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Preparation of Copper Nanoparticles Coated Cotton Fabrics with Durable Antibacterial Properties

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Abstract: When copper nanoparticles (Cu NPs) were applied as an antimicrobial agent to finish cotton fabrics, there are two issues should be solved: the oxidization and the weak adsorbability onto cotton fiber surface. In the present work, we developed a new method that can achieve both immobilization and protection of the Cu NPs at the same time. As an effective binder, thioglycolic acid (TGA) was covalently linked to cotton fiber surface via an 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 TGA and citric acid, the Cu NPs immobilized on the fabric surface showed an excellent antibacterial effect and outstanding laundering durability. Even after 50 consecutive laundering tests, the modified cotton fabrics still showed satisfactory antibacterial ability against both *S. aureus* and *E. coli*, which the bacterial reduction rates are all higher than 96 %. It is believed that this methodology has potential applications in a wide variety of textile productions such as sportswear, socks, and medical textiles.

Keywords: Cotton fabric, Surface modification, Copper nanoparticles, Thioglycolic acid, Antimicrobial effect

Introduction

The cotton fabric is an important member in the textile fabric family for a long time, because its desired cotton natures, e.g., flexibility, water absorptivity, and breathability, make cotton textiles wearing comfortable, and thus favored by people [1-6]. To enhance competitive advantages of cotton products, researchers have been attempting to endow cotton fabric with additional functions. Recently, such studies have been focused on antibacterial activity [7-11], hydrophobic properties [12,13], UV protection [14-16], self-cleaning ability [17], and flame retardance [18,19]. Among these, the research area of antibacterial function is the most active one because bacterial problem is an obvious shortcoming that limits application of cotton fabrics. Cotton fabric generally provides suitable conditions for microorganism growth, leading to bacterial contamination on cotton fabrics and even can become a considerable health concern [20-22]. A lot of antimicrobial agents have been incorporated into the cotton fabrics, and it was found that nanoparticles (NPs) on the cotton fabrics can effectively inhibit the growth of bacterial and fungi [23-26].

Especially, the inorganic nanoparticles of silver [27-31], copper oxide [32,33], gold [34-36], and copper [37] have been extensively studied due to their large surface area and outstanding antimicrobial effect. Copper nanoparticles (Cu NPs) are a class inorganic nanomaterial of interesting potential applications such as catalyst [38-40], electrical conductor [41], and sensor [42]. Due to their high antimicrobial capability and low toxicity [43], they have been widely applied as antimicrobial agents to finish cotton fabrics [44].

However, a number of reports [45-47] have mentioned that there are two drawbacks in the use of Cu NPs for finishing cotton fabric: the oxidization and the weak adsorbability onto cotton fiber surface. To prevent the oxidization of Cu NPs on the cotton fabrics, numerous strategies have been reported [46-48]. For example, Montazer group [46] found that Cu NPs on cotton surface can be effectively protected by introducing of citric acid. Anna group [47] reported a novel method to synthesis of Cu NPs by microwave irradiation. Thirumalaisamy group [48] used stearic acid to cover the surface of Cu NPs, obtaining a good effect on preventing oxidation. 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.

Here, we propose a novel approach using thioglycolic acid (TGA) as a binder. TGA can covalently link to cotton fabric via esterification with the hydroxyl groups of cellulose, and can tightly adhere Cu NPs by coordination bonds. The thiol groups of TGA not only provides Cu NPs with excellent immobilization on cotton surface, but also protects Cu NPs form oxidization [49].

In the present work, antibacterial cotton fabrics are prepared by Cu NPs. Sodium borohydride is used as a reducing agent and citric acid is a stabilizer to prevent Cu NPs agglomeration and oxidation [49]. The resulting cotton fabric samples are characterized using the following methods: field emission scanning electron microscope (FE-SEM), fourier transform infrared spectrum instrument

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(FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). 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

Materials

Thioglycolic acid (TGA) was purchased from Shanghai Aladdin Co., Ltd. (China). The cotton fabric was purchased from Shaoxing Qidong Textile Co., Ltd. (60 ends/cm, 30 picks/cm, 0.42 mm thickness, 120 g/m^2 weight, 35.2 m^2/g specific surface area). Before chemical modification, the cotton fabric samples (3.0 cm×3.0 cm) were cleaned by ultrasonic washing in 2 % sodium laurylsulfonate solution for 30 min, then washing in ethanol (2 h) and deionized water (30 min×3 times). Other reagents were purchased from Shanghai Aladdin Co., Ltd. (China) and used without further purification.

Preparation of TGA-Cotton Fabrics

Raw cotton fabric sample (original cotton) was immersed in TGA solution (1 v/v %, 100 m*l*) for 3 min with the para-toluene sulphonic acid as a catalyst, padded to give a wet pick up of 80±2 %, cured at 130 ^{o}C for 20 min, rinsed with distilled water (50 m*l* × 3 times), and finally dried at 100 ^{o}C for 1 h to obtain TGA-C1 fabric sample. The samples of TGA-C2 and TGA-C3 were prepared via a similar process but with different concentration of the TGA solution (Table 1).

Synthesis of Copper Surface on Cotton Fabrics

For coating of Cu onto cotton fabrics, copper sulfate was dissolved in distilled water (100 m*l*, 0.04 mol/*l*), and citric acid (4.76 mmol) as a protective agent was added to the solution at 50 ^{o}C with stiring. Then the TGA-Cotton fabric sample was immersed into the solution for 30 min, the solution of sodium borohydride (10 m*l*, 0.13 mol/*l*) was introduced into the solution with stiring to reduce the copper salt, the temperature was declined to 40 ^{o}C, and the treament 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 sample of the Cu-TGA-C1 fabric. Samples of Cu-TGA-C2 and Cu-TGA-C3 were prepared using the TGA-C2 and TGA-C3, respectively.

