

Grafted antimicrobial cotton fabrics with N-halamine groups via atom transfer radical polymerization

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Abstract

An *N*-halamine precursor 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate (SCMHBMA) was synthesized and grafted on cotton fabrics via atom transfer radical polymerization for antibacterial function after chlorination. The preparation and chlorinated cotton fabrics (Cotton-g-PSMA-Cl) were characterized with FTIR, XPS, SEM, and TGA. The properties of prepared Cotton-g-PSMA-Cl, including thermal property, antibacterial efficiency, durability, and stability, were systematically evaluated. The results showed that these chlorinated Cotton-g-PSMA-Cl fabrics possessed excellent antibacterial activity against *E. coli* and *S. aureus*. After 10 washing cycles and 60 days of routine storage, active chlorine concentrations (Cl⁺%) were reduced only 22% and 18%, respectively, and the reduced Cl⁺% effectively reverted by simple rechlorination. This new *N*-halamine antibacterial cotton composite with superior antibacterial properties exhibited potential for future application in the long-term antibacterial field.

1. Introduction

As natural cellulose materials, cotton has been used diverse application fields, such as health care, medical treatment, sportswear, and hygienic products, due to being nonirritating to skin and having excellent wearability. However, depending on the environment, natural cotton fibers are more susceptible to bacteria, viruses, and fungi, which can trigger contact infection and damage to cotton fibers (Liang et al. 2007; Liu et al. 2017; Staneva et al. 2019). Fortunately, as a kind of nature cellulose, cotton consists of macropolysaccharides which have plentiful -OH groups and a few carboxylic acid groups (Hou et al. 2017; Przybylak et al. 2016). These polysaccharide structures allow incorporation of various functionalities to cotton, which can result in cotton with new desirable properties, such as antimicrobial activity (Cai et al. 2018; Chen et al. 2016). Thus, several decades of research has focused on the development of antibacterial cotton fabrics to control infection and transmission of diseases (Fei et al. 2018; Humpolicek et al. 2017; Mehrez et al. 2018; Milorad et al. 2018; Mohamed et al. 2017; Ravindra et al. 2010; Srisod et al. 2018).

To date, many types of inorganic, organic, and natural antimicrobial agents, such as silver ions (Maghimaa and Alharbi 2020; Xu et al. 2018), quaternary ammonium salts (Gao et al. 2019; Zhang et al. 2018), *N*-halamine compounds (Ma et al. 2019c; Zhang et al. 2019), and chitosan (Abdou et al. 2010), have been incorporated into cotton fabrics to obtain antibacterial properties. Among these antimicrobial substances, *N*-halamine precursors are the favored biocides in studies because of their high-efficiency, celerity, durable, rechargeability, and broad-spectrum antibacterial properties (Ma et al. 2019a; Si et al. 2018; Wang et al. 2019). These *N*-halamine compounds have the ability to inactivate microorganisms by releasing strong oxidizing free halogen cations after halogenation of the functional -N-H groups to form oxidative -N-Cl or -N-Br antibacterial moieties (Bai et al. 2018; Zheng et al. 2021).

The grafting of *N*-halamine onto cotton using various polymerization techniques has been reported by numerous researchers (Dong et al. 2017; Jiang et al. 2014). An *N*-halamine biocidal monomer VBDMH

has been synthesized and used to form antibacterial thin-films on surfaces of cotton fabrics using an admicellar polymerization method in a three-step process (Ren et al. 2008). After chlorination, polymeric-coated cotton fabrics effectively inactivate both *Staphylococcus aureus* and *Escherichia coli* L. However, the preparation method is relatively complex, which is unfavorable for manufacturing. Inexpensive and commercially available *N*-halamine methylene-bis-acrylamide (MBA) has been bonded onto cotton fabrics via a reliable catalytic solid-state reaction in water (Tian et al. 2017). The properties of these cotton fabrics show powerful antimicrobial properties against representative bacteria, *S. aureus* and *E. coli*, after chlorination, but the grafting rate of antimicrobial cotton is less than satisfactory. To date, the main weakness of the reported preparation methods includes side reactions, uncontrollability due to multistep reactions, and undesired chain degradation of the cotton backbone. Thus, polymerization techniques to bond antimicrobial agents onto cotton have become the subject of intensive research. Atom transfer radical polymerization (ATRP) is a powerful technique to prevent formation of undesired byproducts by effecting fabrication of well-defined polymer brushes on various substrates (Engineering and University 2017; Li et al. 2019; Wang et al. 2020). In addition, the mild polymerization conditions for ATRP protect the substrates, thus avoiding damage to the fiber backbone.

The objective of this study was to obtain and characterize an antibacterial cotton fabrics grafting with *N*-halamine biocidal agent via a homogeneous ATRP under mild conditions. The outline of the synthesis of the *N*-halamine precursor 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido) (SCMHBMA) and the cotton-based ATRP macroinitiator (Cotton-Br) were presented and the *N*-halamine-based antibacterial cotton copolymer (Cotton-g-PSMA) prepared under mild conditions in the presence of the ATRP macroinitiator. With this macroinitiator, the target substance was achieved without the formation of undesired byproducts during polymerization. In addition the antibacterial activity of the functionalized cotton after chlorination was investigated against *S. aureus* and *E. coli*. The stability and recharge ability of antibacterial cotton copolymer were also considered for potential future application value.

