

Silver-nanoparticles dispersed onto cotton fibers: Enhanced surface loading and antibacterial activity by carbene insertion

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Abstract: An amino-substituted bis(aryldiazomethane) was synthesized, and used to modify cotton fibers by a carbene insertion reaction. A subsequent amidation of the modified cotton fibers introduced sulfide groups onto the surface, which was expected to bind silver nanoparticles (Ag NPs). These cotton fibers were characterized by scanning electron microscopy to show the surface morphology, as well as X-ray photoelectron spectroscopy and thermogravimetric analysis to quantify the loading of Ag NPs. A bioassay experiment showed antibacterial activity of the modified cotton fibers. The development of this modification by carbene chemistry followed with the functionalization by amidation reaction opens a new horizon for preparing antibacterial cotton materials for potential biomedical applications.

Key words: Cotton fiber; Silver nanoparticle; Surface modification; Antibacterial activity

1 Introduction

Cotton, as the most widely used natural fiber for textiles, has attracted much attention because of its breathable, soft, and degradable nature¹⁻³. With the development of surface science and composite technology, cotton fibers have been endowed with beautiful colors⁴ and versatile functionality, including super hydrophobicity / superoleophobicity⁵⁻⁸, UV protection⁹, flame retardation¹⁰, and electrical conductivity¹¹. This functionality imparts a completely new dimension for the development of smart cotton fabrics with novel properties, including self cleaning behavior and embedded electronics to monitor human physiological signals.

However, the application of cotton is limited in many areas due to its poor antibacterial activity¹². In order to improve its biological properties, chemical grafting or cross-linking of cottons can be achieved using stable covalent bonds between fiber segments. The creation of diverse antiseptic/antibacterial cotton materials and surfaces has been achieved by the incorporation of biostats/biocides¹³, such as nanosilvers¹⁴, zinc oxides¹⁵⁻¹⁶, tetra-alkyl ammoniums¹⁷⁻¹⁸, and chitins/chitosans¹⁹⁻²⁰. Above all, the surface modification of cottons with silver nanoparticles (Ag NPs) has been widely investigated²¹⁻²³, most of which have been applied in the finishing stage to produce antimicrobial cotton textiles. Ag NPs remain an ideal antiseptic antimicrobial agent due to their favourable properties, which include high specific surface area, effective activity against a wide scope of pathogens, and convenient preparation and application²⁴⁻²⁸.

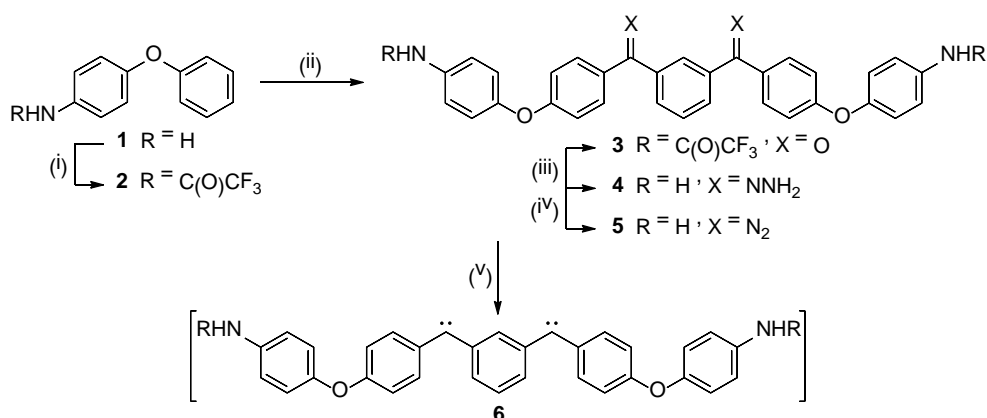
Herein, we report a technically convenient approach which uses an amino-substituted bis(diaryldiazomethane)³³ for functionalization by an amidation reaction to introduce sulfide group on the surface. Solution-dipping is then used to deposit Ag NPs, which increased the loading of Ag NPs and gave significant antibacterial activity²⁹⁻³². The loading of Ag NPs and the antibacterial activity of the cotton materials were compared with samples that were prepared by physical blending.