Characterizations

Surface morphology of the cotton fabrics was investigated using an FE-SEM set (Ultra-55, Zeiss, Germany) with an energy dispersive X-ray spectrometer (EDS). Size distribution of the Cu NPs on fiber surface was calculated by statistically measuring 200 bright points in the SEM image. FTIR measurements were performed on a Nicolet Avatar 370 spectrometer (Nicolet Company, Madison, USA) with an attenuated total reflection (ATR) accessory. The XRD analyses for the modified cotton fabrics were obtained using an X-ray diffractometer (ARL XTRA, Switzerland). The XPS analysis was performed using an AXIS multifunctional X-ray photoelectron spectrometer (ULTRA DLD, Shimadzu Ltd., Japan) at a power of 450 W. The copper content in the Cu-TGA-Cotton fabrics was measured using inductively coupled plasma mass spectrometry (ICP-MS, Aglient 7500a, Australian). Abrasion tests were performed using a Martindale abrasion instrument (HZ-8029A, China) according to DIN EN ISO 12947-3.

Basing on XRD analyses, the average size (D_{cu}) of the Cu NPs in the modified cotton fabrics were calculated using the Debye-Scherrer equation:

$$D = K\lambda\,(\beta\cos\theta)^{-1}$$

where λ is the wavelength of the X-ray radiation (Cu Kα= 0.15418 nm), K is the constant, taken as 0.89, β is the line width at half-maximum height, and q is the diffracting angle.

The detailed method of the antibacterial tests, laundering tests, water absorptivity, water vapor permeability, flexibility, and tensile strength tests [7-9] of the cotton fabric were described in the Supporting Information.

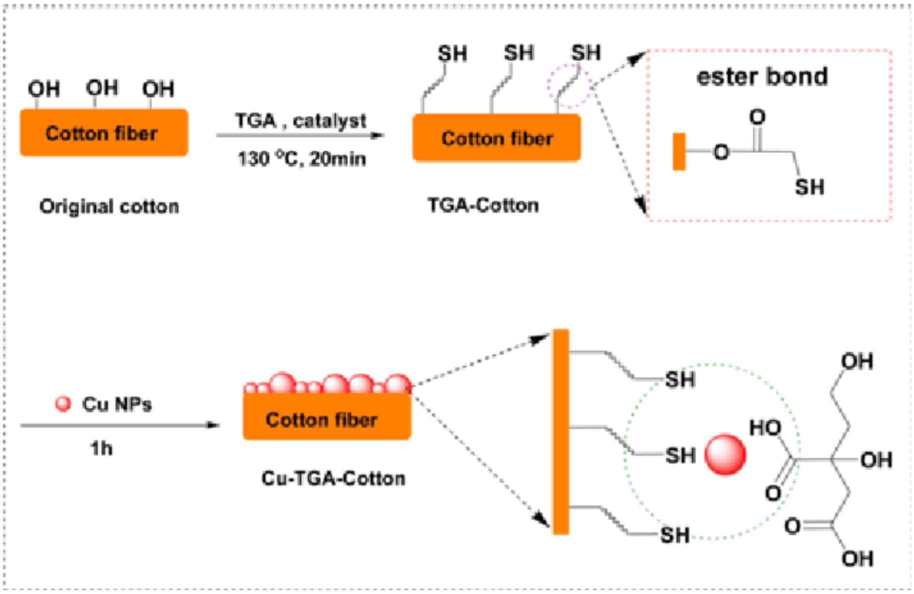
Results and Discussion

Fabrication of the Antimicrobial Cotton Surfaces

Scheme 1 shows the modification process on a cotton fabric sample. First, the carboxylic groups of the TGA were reacted with the hydroxyl groups on the cotton surface at 130 ^{o}C for 20 min. Then the linked TGA acts as a binder to adsorb the Cu^{2+} by the coordination bonds between the thiol groups. 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 adding $NaBH_4$ solution as a reducing agent leads to the generation of Cu^0. As results, the Cu NPs coating on the cotton fabrics were protected by citric acid and thiol groups, thus are well protected from oxidization [49].

Figure 1 compares the ATR-FTIR spectra of the original cotton fabric and modified cotton fabric samples. The cotton fabric sample show the peak at 3329 cm^{-1} can be assigned to the -OH group [14,15,50-52]. However, the modified cotton fabric samples (Figure 1(b), Figure 1(c) and Figure 1(d)) exhibit new peaks appeared at 1746 cm^{-1} and 2530 cm^{-1}, and they are attributable to the C=O (in ester group) and S-H groups, respectively, which suggested that esterification occurs between the TGA molecules and the cotton fabrics. With the increase in the concentration of TGA solution, the peaks of modified cotton fabric is more and more obvious. These results suggest that esterification reaction took place between the TGA and the cotton fabric surface.

Figure 2 shows the XRD spectra of original cotton fabric and the modified cotton fabric samples. The modified cotton



Scheme 1. The surface modification on the cotton fabrics.