2. Experimental

2.1 Materials

Cotton fabric (Cotton), 100% desized and bleached, was purchased from Huafang Group (Zhangjiagang, China). Ethyl acetoacetate (99%), guanidine carbonate (98%), and ethanol (EtOH) were purchased from TCI Development Co., Ltd. (Shanghai, China). Triethylamine (TEA), household bleach (5% sodium hypochlorite), 2-iso-cyanatoethyl methacrylate (ICEMA), dibutyltin dilaurate (BDTDL, 98%), 2-isocyanatoethylmethacrylate, and hydrochloric acid (HCl, 35%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Cupric bromide (CuBr_2), *N,N*-dimethylformamide (DMF), stannous octoate ($\text{Sn}(\text{EH})_2$), 2-bromoisobutyryl-bromide (BiBB), tris[2-(dimethylamino)ethyl]amine (Me_6Tren), ethyl 2-bromoisobutyrate (EBiB), and methanol (CH_3OH) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Unless otherwise stated, all chemicals were used without further purification. A 2-amino-6-methylpyrimidin-4(1H)-one (MIC) was prepared according to the reported literature (Beijer et al. 1998). Unless otherwise stated, all chemicals were of analytical grade and used without further

purification. *S. aureus* ATCC29213 and *E. coli* ATCC25922 used for antibacterial tests were provided by the Institute of Microbiology, Chinese Academy of Science (Beijing, China).

2.2 Preparation of cotton grafted SCMHBMA to achieve antibacterial activity Synthesis of N-halamine precursor

The preparation of N-halamine precursor SCMHBMA was carried out referring to the reported literature (Beijer et al. 1998) and shown in Fig. S1. A 50 mL volume of DMSO and 3.0 g of MIC were added in a 150 mL three-necked flask and the mixture heated at 150 °C with stirring until the MIC was completely dissolved. Then, the flask was quickly removed from the oil bath and 4.1 g of ICEMA added to the flask with stirring and stirred for 10 min. After cooling to room temperature, the resulting solution was poured into 500 mL of methanol and precipitated as white floccules. The product was retrieved by filtration and dried under vacuum at 50 °C for 12 h. The ¹H-NMR spectrum of SCMHBMA is provided in supporting information (Fig. S2)

Preparation of cotton-Br

In a flask, 5 g of cotton fabric (5 × 5 cm pieces), 8 mL of BiBB, and 15 mL of TEA were dispersed in 75 mL of DMF by mechanical stirring. The solution was stirred in a sealed flask at room temperature for 24 h. Then, the product (Cotton-BR) was washed alternately thoroughly with acetone and water and dried under vacuum at 50 °C for 12 h (Fig. 1).

Preparation of cotton-g-PSMA

In this preparation process, 4 g of cotton-BR (3×3 cm pieces), 2.3 g SCMHBMA, and 30 mL of DMF were added in a 100 mL Schlenk flask under mechanical stirring. Then, 2.5 mg of CuBr₂ (0.011 mmol), 10 mg of EBiB, and 23 μL Me₆Tren (0.086 mmol) were added sequentially to the flask. After 30 min of purged with N₂, 5 mg of deoxygenated Sn(EH)₂ was added in the mixture. Next, the flask was held in a 60 °C water bath with uninterrupted stirring for 48 h to allow polymerization. The molecular weight of the grafted polymer could be tailored by the addition of EBiB, as a sacrificial initiator (Table S1). Finally, the obtained Cotton-g-PSMA was washed several times with DMF and acetone and dried under vacuum to a constant weight (Fig. 1). The free polymer of PSMA initiated by EBiB was precipitated into methanol, filtered, and dried under vacuum to a constant weight.

2.3 Chlorination and titration analytical procedure

The resulting cotton fabric samples grafted with SCMHBMA were chlorinated by soaking in 2% NaClO at room temperature for 1 h. The pH of the bleaching solution was adjusted to ~7 by adding HCl (1 mol/L). After chlorination, the chlorination fabric (Cotton-g-PSMA-Cl) swatches were washed thoroughly with abundant distilled water to remove free oxidative chlorine on the fabric surfaces and then dried at 50°C in a vacuum oven overnight before subsequent use. The active chlorine concentration of the final product

Cotton-g-PSMA-Cl was determined by an iodometric titration method (Li et al. 2015; Liu et al. 2016) and calculated using the equation (Fig. 1).

$$Cl^+(\%) = \frac{35.45 \times N \times V}{2 \times W}$$

where $Cl^+\%$ was the weight percentage of oxidative chlorine on the chlorinated swatch, N and V the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and W the weight (g) of the chlorinated fabric swatch. Testing of each specimen was repeated three times and the mean values were calculated.

2.4 Washing durability and storage stability tests

The washing durability of these Cotton-g-PSMA-Cl fabrics was evaluated using the American Association of Textile Chemists and Colorists Test Method 61-1996 (Ma et al. 2019b). In brief, 150 mL of water solution containing 0.15% AATCC detergent and 50 stainless steel balls were added in a stainless-steel canister (1.5×2 in.). After cotton samples were put into the canister, it was powered at 42 rpm and 49 °C for 45 min, with each present washing cycle equal to 5 machine washes. After 0, 1, 3, 5, and 10 washing cycles, the active chlorine concentration was determined by iodometric titration, with each cotton sample tested three times and the mean obtained.

The storage stability of these Cotton-g-PSMA-Cl fabrics was evaluated using a reported method. Cotton-g-PSMA-Cl fabric samples were stored in a dark environment at room temperature (Liu et al. 2017). After 0, 15, 30, and 60 d of static storage duration, the oxidative chlorine contents of the samples were measured. Each test was repeated three times and the mean obtained.

2.5 Antimicrobial efficacy test

A modified AATCC 100-2004 Test Method was used to evaluate the antimicrobial efficacies of pristine cotton, chlorinated Cotton-g-PSMA-Cl, and unchlorinated Cotton-g-PSMA, with the latter having been reported by other researchers (Li et al. 2014). *E. coli* (ATCC 43895) and *S. aureus* (ATCC 6538) were chosen as models for Gram-negative and Gram-positive bacteria, respectively. Test cotton samples were cut into 2.54 × 2.54 cm squares and sterilized using UV-light. Then, 25 μL of a bacterial suspension (10^8 cfu/mL), prepared in advance, was added on test sample centers and a piece of sterilized cotton sample of the same size used to cover the first one. A sterilized glass slide was placed upon the two pieces of cotton samples to achieve full contact with the bacterial piece. All of the operations were performed in the sterile glove. After a period of contact, the cotton samples were transferred to a test-tube containing 0.02 N sodium thiosulfate solution and swirled for 3 min. Finally, 100 μL of bacterial suspension in the test-tube was transferred onto trypticase agar plates and covered with glass lid. After incubation in a constant 37 °C temperature and humidity incubator for 24 h, the antimicrobial efficacy was evaluated according to the bacterial colony count. Each specimen was tested three times to calculate the mean values.

