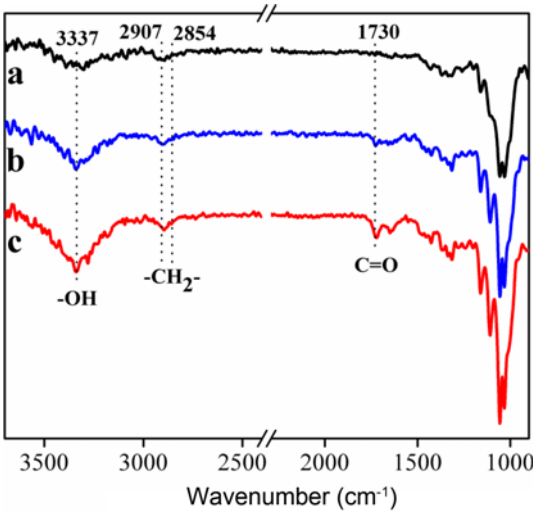


Figure 3. ATR-FTIR spectra of the original cotton fabric sample (a), the Cu-Cys-Cotton fabric sample (b), and the Cys-Cotton fabric sample (c).

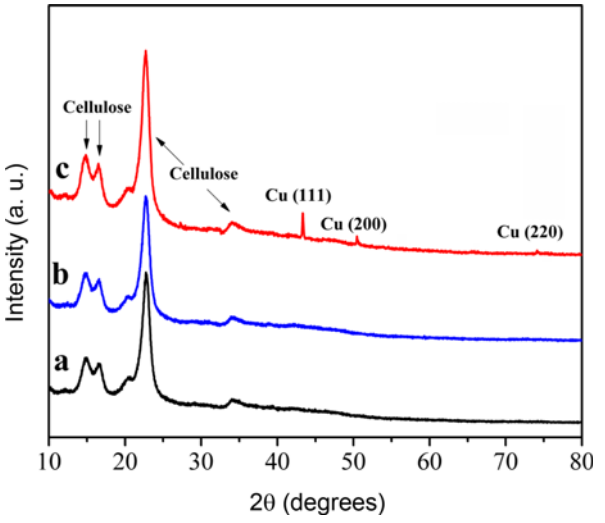


Figure 4. X-ray diffraction pattern of the original cotton fabric sample (a), the Cys-Cotton fabric sample (b), and the Cu-Cys-Cotton fabric sample (c).

and 74.5° for the index (111), (200) and (220) planes of Cu particles, respectively. The results clearly showed that Cu NPs were successfully immobilized on the cotton fabric surface [51]. Based on XRD pattern and Debye-Scherrer equation, it was calculated that the average diameter of Cu NPs is 60.4 nm on the Cu-Cys-Cotton fabric surface [52].

Figure 5 shows the SEM images of the cotton fabrics. The surface of original cotton fabric (Figure 5(a) and 5(b)) is clean and smooth. However, there are many filaments on the Cys-Cotton fabric surface (Figure 5(c) and 5(d)), which may due to Cys and cotton fabric surface reaction generated. Compare with the Cys-Cotton, the Cu-Cys-Cotton fabric surface (Figure 5(e) and 5(f)) not only have many filaments but also have a lot of particles, meaning that Cu NPs were coated on the cotton fabric surface [53].

To further determine the Cys and Cu NPs were successful linked to the cotton surface, we performed XPS analysis. Figure 6 shows the XPS survey spectra of the original cotton (Figure 6(a)), Cys-Cotton (Figure 6(b)), and Cu-Cys-Cotton