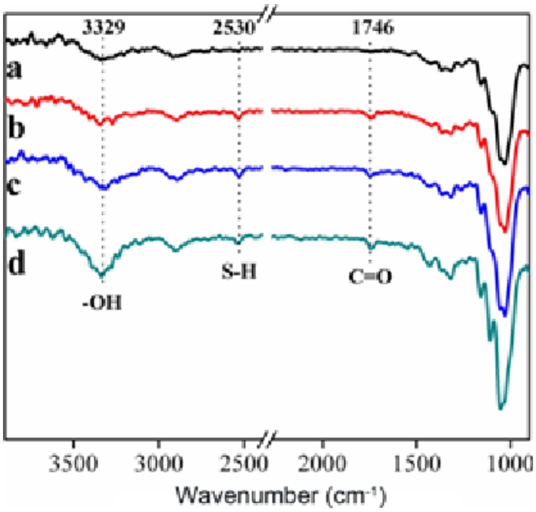


Figure 1. ATR-FTIR spectra of the (a) original cotton, (b) Cu-TGA-C1, (c) Cu-TGA-C2, and (d) Cu-TGA-C3 fabric samples.

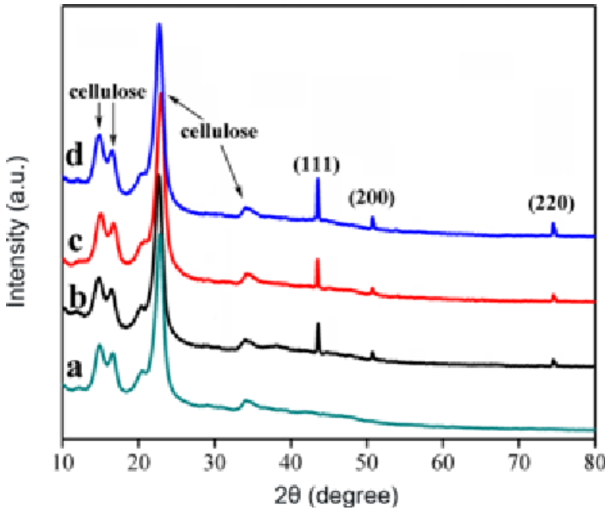


Figure 2. XRD patterns of the (a) original cotton, (b) Cu-TGA-C1, (c) Cu-TGA-C2, and (d) Cu-TGA-C3 fabric samples.

fabric samples show the typical peaks at 43.7 °, 50.9 ° and 74.5 ° for the index (111), (200) and (220) planes of Cu particles, respectively. Based on XRD pattern and Debye-Scherrer equation, it was calculated the Cu NPs on the modified cotton fabric samples as shown in the Table 1. The average size of the Cu-TGA-C1, Cu-TGA-C2, and Cu-TGA-C3 fabric samples is 56.4 nm, 65.1 nm and 70.5 nm, respectively.

Figure 3(a) and Figure 3(b) show the wide-range XPS spectra of the original cotton fabric and the Cu-TGA-C1 fabric samples. The original cotton fabric displays C 1s and O 1s signals, but the modified cotton fabric (Cu-TGA-C1) has additional S 2p and Cu 2p signals. The C1s high resolution XPS spectra of original cotton fabric and Cu-TGA-C1 fabric samples are shown in Figure 3(c) and Figure 3(d). The peak for original cotton fabric is decomposed to three peaks with binding energy of 284.1 eV (C-C), 286.2 eV (C-OH), and 288.7 eV (C-O-C). In the case of the Cu-TGA-C1 fabric, new peaks observe at 287.2 eV and 288.8 eV, which are assigned to C-S and C=O/C-O-C bonds, respectively. The coordination of the Cu NPs and the thiol groups which grafted on the cotton fabrics were investigated in Figure 3(e) and Figure 3(f), the peaks at 168.5 eV and 161.9 eV is attributable to the highly de-electronated S elements, and the Cu signals can be fit in two peaks (centered at 933.2 eV and 953.1 eV), which are consistent