2.6 Characterization and Instrumentation

A Fourier transform-infrared spectroscopy (FT-IR; NEXUS-870, Nicolet Instrument Corp., Madison, WI, USA) was used to verify polymer grafting using the standard KBr disk method and a frequency region of 4000–600 cm^{-1} . The surface chemical compositions of samples were recorded by X-ray photoelectron spectrometer (XPS; Axis Ultra DLD/ESCA, Kratos Analytical, Ltd., Manchester, UK). The surface structures of fabric samples were evaluated by scanning electron microscope (SEM; S-4800, Hitachi, Japan) operated at 15 kV. The thermal stability of the cotton fabrics was studied thermogravimetric analysis (TGA; Pyris-1, PerkinElmer, Inc., Waltham, MA, USA), with samples heated at a rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 to 800 $^{\circ}\text{C}$ under a nitrogen flow (20 mL/min).

2.7 Statistical analysis

Data management and analysis was performed using the SPSS software (v.17.0, SPSS Inc., Chicago, IL). The results are reported as the mean \pm standard deviation (SD), and the statistical significance was set at the customary level of $p < 0.05$.

3 Results And Discussion

3.1 Characterization of polymer-grafted cotton via ATRP

Polymer grafting and surface chemical modification were confirmed by characterizing pristine cotton, Cotton-Br, Cotton-g-PSMA, and Cotton-g-PSMA-Cl by FT-IR (Fig.1). Compared to pristine cotton, a new absorption peak, located at 1725 cm^{-1} resulted from stretching vibrations of carbonyl groups, appeared after preparation of Cotton-Br. This indicated that cotton-based ATRP macroinitiator Cotton-Br was successfully obtained, as cotton modified by BiBB via α -bromoisobutyryl group bond linking. After polymer grafting, new absorption bands that appeared at 1582 and 1662 cm^{-1} were attributed to SCMHBMA's amide ν band and urea carbonyls, respectively (Lewis and Anthamatten 2013). These characteristic spectra verified successful polymer grafting of SCMHBMA on cotton surfaces.

The surface chemical compositions of cotton samples were further confirmed by XPS analysis. The chemical states of pristine Cotton, Cotton-Br, and Cotton-g-PSMA showed only O-1s and C-1s peaks in pristine Cotton, which was because the main chemical constituent elements of pristine Cotton were C, O, and H (Fig. 2). Compared to pristine cotton, the spectrum of Cotton-Br showed new peaks at 70.1 and 400.3 eV, which corresponded to Br-3d and N-1s, respectively, and indicated that the cotton had been successfully modified by BiBB (Yu et al. 2020). After polymer grafting modification, no remarkable variations in the position and intensity of peaks were observed between Cotton-Br and Cotton-g-PSMA. This was mainly due to the similar chemical compositions of Cotton-Br and Cotton-g-PSMA, as SCMHBMA was constituted completely of C, N, O, and H.

SEM was employed to investigate the surface morphology of raw and decorated cotton fabrics. The surfaces of pristine cotton fibers were smooth and had grained, ravined, and distortional nature

morphology (Fig. 3a) (Wu et al. 2014). However, after α -bromopropionyl group bonding, Cotton-Br surfaces showed roughness and were fuzzy, which resulted from surface hydrogen bond disruption (Fig. 3b). After polymer grafting, irregular and lumpy protuberances were observed on Cotton-g-PSMA surfaces (Fig. 3c) and, from a partial enlarged view, the surfaces of SCMHBMA-treated cotton fibers were observed to be covered with large numbers of small grains, which were probably caused by SCMHBMA deposition (Fig. 3d).

3.2 Characterization of the chlorination process

Cotton-g-PSMA-Cl was obtained by a simple chlorination in 2% sodium hypochlorite solution, per the experimental section. FT-IR spectroscopy was used to characterize this material and, compared to the spectrum of unchlorinated cotton-g-PSMA, the carbonyl stretching vibrational bands of chlorinated Cotton-g-PSMA-Cl were shifted from 1725 to 1731 cm^{-1} (Fig. 1d). This corresponded with previously reported literature, in which a higher wavenumber shift always occurs for carbonyl bands upon chlorination (Li et al. 2013; Ma et al. 2013). Also, the peak at 1582 cm^{-1} , corresponding to bending vibrations of C-H, faded away, indicating that the N-H bonds on cotton-g-PSMA were converted to N-Cl bonds during chlorination .

Elements characteristic of chlorinated Cotton-g-PSMA-Cl were identified in XPS spectra for further confirmation of the chlorination process (Fig. 2). Compared to the spectrum of cotton-g-PSMA, that of Cotton-g-PSMA-Cl showed a new absorption band at 200.3 eV, which corresponded to Cl-2p and indicated the existence of chlorine atoms on Cotton-g-PSMA-Cl surfaces. In addition, high resolution XPS spectrum of N-1s showed that the peak at ~ 400 eV in unchlorinated Cotton-g-PSMA-Cl was assigned to amide N-H. However, after chlorination, the peak of N-1s shifted to 402 eV, which was ascribed to N-halamine nitrogen atom, N-Cl. This characteristic shift to higher binding energy has been reported from other studies [], which was interpreted as Cl electronegativity being higher than H (Wu et al. 2014). Thus, FT-IR and XPS spectra indicated that N-halamine functional groups had been formed by the chlorination process.