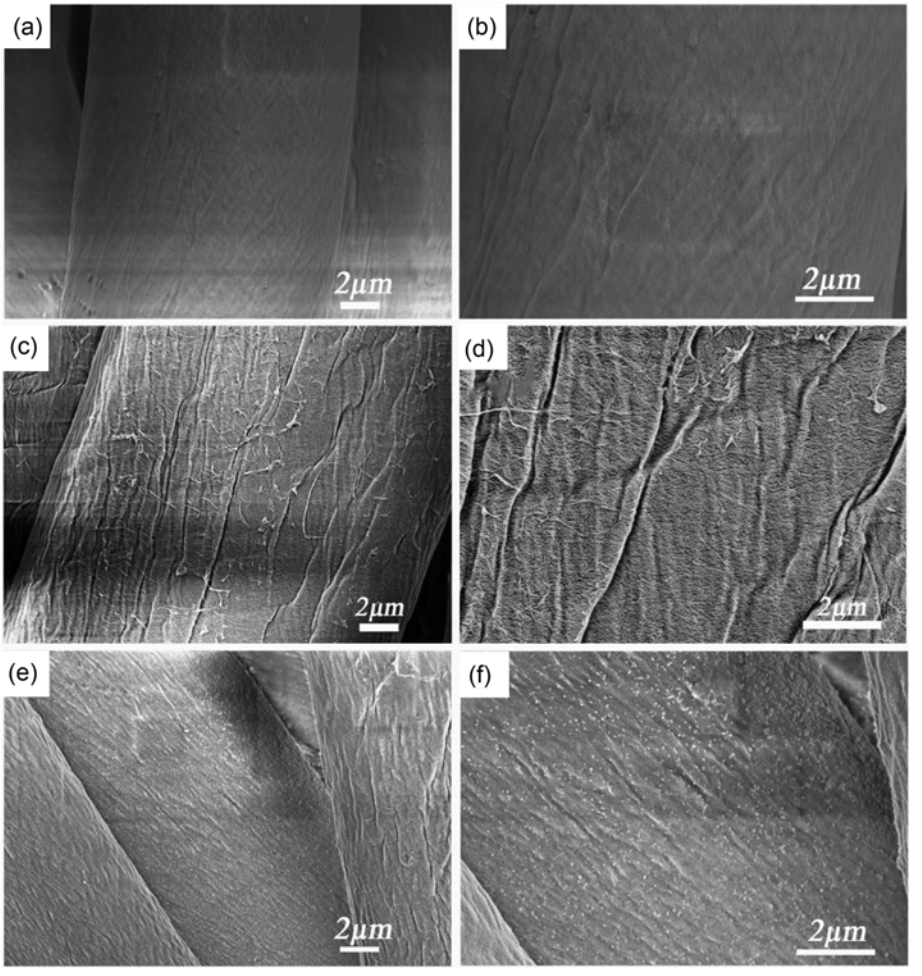


Figure 5. SEM images of the original cotton fabric sample (a, b), the Cys-Cotton fabric sample (c, d), and the Cu-Cys-Cotton fabric sample (e, f).

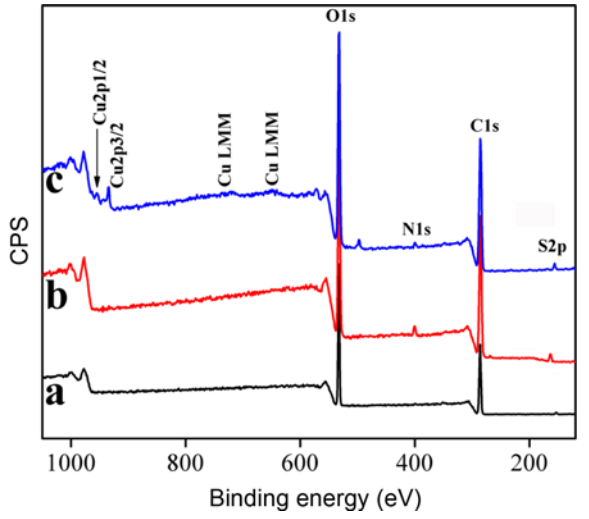


Figure 6. XPS survey spectra of the original cotton fabric sample (a), the Cys-Cotton fabric sample (b), and the Cu-Cys-Cotton fabric sample (c).

samples (Figure 6(c)). The original cotton displays C 1s and O 1s signals, and the Cys-Cotton displays C 1s, O 1s, N 1s, and S 2p signals. However, the signal of C 1s, O 1s, N 1s, S 2p, and Cu 2p was showed in the Cu-Cys-Cotton fabric. Figure 7(a) shows the deconvoluted C1s spectrum of the original cotton fabric contained three peaks at 284.1, 286.2, 288.7 eV, corresponding to C-C, C-OH and C-O-C respectively. However, the Cu-Cys-Cotton fabric (Figure 7(b)) shows the extra peaks at 285.7 eV, 287.5 and 288.8 eV, which are assigned to C-N, C-S and C=O/C-O-C bonds, respectively. The coordination force of the amino groups and thiol groups of Cys with Cu was verified by N 1s and S 2p XPS spectroscopy study in Figure 7(c) and 7(d), suggesting the happening of the electron transfer between Cys and Cu elements. These results providing further evidence of the Cys and Cu NPs were immobilized onto the cotton fabric surface [53].

We next studied the coating stability using washing test resembling that in laundry applications. Figure 8 compares the high-magnification SEM images, S mapping, and Cu