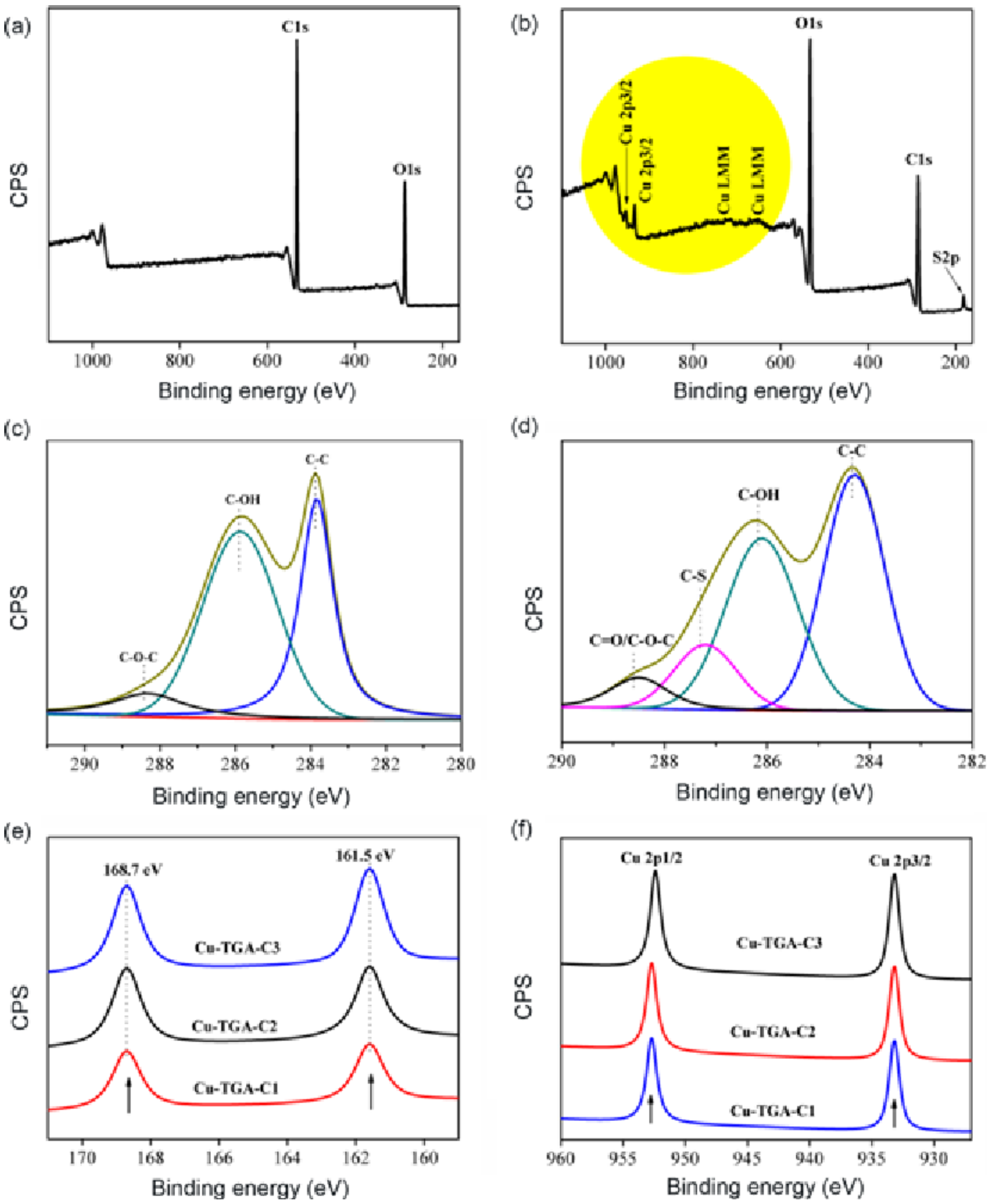


Figure 3. XPS survey and deconvoluted Cls XPS spectra of the (a, c) original cotton fabric sample, (b, d) Cu-TGA-C1 fabric sample. The S 2p XPS spectra (e) and Cu 2p XPS spectra (f) of the cotton fabric samples.

with Cu 2p3/2 and Cu 2p1/2, respectively. It's suggests that electron transfer happened between the S and Cu elements. These XPS analyses suggest that the TGA was covalently linked on the cotton fiber surface via formation of ester groups, and the Cu NPs has been immobilized on the modified cotton fabric surface by coordination bonds.

The low-magnification and high-magnification SEM images of the cotton fabric surfaces were showed in Figure 4. The low-magnification SEM of the cotton fabric samples showed insignificant changes after the modifications with TGA and Cu NPs, which implied that the Cu NPs mainly coated the fiber surface and did not occupy the voids between the fibers. In the high-magnification SEM of the cotton fabric samples, there are many small white particle on the modified cotton fabric surface, it was indicated that the Cu NPs was successfully immobilized on the cotton fabric surfaces. The dispersion of Cu NPs coating on the cotton fiber surface was confirmed by the high-magnification (×20000) SEM images (Figure 5(a), Figure 5(b), and Figure 5(c)), the EDS mapping images (Figure 5(d-i)) of the

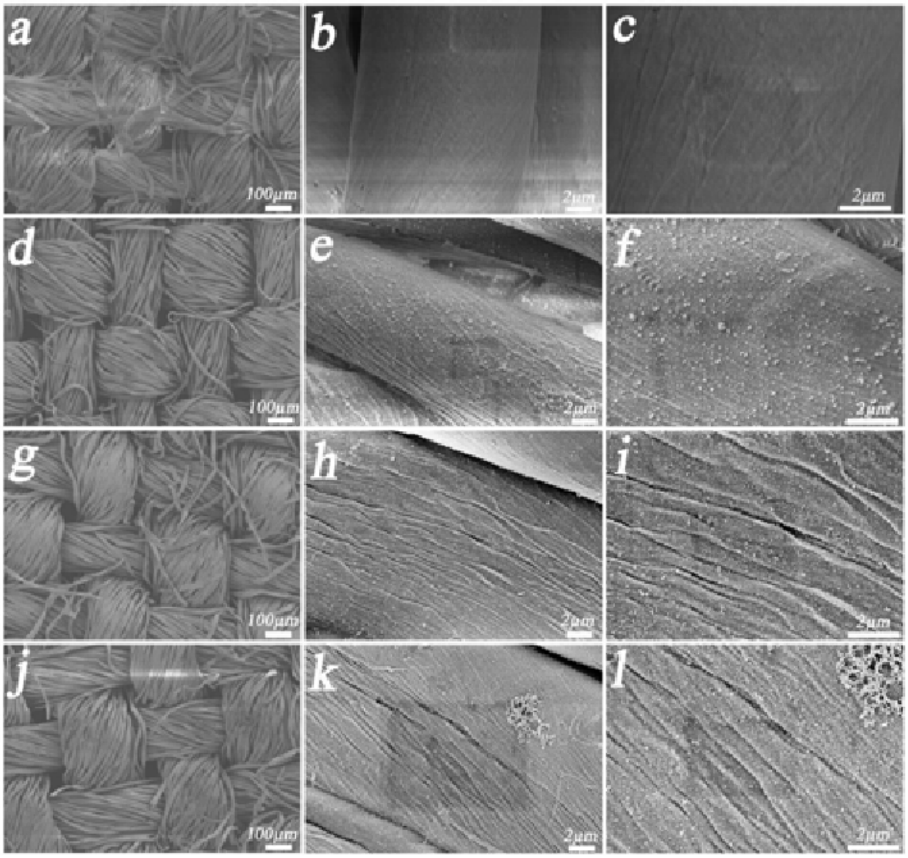


Figure 4. SEM images of the (a, b, c) original cotton, (d, e, f) Cu-TGA-C1, (g, h, i) Cu-TGA-C2, and (j, k, l) Cu-TGA-C3 fabric samples.