3.3 Thermal properties of the cotton fabrics before and after decoration

The decomposition process and thermal stability of pristine and treated cotton fabrics were examined by TGA (Fig. 5). The initial decomposition for all samples below 100°C was considered evaporation of adsorbed water. From Fig.5a, Thermal decomposition of virgin cotton occurred via a one-step mechanism, with the maximum degradation temperature at 294.6°C. After α -bromopropionyl group bonding, the macroinitiator cotton-Br showed a significant drop in thermal stability. It was expected that the introduction of bromoalkyl units might release HBr upon heating and then catalyze further degradation (Sui et al. 2008). After polymer grafting, Cotton-g-PSMA displayed better thermal stability than that of Cotton-Br, but it was still worse than that of pristine cotton. The thermal decomposition temperature of Cotton-g-PSMA-Cl was dramatically reduced relative to pristine cotton and cotton-Br (Fig. 5d). The impact of chlorination was thought to cause some Surface structure changes which finally led

to decreased decomposition temperature (Dong et al. 2010). However, notably, the residue of cotton fabric samples after surface modification and polymer grafting was much higher than that of the pristine cotton samples, indicating that the decorated cotton fabrics possessed better flame-retardant property.

3.4 Washing durability and storage stability of Cotton-g-PSMA-Cl

The washing durability and storage stability of Cotton-g-PSMA-Cl was evaluated using the iodometric titration method. Cotton-g-PSMA-Cl fabric samples with increasing numbers of washing cycles possessed oxidative chlorine losses from 0.36 to 0.28% after 10 standard washing cycles (Table 1). This verified that N-Cl bonds in Cotton-g-PSMA-Cl were relatively stable during the washing process. In addition, over 80% of oxidative chlorine was retained after 60 d of storage, indicating that the storage stability of Cotton-g-PSMA-Cl was excellent.

Interestingly, the percentage of oxidative chlorine, after 10 washing cycles and 60 d of storage, reached 0.35 and 0.36%, respectively, using a simple rechlorination in 2% sodium hypochlorite solution for 1 h. This demonstrated that decreased Cl⁺% was mainly caused by conversion of -N-Cl to -N-H groups during washing and long-term storage. Furthermore, the material's good washing durability and storage stability were explained in terms of the stability of *N*-halamine biocidal agent SCMHBMA grafted onto cotton via ATPR, thus possessing good resistance to hydrolysis.

Table 1. Cotton-g-PSMA-Cl standard chlorine content after washing and after rechlorination

No. of washing cycles	Chlorine content (Cl ⁺ %)	Chlorine content after rechlorination (Cl ⁺ %)
0	0.36 ±0.01	-
1	0.35 ±0.01	-
3	0.33 ±0.01	0.35 ±0.01
5	0.28 ±0.01	0.32 ±0.01
10	0.20 ±0.01	0.27 ±0.01

Table 2. Chlorine content of Cotton-g-PSMA-Cl for different storage times and after rechlorination

Storage time (d)	Chlorine content (Cl ⁺ %)	Chlorine content after rechlorination (Cl ⁺ %)
0	0.36 ±0.01	-
7	0.35 ±0.01	-
15	0.32 ±0.01	-
30	0.30 ±0.01	-
60	0.29 ±0.01	0.36 ±0.01

3.5 Antimicrobial evaluation

To highlight the antimicrobial efficacies of these cotton fabrics, pristine Cotton, Cotton-g-PSMA, and Cotton-g-PSMA-Cl were challenged with *E. coli* and *S. aureus* under the same conditions. Untreated cotton exhibited very poor antibacterial efficacy no matter what kind of bacterial exposure with 15 min of contact (Table 3). The inapparent bacterial reduction was explained as bacterial adhesion on pristine cotton surfaces, instead of inactivation. For treated Cotton-g-PSMA without chlorination, the antibacterial efficacy was still low after 15 min of contact. However, after chlorination, Cotton-g-PSMA exhibited excellent antibacterial properties. This activity originated from the strong oxidative nature of the halogen atoms in the N-Cl bonds of the *N*-halamine components, which are known to demonstrate antibacterial activity against pathogens. The reasonable interpretation was that (i) prevent the growth of microorganisms by releasing free oxidative chlorines, and (ii) deactivate bacteria via direct contact in the presence of the *N*-halamine monomers, as reported previously (Dong et al. 2015; Eknoian et al. 1999).

Table 3. Antibacterial test with contact time for different cotton fabric samples

Sample	Contact time (min)	Bacterial reduction	
		<i>S. aureus</i> (%)	<i>E. coli</i> (%)
Cotton	15	12.1	9.5
Cotton-g-PSMA	15	13.2	9.9
Cotton-g-PSMA-Cl	1	100	100
	5	100	100
	15	100	100

To demonstrate antibacterial properties of the grafted cotton, the representative antibacterial pictures of cotton samples exposing to *E. coli* and *S. aureus* for 1 min were showed in Fig. 6. Almost of *E. coli* and *S. aureus* were inactivated after 1 min of contacting with Cotton-g-PSMA-Cl (Fig. 6 c and f). However, they could survive in the culture medium after 1 min of contact with pristine Cotton and Cotton-g-PSMA, which confirmed the previous assumption that the cotton-g-PSMA-Cl gained excellent antibacterial efficacy after chlorination.

Conclusions

The *N*-halamine biocidal agent precursor SCMHBMA was successfully grafted on cotton via ATRP under mild conditions. The resulting Cotton-g-PSMA was chlorinated by soaking in dilute sodium hypochlorite solution to convert -N-H to -N-Cl. The preparation and chlorination processes were characterized with FT-IR, XPS, SEM, and TGA. After chlorination Cotton-g-PSMA-Cl fabric samples exhibited excellent antibacterial properties against *E. coli* and *S. aureus*, which inactivated almost all test organisms within 1 min of sample contact time. Moreover, these antibacterial Cotton-g-PSMA-Cl fabrics were confirmed to

be stable after 10 washing cycles and 60 d of routine storage and the Cl⁺% could be effectively promoted or recharged by simple rechlorination. These encouraging outcomes pointed to the great potential of these new antibacterial N-halamine-based cotton composites for extensive and long-term antimicrobial control applications.