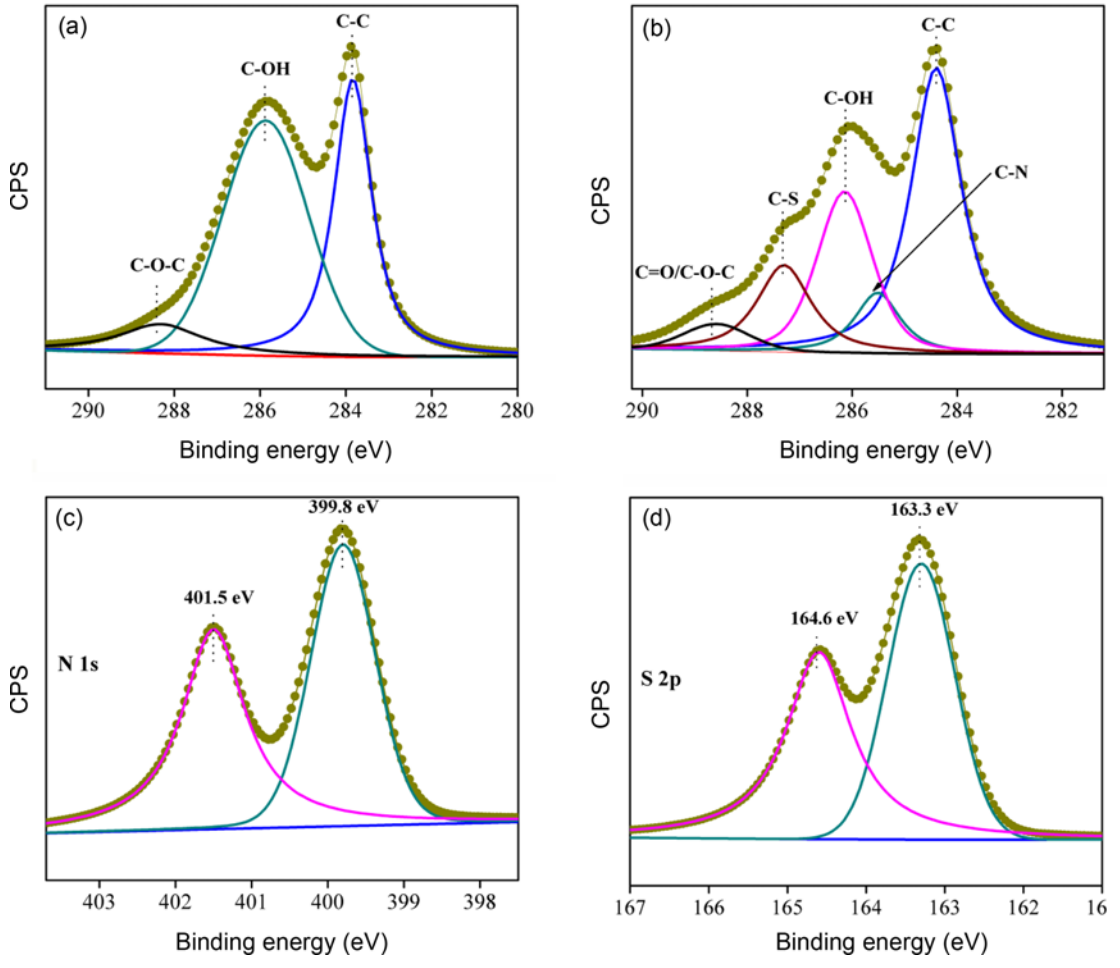


Figure 7. Deconvoluted Cls XPS spectra of the original cotton fabric sample (a), the Cu-Cys-Cotton fabric sample (b), N 1s XPS spectra (c), and S 2p XPS spectra (d) of the Cu-Cys-Cotton fabric.

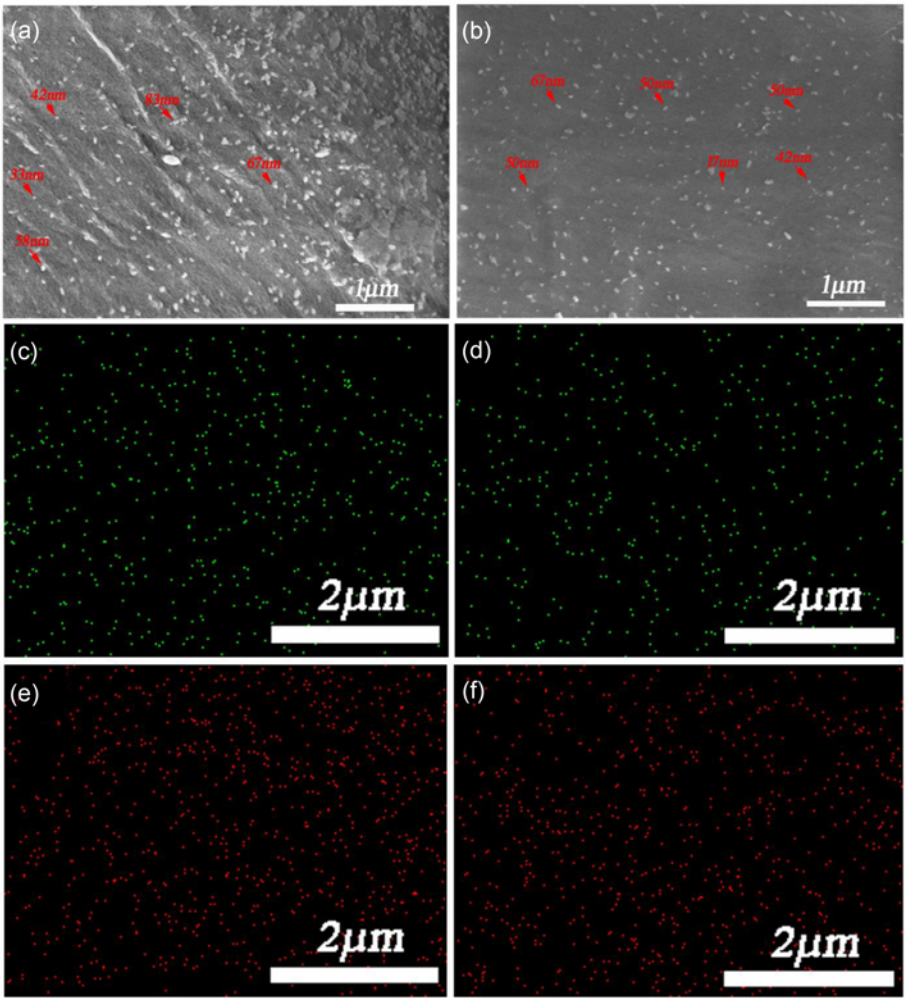


Figure 8. High magnification (×20000) SEM images, S mapping image, Cu mapping images of the Cu-Cys-Cotton fabric before (a, c, e) and after (b, d, f) 50 washing samples.