2 Results and discussion

2.1 Synthesis of amino-substituted bis(diazomethane)

As shown in Scheme 1, trifluoroacetic anhydride (TFAA) was used to protect the amino

group in 4-phenoxyaniline **1** to give amide **2**, which was subsequently converted by Friedel-Crafts reaction to bis(arylketone) **3** in relatively high yield. The ketone groups of **3** were treated with hydrazine monohydrate to generate hydrazone **4**, and oxidation with manganese dioxide gave the bis(diaryldiazomethane) **5**. The diazomethane is suitable for conversion into carbene **6** by heating, and the derived active carbene intermediate could react with many polymers and introduce diverse chemical functionality onto the substrate efficiently^{17, 34-36}.

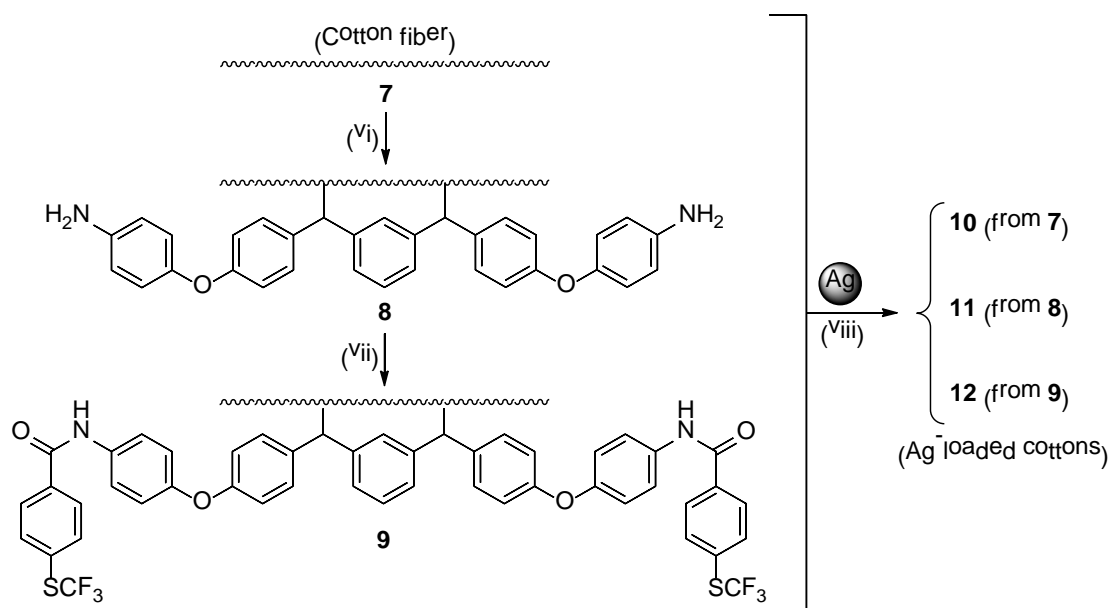


Scheme 1 The synthetic route of amino-substituted bis(diaryldiazomethane). Conditions:

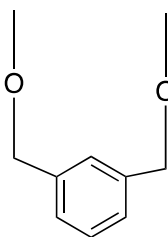
(i) TFAA, pyridine, DCM, 5°C-r.t., overnight (96%); (ii) isophthaloyl chloride or terephthaloyl chloride, AlCl₃, DCM, 5°C-r.t., 2h (89%); (iii) NH₂NH₂, H₂O, HAc, EtOH, reflux, 40h (87%); (iv) MnO₂, Na₂SO₄, KOH, DCM, r.t., 5h (89%); (v) 120°C.

2.2 Surface modification of cotton fibers

As shown in Scheme 2, cotton fiber **7** was mixed with bis(diaryldiazomethane) **5** evenly before being heated to 120°C, from which carbenes were generated. The insertion reaction of carbene with O-H bonds on the surface of cottons gave the modified cotton fiber **8**, now with amino groups on the surface. The amino-substituted cotton fiber **8** was subsequently reacted with 4-(trifluoromethylthio)benzoyl chloride to generate sulfide-functionalized cotton fiber **9**.



Can you change 8 and 9 to include the O atoms on the new bond with cellulose ie.



Scheme 2 Surface modification route of cotton fibers. Conditions: (vi) **5**, 120°C; (vii) 4-(trifluoromethylthio)benzoyl chloride, DCM, 0°C-r.t., overnight; (viii) Ag NPs, DMF, 120°C, 1h.