Declarations

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Figures

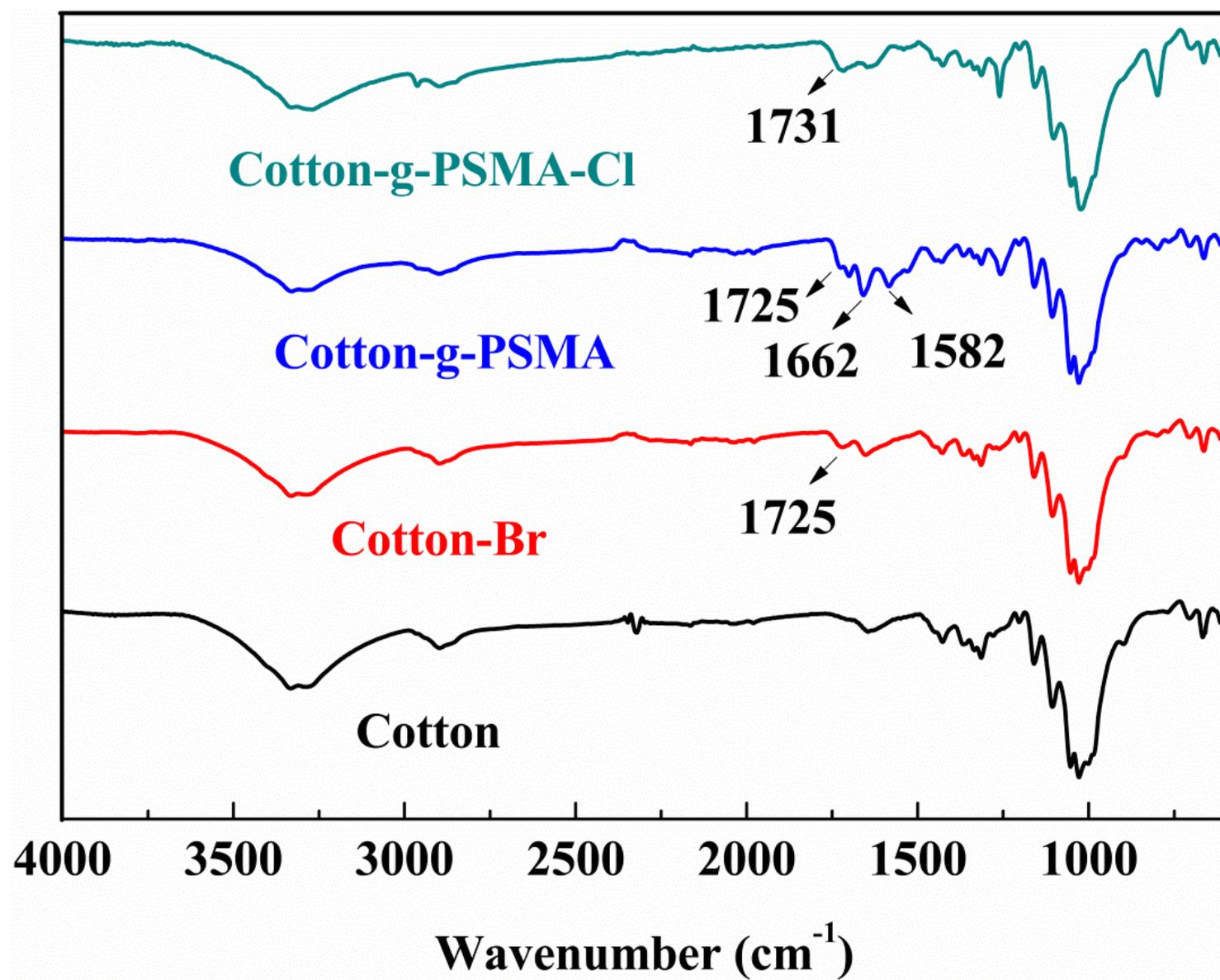


Figure 1

FT-IR curves of pristine Cotton, Cotton-Br, Cotton-g-PSMA, and Cotton-g-PSMA-Cl.