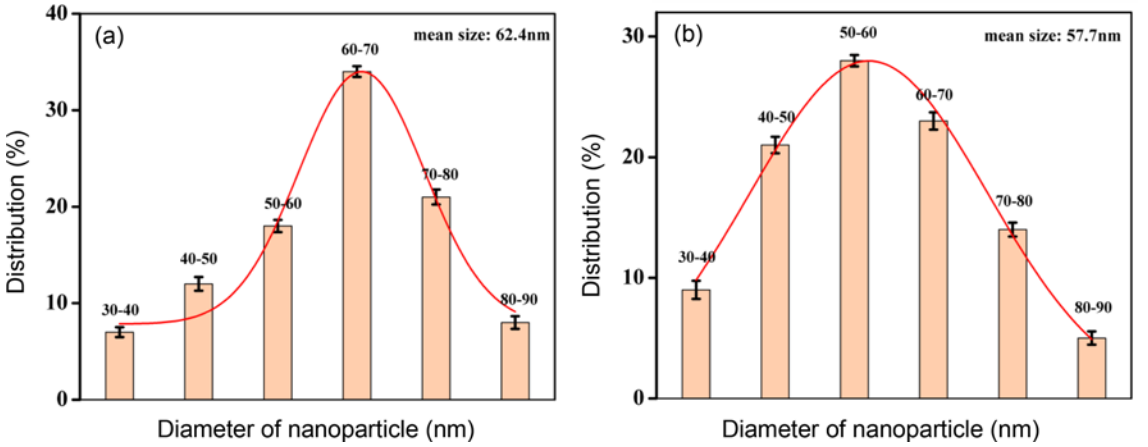


Figure 9. Size distribution of of the Cu-Cys-Cotton fabric before (a) and after (b) 50 washing samples.

mapping images of Cu-Cys-Cotton before and after 50 washing tests. Compare Figure 8(a) and 8(b), it was founded that a lot of Cu NPs still exist on the surface of the modified cotton fiber (Cu-Cys-Cotton) even after withstand 50

Table 1. ICP-MS results of the Cu-Cys-Cotton before and after washing samples

Washing cycle[a]	Cu content (mg/g)	Remaining of Cu (%)
0	13.8	-
10	13.5	97.8
20	13.1	94.9
30	12.9	93.5
40	12.6	91.3
50	12.5	91.1

[a]The washing period of the modified cotton fibers is ten min.

washing cycles. Figure 8(c) and 8(f) show the EDS mapping images of the Cu-Cys-Cotton before and after 50 washing cycles, it was confirmed again that the Cys and Cu NPs were immobilized on the cotton fabric even withstand 50 washing cycles. According high magnification SEM image of the Cu-Cys-Cotton fabric, we make a statistical analysis of the bright points on the Cu-Cys-Cotton before and after 50 laundering cycles, giving a size distribution diagrams shown in Figure 9. It was found that average size of the Cu NPs become smaller, this results indicate that the size of the Cu NPs decreases by the washing. To examine the reduction in quantities of Cu element coated on the fabric surface, the modified fabrics (Cu-Cys-Cotton) were further investigated using ICP-MS analysis. The loss of Cu element caused by the 50 washing tests is about 8.9 % (Table 1), this result indicating the Cu NPs with the Cys binder are durable for the abrasion force occurred during the washing process.

Antibacterial Efficacy and Laundering Durability

Figure 10 shows the antibacterial effect of the cotton fabric samples. There are no obvious inhibition zones around original cotton and Cys-Cotton, but the Cu-Cys-Cotton show the obvious inhibition zones (Figure 10(a) and 10(b)). Similarly, the bacterial growth tests (Figure 10(c) and 10(d)) shows that the Cu-Cys-Cotton has positive effect in suppressing the microbial growth. However, the Cys-Cotton shows a weak inhibitory effect on bacterial growth compare with the original cotton. Figure 11(a) and 11(b) show the BR rates of the cotton fabric samples, the Cys-Cotton showed poor antimicrobial effect with BR rates lower than 7 %. However, the BR values of the Cu-Cys-Cotton for both bacteria after 1 h contact period are all higher than 100 %. It is obvious that the loading of Cu NPs on the cotton fabric significantly contributes to the antimicrobial behavior