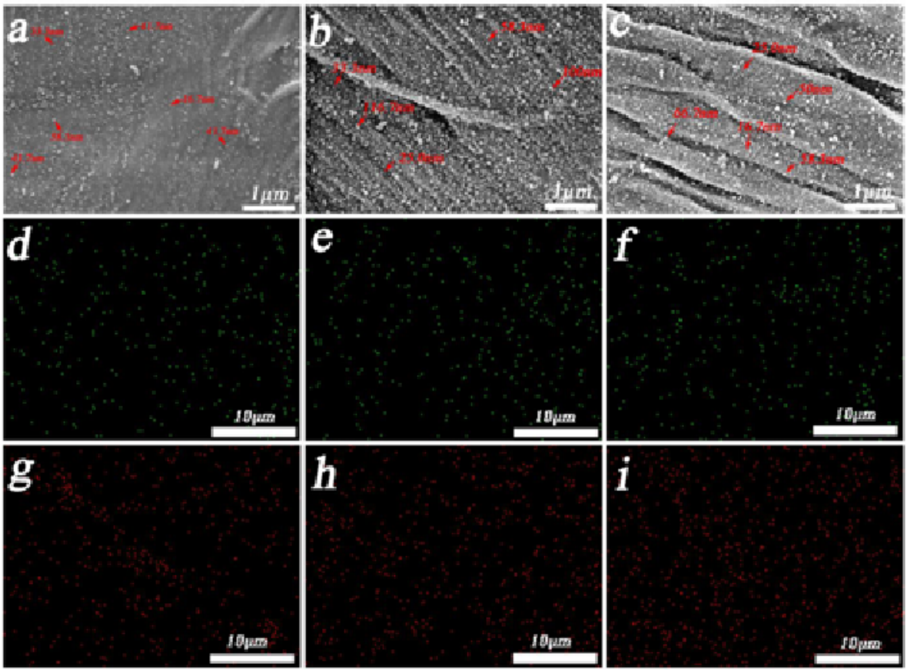


Figure 5. High magnification SEM images (a, b, c), S mapping (d, e, f), and Cu mapping (g, h, i) images of the Cu-TGA-C1 (a, d, g), Cu-TGA-C2 (b, e, h), and Cu-TGA-C3 (c, f, i) fabric samples.

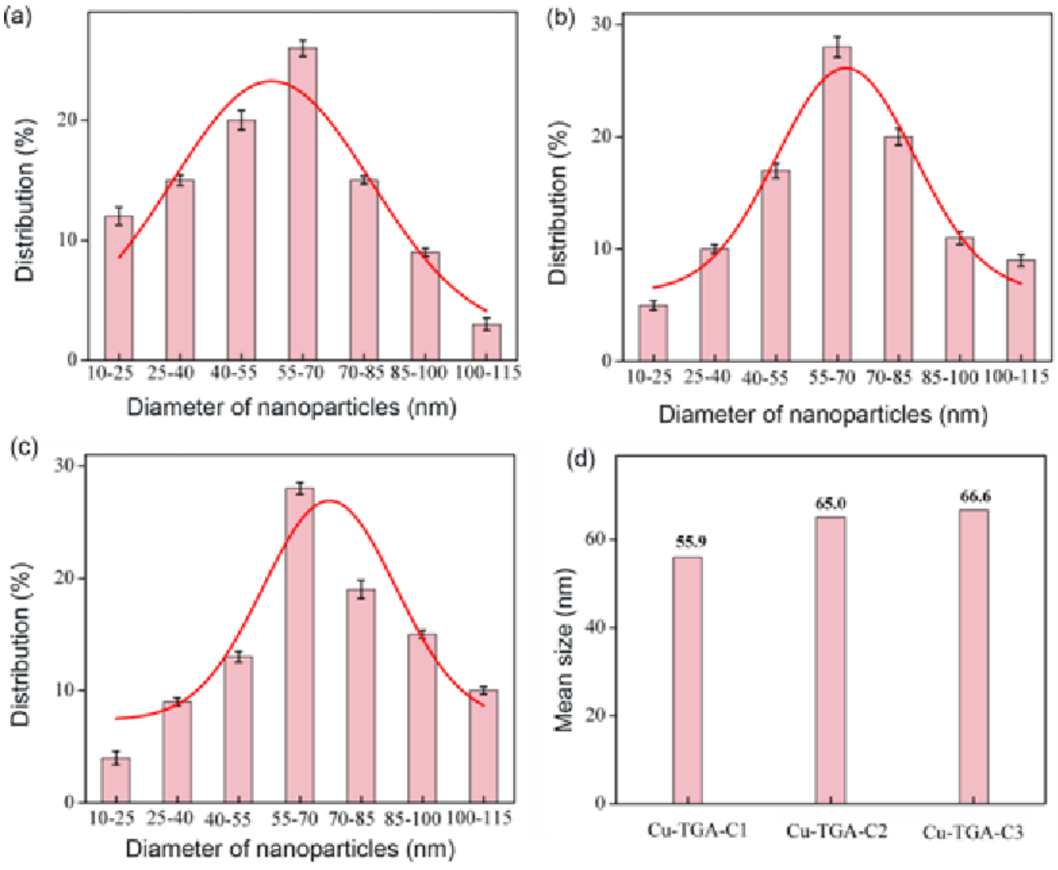


Figure 6. Size distribution (a, b, c) and mean size (d) of the Cu-TGA-C1 (a), Cu-TGA-C2 (b), and Cu-TGA-C3 (c) fabric samples.