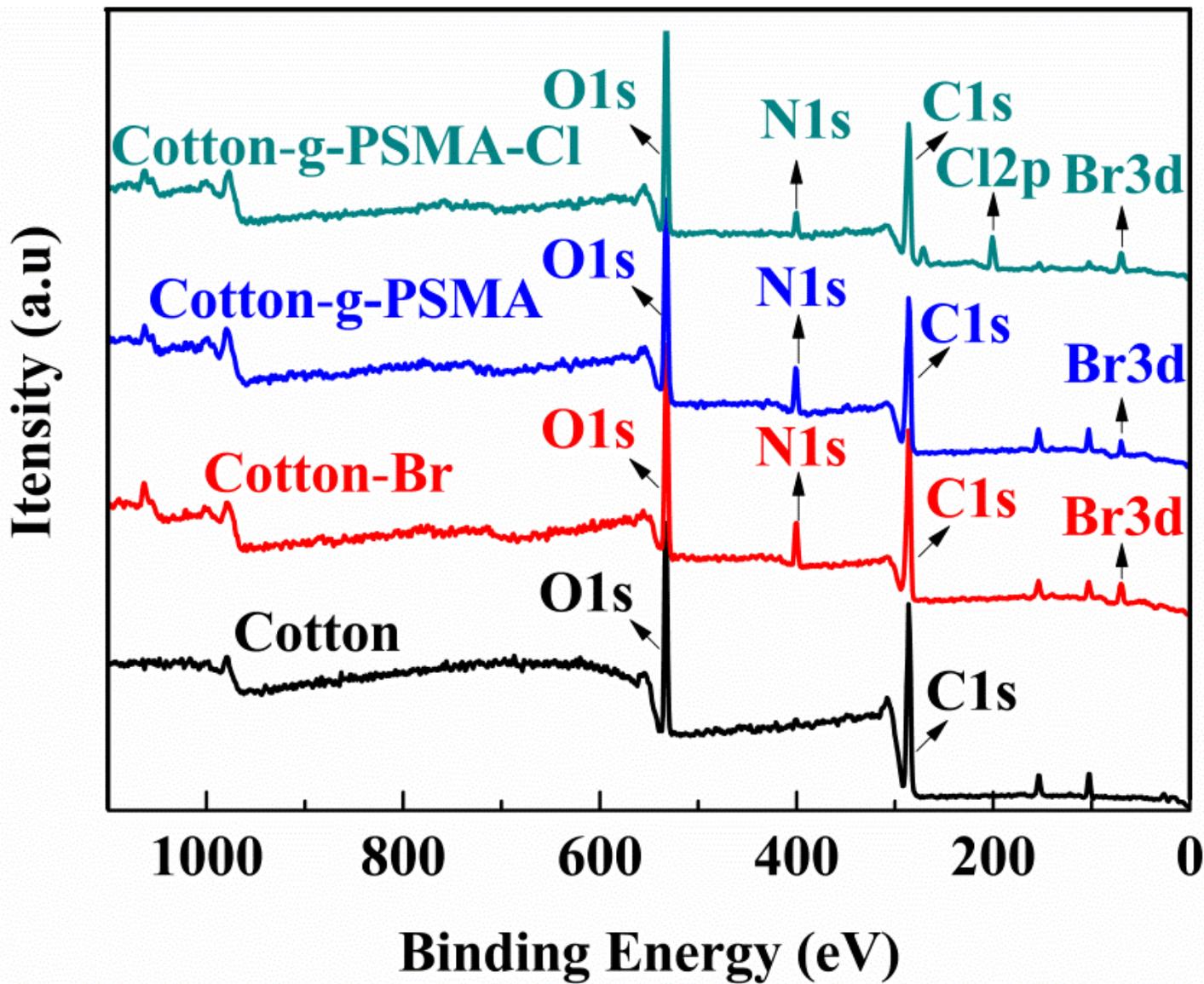


Figure 2

XPS spectra of pristine Cotton, Cotton-Br, Cotton-g-PSMA, and Cotton-g-PSMA-Cl.

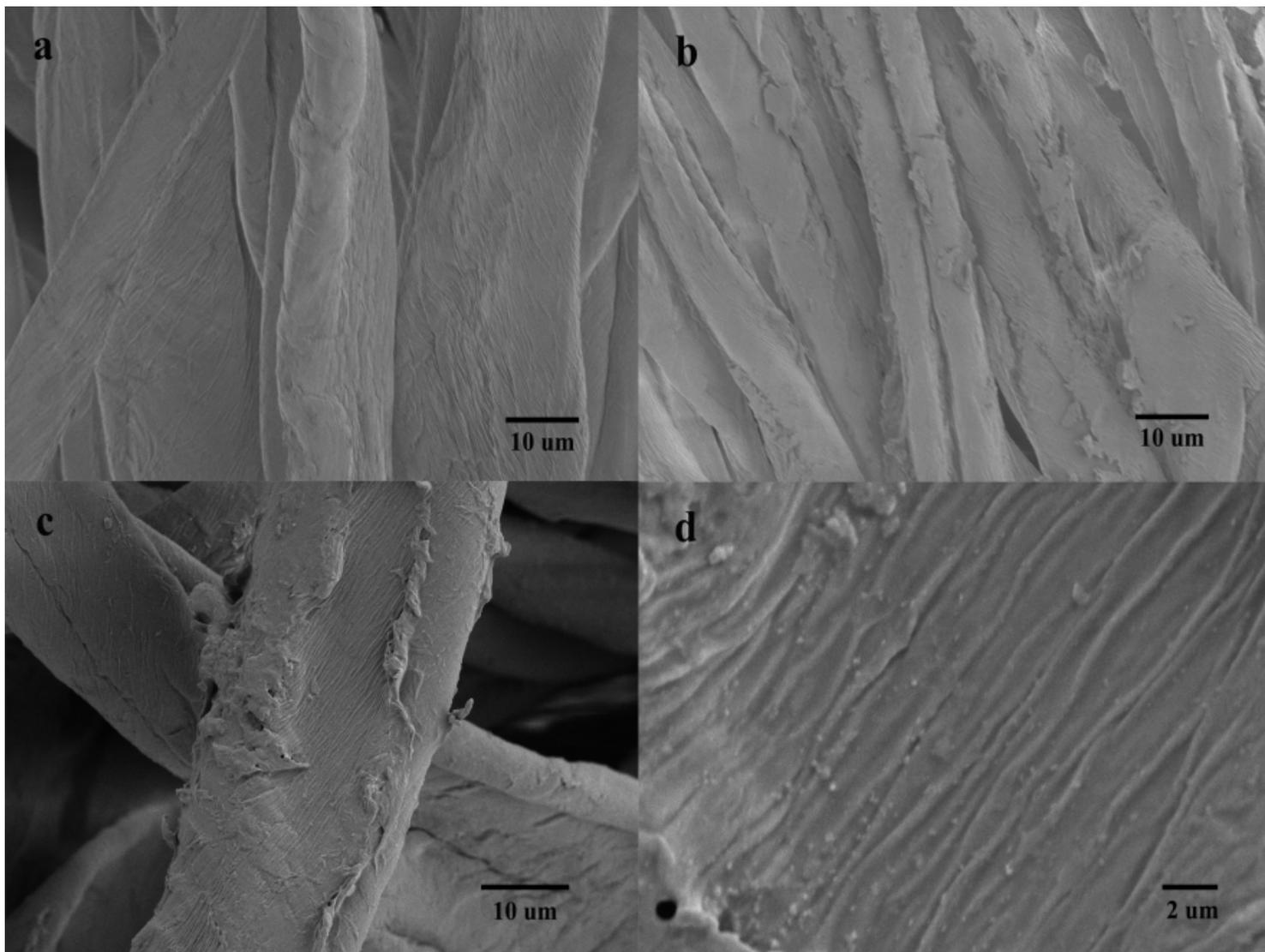


Figure 3

SEM images of pristine Cotton, Cotton-Br, Cotton-g-PSMA, and partial enlarged view of Cotton-g-PSMA (a–d, respectively)