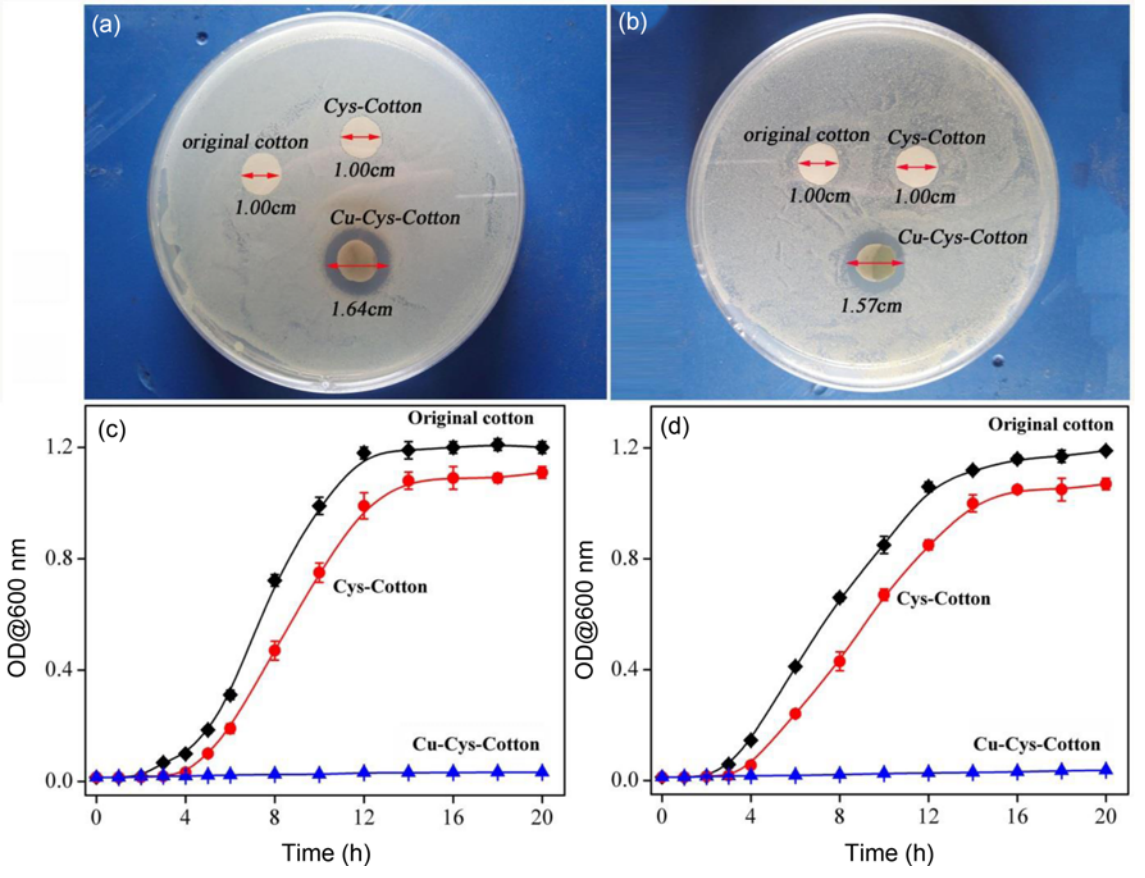


Figure 10. Zone of inhibition (a, b) and bacterial growth curve (c, d) against *E. coli* (a, c) and *S. aureus* (b, d) in the presence of the cotton fabric samples.