modified cotton fabric surfaces show the distribution of S and Cu, this results was confirmed again that the TGA and Cu NPs were immobilized on the cotton fabric surfaces. We make a statistical analysis of the bright points, giving a size distribution diagrams based on the high magnification (×20000) SEM images as shown in Figure 6. It was found that the Cu NPs on the modified cotton fabric samples, Cu-TGA-C1, Cu-TGA-C2, and Cu-TGA-C3 have average size of 74.0 nm, 74.6 nm and 75.2 nm, respectively. This result is in good agreement with the particle size data calculated by Debye-Scherrer equation according the XRD images.

Antibacterial Durability of the Modified Cotton Fabrics

To investigate the antimicrobial behavior of the modified cotton fabrics, antimicrobial tests were performed. Figure 7(a) and Table 1 shows the antimicrobial effect of the modified cotton fabrics, the BR values of the three modified cotton fabric for both bacteria after 1 h contact period are all 99 %. Whereas the TGA modified cotton without Cu NPs showed poor antimicrobial effect with BR rates lower than 10 %. These results indicating that the loading Cu NPs on the cotton fabric significantly contributes to the anti-microbial behavior against both *E. coli* and *S. aureus.*

The laundering durability is another important parameter for the modified cotton fabrics. In this work, sample of the Cu-TGA-C1 fabric was investigated antimicrobial laundering test. The Cu-TGA-C1 fabric was washed through many laundering cycles and their antibacterial performance was retested. As shown in Figure 7(b) and Figure 7(c), after 50 washing cycles, the antimicrobial rate remains 96 % both *E. coli* and *S. aureus*. This results show that the washing process has a little effect on antimicrobial property of modified cotton fabric.

Figure 8(a) shows the inhibition zones of the Cu-TGA-C1 fabrics before and after withstand different abrasion cycles, indicating that the antimicrobial effect of these cotton fabrics against both *E. coli* and *S. aureus* are very effective when compared with the original cotton. As shown in Figure 8(b) and Figure 8(c), the antimicrobial rate remains 90 % both *E. coli* and *S. aureus* of the Cu-TGA-C1 fabric even after withstand 600 abrasion cycles. It means that the abrasion process has a little damaging effect on antimicrobial property of the modified cotton fabrics.

ICP-MS Analysis Cu Quality of the Cotton Fabrics before and after Laundering Cycles

To examine the quality of Cu NPs on the cotton fabric surface, elemental analyses of the modified cotton fabric by

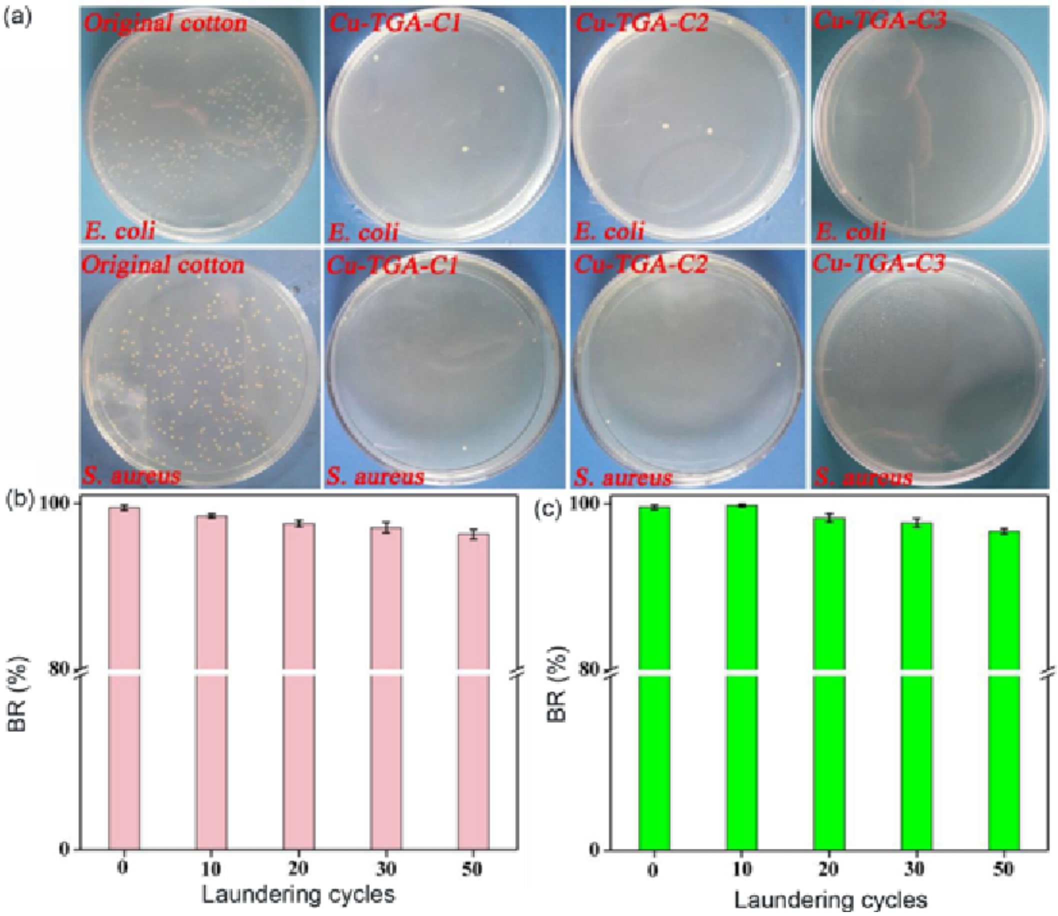


Figure 7. The antibacterial effect of the cotton fabric samples, (a) the optical images of the antibacterial tests, and the antibacterial durability results of the Cu-TGA-C1 against (b) *E. coli* and (c) *S. aureus*.