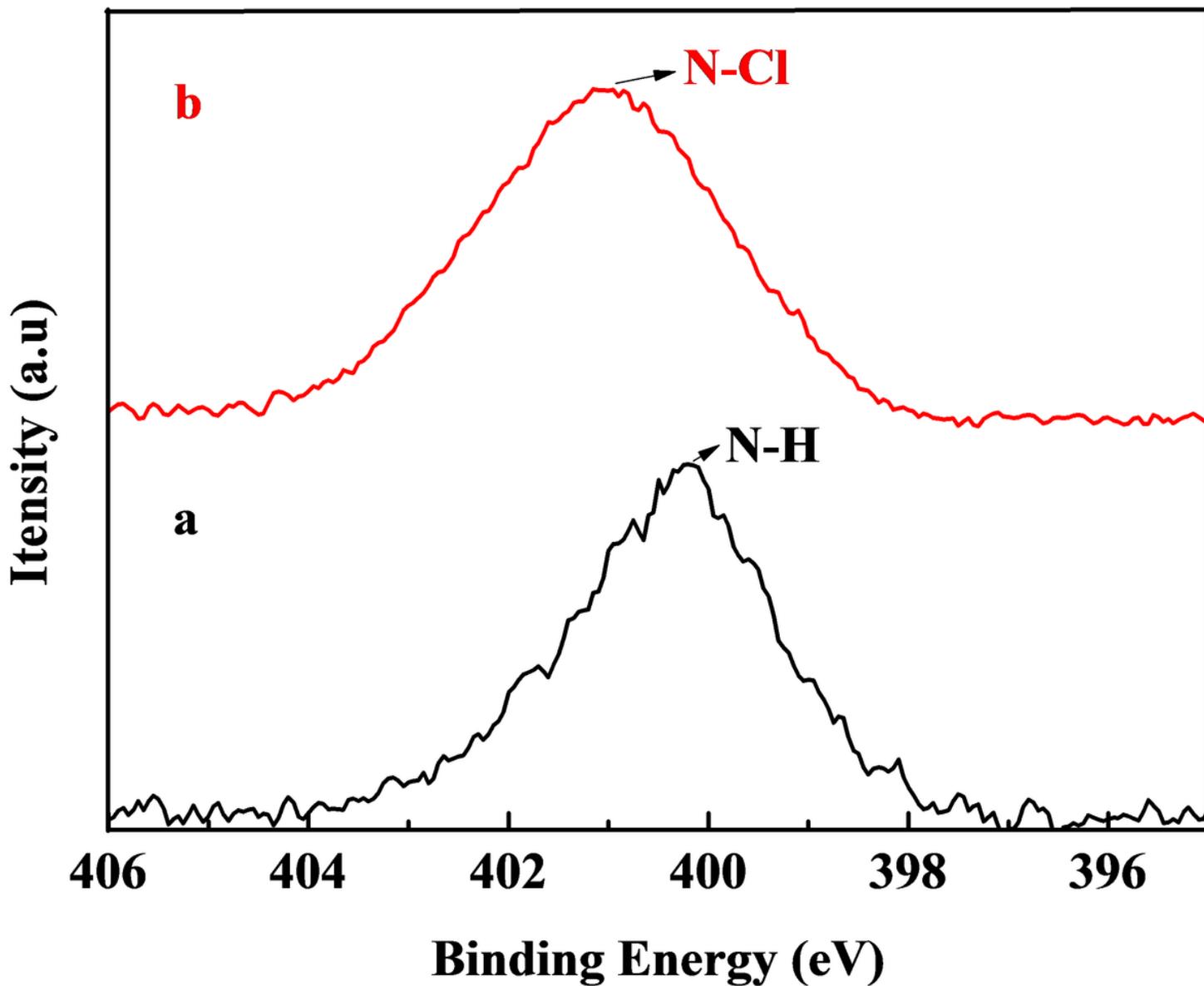


Figure 4

N-1s core-level spectra of Cotton-g-PSMA (a) and Cotton-g-PSMA-Cl (b).