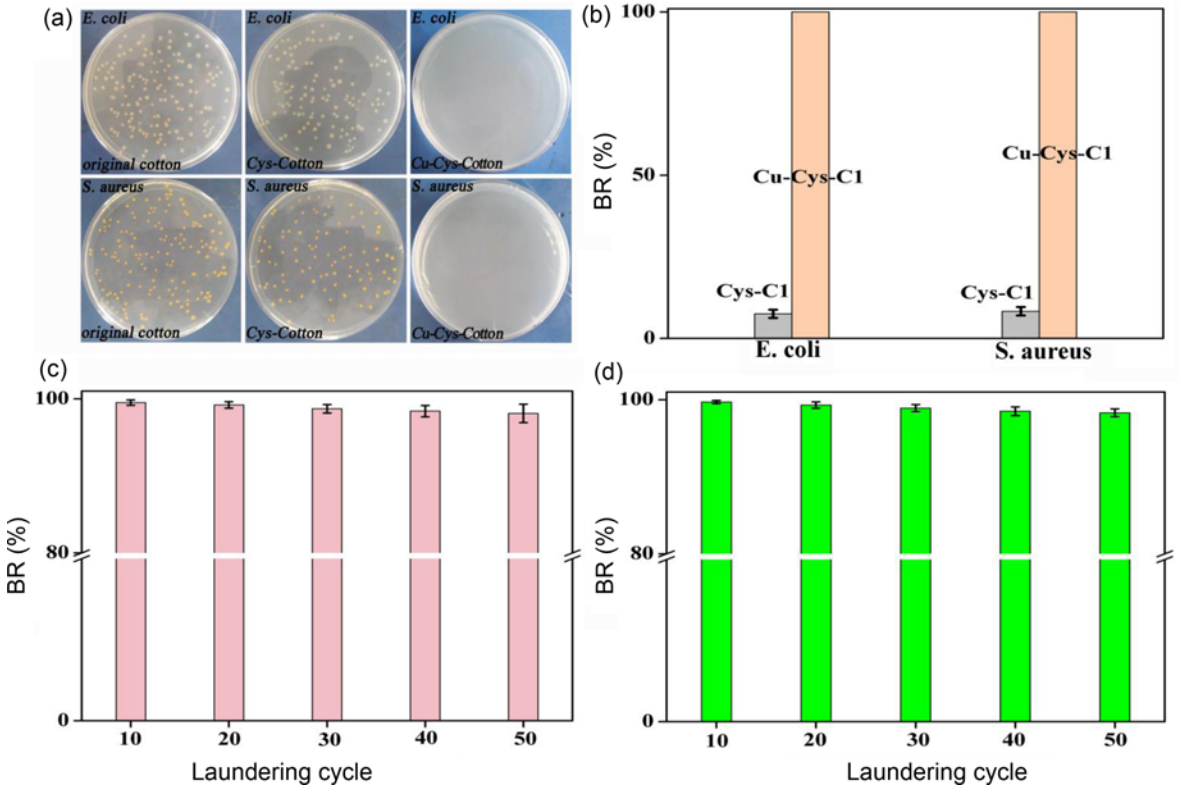


Figure 11. The antibacterial effect of the modified cotton fabrics, (a) the optical images of the antibacterial tests, (b) the BR rates of Cys-Cotton and Cu-Cys-Cotton, and the antibacterial durability results against (c) *E. coli* and (d) *S. aureus* of the Cu-Cys-Cotton fabric sample.

against both *E. coli* and *S. aureus*. These results show that coating Cu NPs on the cotton fabrics can be significantly contributes to the antimicrobial behavior against both *E. coli* and *S. aureus.*

Considering practical applications, it is necessary to monitor laundering durability of the modified cotton fabrics. Herein, the Cu-Cys-Cotton fabric sample was washed through many laundering cycles, and retest it antibacterial effect. The results were given in Figure 11(c) and 11(d), the BR values was maintained 98 % both *E. coli* and *S. aureus* after withstand 50 laundering cycles. It means that the washing process has little effect on antimicrobial property of the Cu-Cys-Cotton fabric sample.

Stability of the Cu NPs

Figure 12 shows the Cu 2p XPS spectra of the cotton fabric sample, unlike with original cotton fabric, the peaks at 932.3 eV and 952.1 eV of the Cu-Cys-Cotton fabric (before and after 50 washing cycles) can be assigned Cu 2p3/2 and Cu 2p1/2 [53] compare with the original cotton fabric. Observed from Cu 2p XPS spectra of the Cu-Cys-Cotton fabric before and withstand 50 washing cycles, it was shown that the Cu NPs which immobilized on the cotton fabric surface have a good oxidation resistance even withstand 50 washing cycles.

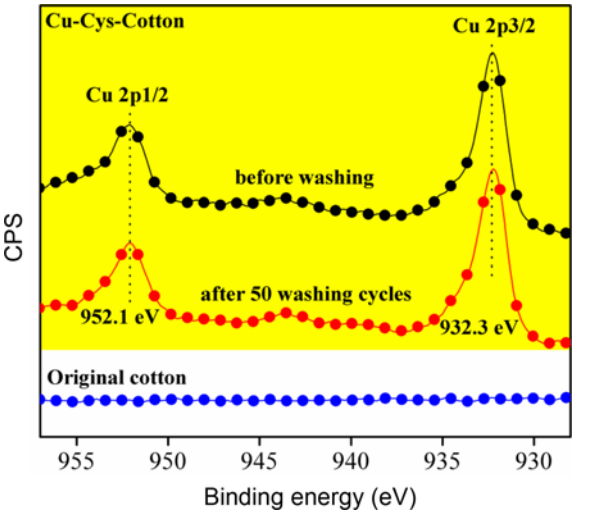


Figure 12. Cu 2p XPS spectra of the original cotton and Cu-Cys-Cotton fabric before and withstand 50 laundering cycles.

Influences on the Intrinsic Properties of Cotton

Consider practical application of the cotton fabrics, it is necessary to test the intrinsic properties such as water vapor permeability, water absorbability, and the mechanical strength. The results were given in Table 2. The vapor permeability

Table 2. Important natures of the cotton fabrics

Sample	Water vapor permeability ($g/m^2/d$)	Water absorption (%)	Tensile strength (MPa)
Original cotton	1145.0±15.0	275.0±3.0	19.7±0.4
Cys-Cotton	1137.0±20.0	281.0±4.0	17.5±0.1
Cu-Cys-Cotton	1128.0±10.0	267.0±6.0	16.8±0.3

value of the Cu-Cys-Cotton fabric is 1145±15 $g/m^2/d$, which approximate equal to the original cotton fabric. Similarity, the Cu-Cys-Cotton fabric also show good water absorbability, which approximate equal to that of the original cotton (the water absorbability of 275.0±3.0 %). The mechanical properties of the cotton fabrics were also studied by measuring the breaking tensile strength. Compare with the original cotton fabric, the tensile breaking strength of the modified cotton were slightly reduced. Figure S1 compares the flexibilities of the original cotton and the Cu-Cys-Cotton fabrics. The original cotton fabric exhibited a good flexibility, as the height of the loop less than 10.9 mm. The Cu-Cys-Cotton showed a small loop height of 12.3 mm, which is similar to original cotton fabric. Considering of those results, the modifications on the cotton fabrics are desirable for the practical wearing.