Table 1. Information and antibacterial effect of the cotton fabric samples

Sample	TGA (V/V %)	W_{Cu}[a] (mg/g)	$D_{Cu\ NPs}$[b] (nm)	BR (%)	
				E. coli	*S. aureus*
TGA-C1	1.00	-	-	5.2±0.47	6.3±0.68
TGA-C2	2.00	-	-	7.1±0.33	7.9±0.65
TGA-C3	4.00	-	-	8.9±0.72	9.4±0.47
Cu-TGA-C1	1.00	1.613	56.4	99.5±0.33	99.6±0.28
Cu-TGA-C2	2.00	1.817	65.1	99.8±0.12	99.9±0.10
Cu-TGA-C3	4.00	1.904	70.5	100	100

[a]W_{Cu} was determined by the ICP-MS analysis and [b]The mean size of the crystal particles was calculated by Debye-Scherrer equation.

ICP-MS. It was found that the quality of Cu NPs on the modified cotton fabric samples, Cu-TGA-C1, Cu-TGA-C2, and Cu-TGA-C3 is 1.613 mg/g, 1.817 mg/g and 1.903 mg/g, respectively. These results were indicated that increase amount of the TGA during the modification process, it can effectively increase the amount of Cu NPs which immobilized on the cotton fabric surface. In order to study stability of the Cu NPs which coating on the Cu-TGA-C1 fabric before and after laundering cycles. As shown in Table 2, it is obvious that the quality of Cu element loss is severe in the first 20 cycles, and it becomes steady in the subsequent washing cycles. After 50 laundering tests, the quantities of Cu NPs about 91.8 % on the cotton surfaces compare with no washing cotton fabrics. The results show that the Cu loss from the modified cotton fabrics is insignificant during the washing process.

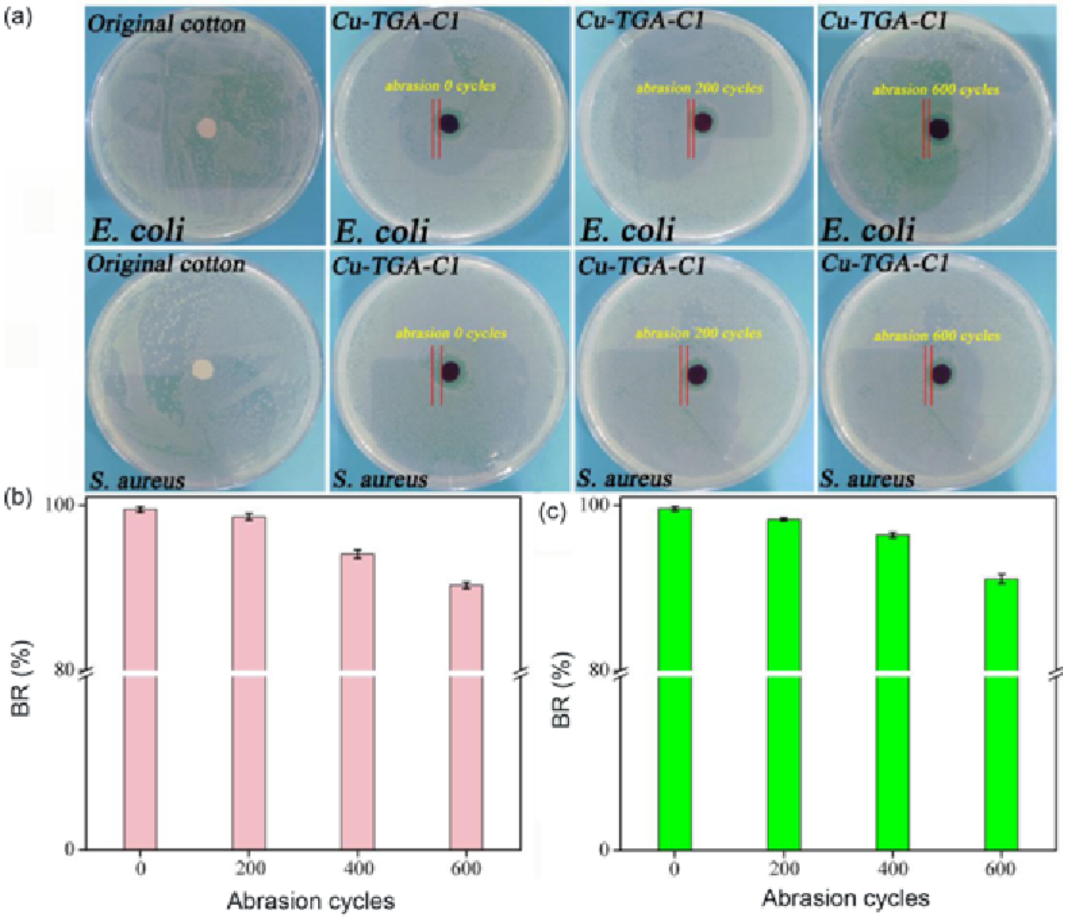


Figure 8. Inhibition zone test of the cotton fabric samples (a) and the antibacterial results of the Cu-TGA-C1 against *E. coli* (b) and *S. aureus* (c) after withstand abrasion tests.