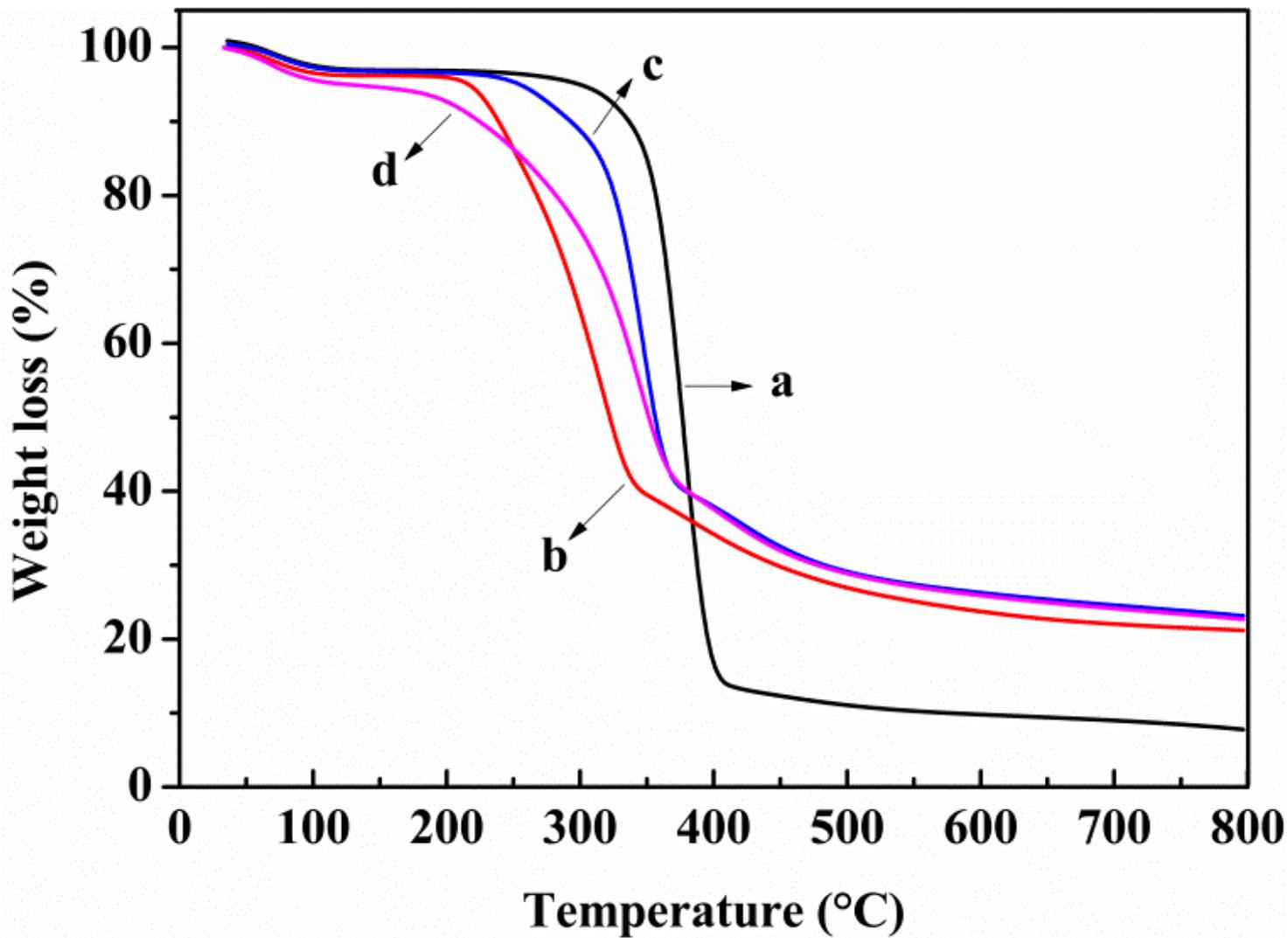


Figure 5

TGA images of pristine Cotton, Cotton-Br, Cotton-g-PSMA, and Cotton-g-PSMA-Cl (a–d, respectively).

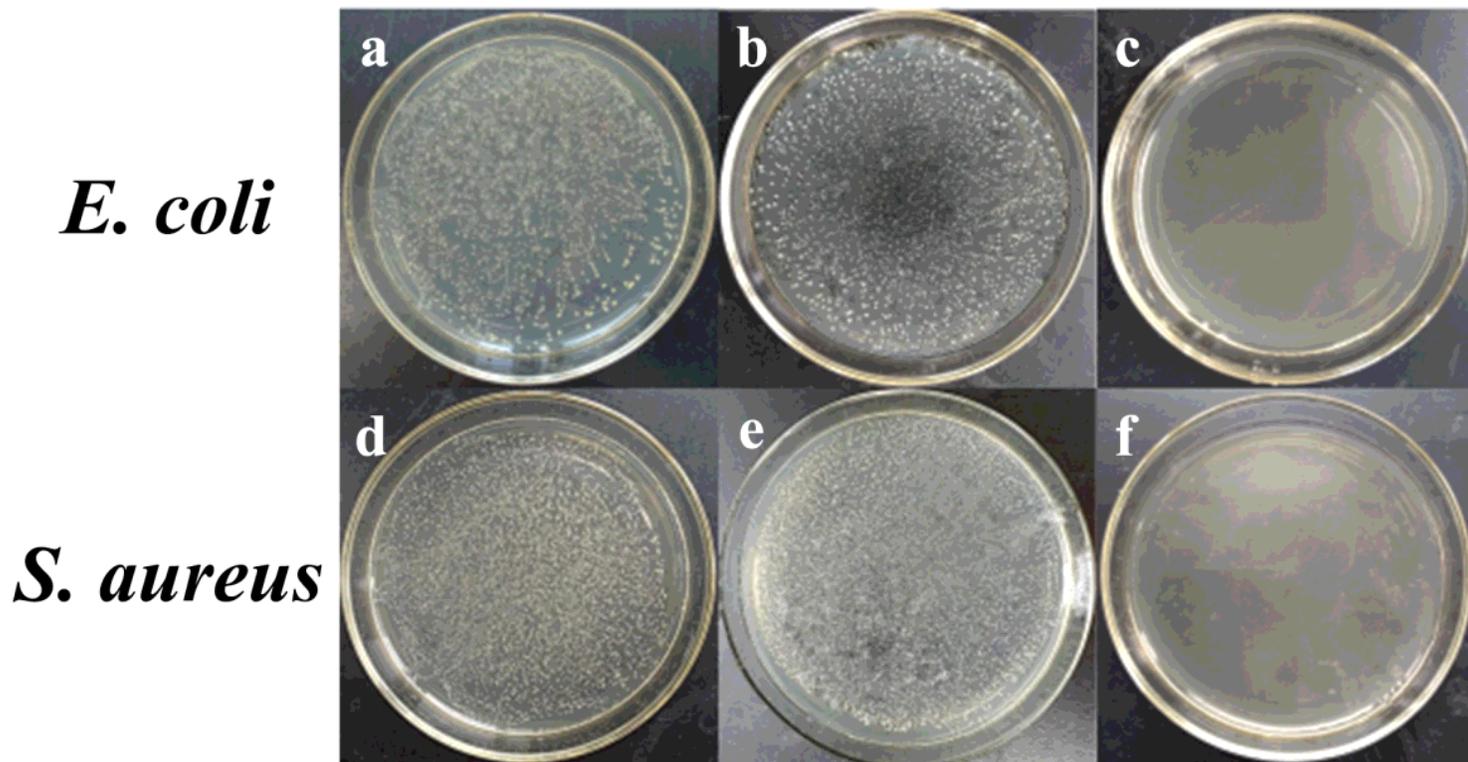


Figure 6

Antibacterial activity of pristine Cotton (a), Cotton-g-PSMA (b), Cotton-g-PSMA-Cl (c) against *E. coli* and Cotton (d), Cotton-g-PSMA (e), Cotton-g-PSMA-Cl (f) against *S. aureus* after 1 min of contact.

Supplementary Files

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