Conclusion

The durable antibacterial properties were successfully imparted on the cotton fabrics by immobilized particles of Cu NPs. The results clearly revealed that Cys binder can be covalently grafted on the cotton fabrics, and demonstrated it can tightly adhered Cu NPs. ICP-MS analysis determined the loss of the Cu quantity by the 50 washing tests is about 8.9 %, it was explained again that the Cys moieties enhance adhesion capability of the Cu NPs on the cotton fabrics. This method is simple operated and it has large potential applications in biomedical textiles market.

Acknowledgements

This work was financially supported by Public Welfare Technology Application Research Project of Zhejiang Province (2017C31035) and the Natural Science Foundation of China (51573167).

Electronic Supplementary Material (ESM) The online version of this article (doi: 10.1007/s12221-018-8621-1) contains supplementary material, which is available to authorized users.

References

1. G. Y. Luo, G. H. Xi, X. Y. Wang, D. D. Qin, Y. Y. Zhang, F. Y. Fu, and X. D. Liu, *J. Appl. Polym. Sci.,* **134**, 44897 (2017).
2. A. L. Mohamed, M. A. El-Sheikh, and A. I. Waly, *Carbohydr. Polym.,* **102**, 727 (2014).
3. H. E. Emam and R. M. Abdelhameed, *ACS Appl. Mater. Interfaces*, **9**, 28034 (2017).
4. H. E. Emam and T. Bechtold, *Appl. Surf. Sci.,* **357**, 1878 (2015).
5. Q. B. Xu, Y. H. Wu, Y. Y. Zhang, F. Y. Fu, and X. D. Liu, *Fiber. Polym.,* **17**, 1782 (2016).
6. Y. Y. Zhang, Q. B. Xu, F. Y. Fu, and X. D. Liu, *Cellulose,* **23**, 2791 (2016).
7. G. H. Xi, Y. L. Xiu, L. Wang, and X. D. Liu, *J. Appl. Polym. Sci.,* **132**, 41824 (2015).
8. R. Khajavi and A. Berendjchi, *ACS Appl. Mater. Interfaces,* **6**, 18795 (2014).
9. L. Wang, G. H. Xi, S. J. Wan, C. H. Zhao, and X. D. Liu, *Cellulose,* **21**, 2983 (2014).
10. G. H. Xi, W. C. Fan, L. Wang, X. D. Liu, and T. Endo, *J. Polym. Sci. Pol. Chem.,* **53**, 1862 (2015).
11. G. H. Xi, J. Wang, G. H. Luo, Y. H. Zhu, W. C. Fan, M. Q. Huang, and X. D. Liu, *Cellulose,* **23**, 915 (2016).
12. M. Yu, Z. Wang, M. Lv, R. Hao, R. Zhao, L. Qi, and J. Li, *ACS Appl. Mater. Interfaces,* **8**, 19866 (2016).
13. H. E. Emam, M. Rehan, H. M. Mashaly, and H. B. Ahmed, *Dyes Pigment.,* **133**, 173 (2016).
14. H. B. Ahmed and H. E. Emam, *Fiber. Polym.,* **17**, 418 (2016).
15. H. E. Emam, S. Mowafi, H. M. Mashaly, and M. Rehan, *Carbohydr. Polym.,* **110**, 148 (2014).
16. H. E. Emam and M. K. El-Bisi, *Cellulose,* **21**, 4219 (2014).
17. H. E. Emam, N. H. Saleh, K. S. Nagy, and M. K. Zahran, *Int. J. Biol. Macromol.,* **84**, 308 (2016).
18. H. E. Emam, A. P. Manian, B. Široká, H. Duelli, P. Merschak, B. Redl, and T. Bechtold, *Surf. Coat. Tech.,* **254**, 344 (2014).
19. H. E. Emam, H. B. Ahmed, and T. Bechtold, *Carbohydr. Polym.,* **165**, 255 (2017).
20. H. E. Emam, N. S. El-Hawary, and H. B. Ahmed, *Int. J. Biol. Macromol.,* **96**, 697 (2017).
21. H. E. Emam, M. M. El-Zawahry, and H. B. Ahmed, *Carbohydr. Polym.,* **166**, 1 (2017).
22. H. B. Ahmed, N. S. El-Hawary, and H. E. Emam, *Int. J. Biol. Macromol.,* **105**, 720 (2017).
23. H. E. Emam, A. P. Manian, B. Široká, and T. Bechtold, *Carbohydr. Polym.,* **90**, 1345 (2012).
24. C. K. Kang, S. S. Kim, S. Kim, J. Lee, J. H. Lee, C. Roh, and J. Lee, *Carbohydr. Polym.,* **151**, 1012 (2016).
25. A. Errokh, A. M. Ferraria, D. S. Conceição, L. V. Ferreira, A. B. do Rego, M. R. Vilar, and S. Boufi, *Carbohydr. Polym.,* **141**, 229 (2016).
26. C. Wang, J. Lv, Y. Ren, Q. Zhou, J. Chen, T. Zhi, and L. Jin, *Carbohydr. Polym.,* **138**, 106 (2016).
27. M. Faraji, Y. Yamini, and S. Shariati, *J. Hazard. Mater.,*