Table 2. The Cu loss of the Cu-TGA-C1 fabric against the washing by ICP-MS

Washing cycles[a]	Cu content (mg/g)	Remaining of Cu (%)
0	1.613	-
10	1.586	98.3
20	1.557	96.5
30	1.496	92.7
40	1.482	91.9
50	1.480	91.8

[a] The washing period of the cotton fabric sample is ten min.

Influences on the Intrinsic Properties of Cotton Fabric

The modifications on cotton fabrics should not give significant damages on the desired cotton natures such as vapor permeability and water absorbability, which are comfortable to the human skin [53-57]. Therefore, these two properties were tested in this work for the modified cotton fabrics. As shown in the Figure 9(1) and Figure 9(2), the modified cotton fabrics show the good vapor permeability of which is close to the original cotton fabric (the vapor permeability of 1155±20 g/m^2/d). In the water absorbability test, the modified cotton has lower water absorbability when compared with the original cotton fabric (the water absorbability of 275±6.2 %). Especially the water absorbability of Cu-TGA-C3 fabric decreased 22.6 % by comparing with the original cotton fabric. The mechanical properties (Figure 9(3)) of the cotton fabrics were also studied by measuring the breaking tensile strength. The increase on concentration of TGA during the modification process causes the tensile breaking strength of the cotton fabric reduced obviously. Moreover, when compared with the original cotton fabric, the tensile breaking strength of the Cu-TGA-C3 was decreased 26.3 %. Figure 9(4) compares the flexibilities of the original cotton fabric and the Cu-TGA-C1 fabric. The original cotton fabric exhibited a good flexibility, as the height of the loop less than 14.3 mm. The Cu-TGA-C1 showed a small loop height of 17.8 mm, which is similar to original cotton fabric. The vapor permeability, water absorbability, tensile breaking strength, and flexibility of the modified cotton are almost not adversely affected. This is

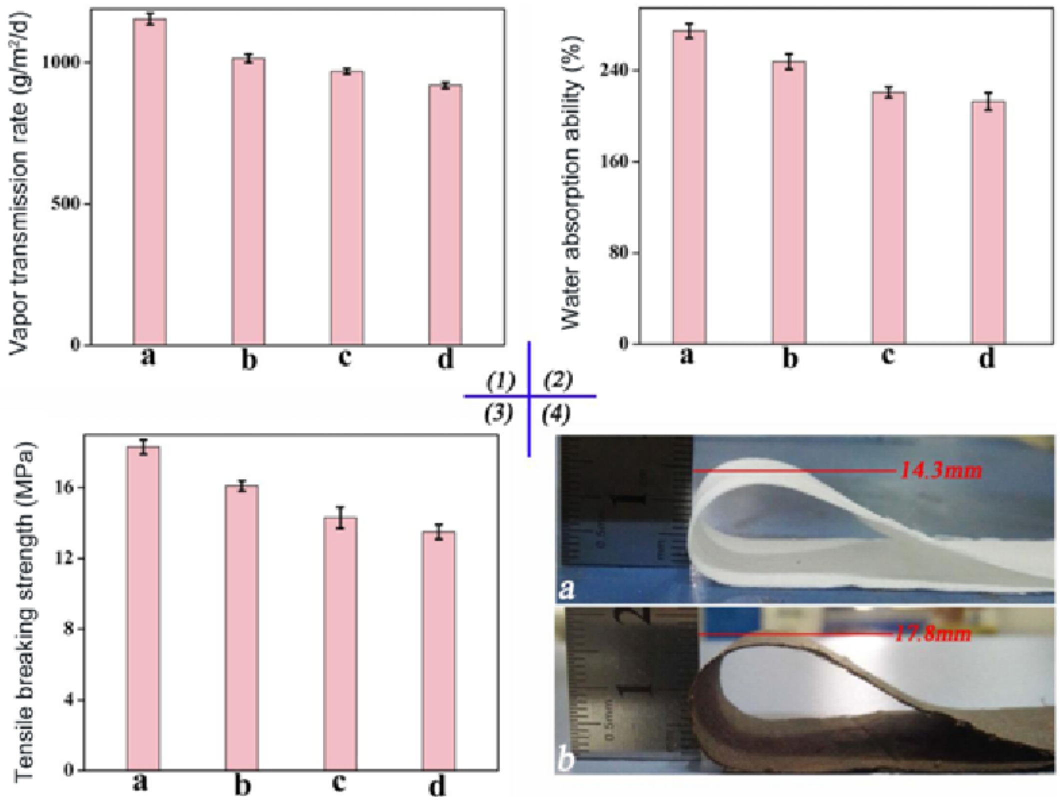


Figure 9. Influence of the surface modification on several cotton natures, including (1) water vapor transmissibility, (2) water absorbability, (3) tensile strength, and (4) flexibility. (a) Original cotton, (b) Cu-TGA-C1, (c) Cu-TGA-C2, and (d) Cu-TGA-C3 fabric samples.

desirable for the practical wearing.

Conclusion

In situ synthesis of Cu NPs on cotton fabrics has been successfully achieved by a chemical reduction method. The TGA moieties were covalently linked on the cotton fabric surface showed a remarkable adhesion effect with the Cu NPs, endowing the modified cotton fabric with outstanding antibacterial durability. The BR values of the modified cotton remained over 96 % with further 50 washing cycles. The ICP-MS analysis indicated that the Cu loss during the 50 washing tests was approximately 8.1 %. These results suggest that TGA binder enhance adhesion capability of the Cu NPs on the cotton fabrics. It has great potential for practical applications in biomedical textiles.

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