166, 1383 (2009).
28. J. Wen, J. Li, S. Liu, and Q. Y. Chen, *Colloid. Surface A.,* **373**, 29 (2011).
29. Q. Xu, Y. Zhao, J. Z. Xu, and J. J. Zhu, *Sensor. Actuat. B-Chem.,* **114**, 379 (2006).
30. W. M. Lee, Y. J. An, H. Yoon, and H. S. Kweon, *Environ. Toxicol. Chem.,* **27**, 1915 (2008).
31. M. Grace, N. Chand, and S. K. Bajpai, *J. Eng. Fiber. Fabr.,* **4**, 1 (2009).
32. D. P. Chattopadhyay and B. H. Patel, *J. Eng. Fiber. Fabr.,* **5**, 1 (2010).
33. P. Kanhed, S. Birla, S. Gaikwad, A. Gade, A. B. Seabra, O. Rubilar, and M. Rai, *Mater. Lett.,* **115**, 13 (2014).
34. M. Sampath, R. Vijayan, E. Tamilarasu, A. Tamilselvan, and B. Sengottuvelan, *J. Nanotech.,* **2014**, 626523 (2014).
35. S. K. Bajpai, P. Das, and B. Soni, *J. Ind. Text.,* **45**, 495 (2016).
36. C. Sun, Y. Li, Z. Li, Q. Su, Y. Wang, and X. Liu, *J. Nanomater.,* **2018**, 6546193 (2018).
37. J. Yang, H. Xu, L. Zhang, Y. Zhong, X. Sui, and Z. Mao, *Surf. Coat. Tech.,* **309**, 149 (2017).
38. V. Sadanand, T. H. Feng, A. V. Rajulu, and B. Satyanarayana, *Int. J. Polym. Anal. Ch.,* **22**, 587 (2017).
39. Q. B. Xu, X. T. Ke, D. R. Cai, Y. Y. Zhang, F. Y. Fu, T. Endo, and X. D. Liu, *Cellulose,* **25**, 2129 (2018).
40. R. A. Soomro, A. Nafady, N. Memon, T. H. Sherazi, and N. H. Kalwar, *Talanta,* **130**, 415 (2014).
41. H. Zhao, Q. Liang, and Y. Lu, *Fiber. Polym.,* **16**, 593 (2015).
42. Q. B. Xu, X. T. Ke, L. W. Shen, N. Q. Ge, Y. Y. Zhang, F. Y. Fu, and X. D. Liu, *Int. J. Biol. Macromol.,* **111**, 796 (2018).
43. Q. B. Xu, L. J. Xie, H. Diao, F. Li, Y. Y. Zhang, F. Y. Fu, and X. D. Liu, *Carbohydr. Polym.,* **177**, 187 (2017).
44. Q. B. Xu, J. Y. Gu, Y. Zhao, X. T. Ke, and X. D. Liu, *Fiber. Polym.,* **18**, 2204 (2017).
45. J. Jaczynski and A. T. Tesfai, *Wood, Fiber, Sci.,* **45**, 215 (2013).
46. H. Zhu, G. John, and B. Wei, *Chem. Phys. Lett.,* **405**, 49 (2005).
47. M. Abdulla-Al-Mamun, Y. Kusumoto, and M. Muruganandham, *Mater. Lett.,* **63**, 2007 (2009).
48. R. M. Abdelhameed, H. Abdel-Gawad, M. Elshahat, and H. E. Emam, *RSC Adv.,* **6**, 42324 (2016).
49. H. E. Emam and R. M. Abdelhameed, *J. Porous Mat.,* **24**, 1175 (2017).
50. R. M. Abdelhameed, H. E. Emam, J. Rocha, and A. M. Silva, *Fuel Process. Technol.,* **159**, 306 (2017).
51. A. K. Sasmal, C. Mondal, A. K. Sinha, S. S. Gauri, J. Pal, T. Aditya, and T. Pal, *ACS Appl. Mater. Interfaces,* **6**, 22034 (2014).
52. M. Zhang, J. Pang, W. Bao, W. Zhang, H. Gao, C. Wang, and J. Li, *Appl. Surf. Sci.,* **419**, 16 (2017).
53. Z. Komeily-Nia, M. Montazer, and M. Latifi, *Colloid. Surface A.,* **439**, 167 (2013).