2.3 Preparation of the Ag NPs-loaded cottons

There are only hydroxyl groups on the surface of cotton fibers, which have very limited binding capacity with Ag NPs. Therefore, sulfide groups were introduced onto the surface of cotton fibers, which gave much better binding with Ag NPs. As shown in Scheme 2, three silver-loaded cottons **10~12** were prepared by treating the different cotton fibers **7~9** with silver nanoparticles in DMF at 120°C. It was expected that **12** would show the best loading efficiency of Ag NPs since the sulfide groups on the surface could link Ag NPs with the modified cotton fibers by coordination. For comparison, the Ag NPs - loaded cottons **10~11** were prepared with similar treatment, allowing comparison of the different binding of Ag NPs with hydroxyl, amine, or sulfide groups.

2.4 Morphology of cotton fibers

It is interesting that the modified cotton **8** appeared yellow in color, which is very different from the white color of the initial cotton **7** (Figure 1), and this is consistent with the presence of the introduced aromatic residues of carbene **6**. In addition, the silver-loaded cotton **12** appeared much darker color.

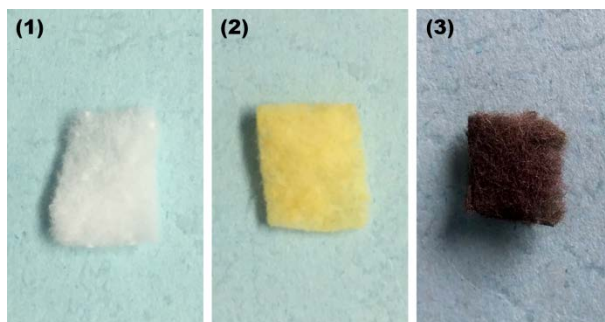
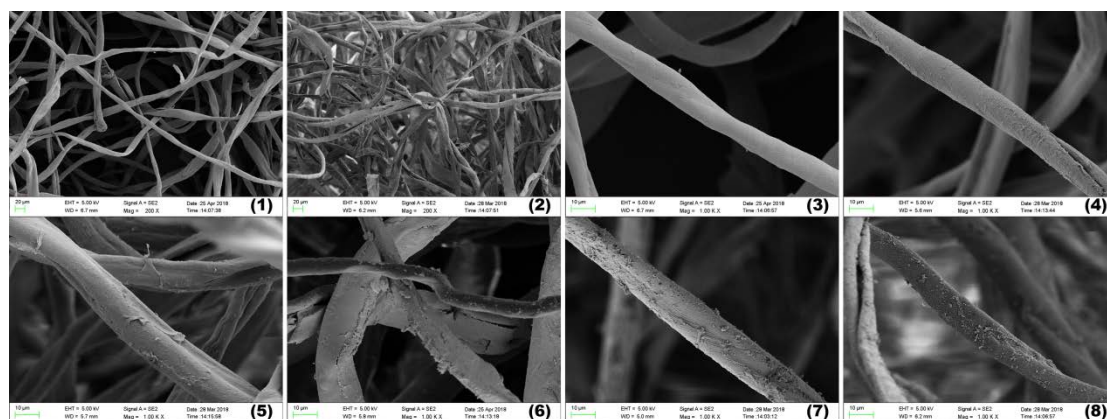


Figure 1 Photographs of cottons with different color: (1) **7**; (2) **8**; (3) **12**. Can you put a scale bar on these pictures to indicate 1cm length?

This immediately suggested that the modification had been successful, but scanning electron microscopy (SEM) is a direct way to show the dispersion of Ag NPs on the surface of cotton fibers, and provide additional confirmation of surface modification. Figure 2(1) and Figure 2(2) shows the pure cotton fibers and the Ag NPs - loaded cotton **12** under low magnification, respectively, from which it is clear that silver nanoparticles were dispersed on the surface of the cotton. SEM photos of different cotton fibers **7**~**12** at high magnification were recorded (Figure 2(3)~(8)) (Scheme 2). The surface of pure cotton **7**, amino-modified cotton **8**, and sulfide-functionalized cotton **9** were very different, which clearly demonstrated the carbene insertion modification and the subsequent amidation reaction. The surface of pure cotton fibers was very smooth (Figure 2(a)), and very few Ag NPs were detected (Figure 2(d)), but a significant number of Ag NPs were loaded on the surface of cotton fibers with amino groups (Figure 2(f)) or sulfide groups (Figure 2(h)). It indicated that the binding of Ag NPs with amines or sulfides was much improved, as has been formerly reported in the literature³⁷⁻⁴⁰.



Better to renumber as (a), (b) rather than (1), (2) as this is confusing with compound nos

Figure 2 SEM pictures of cotton fibers and cotton/Ag NPs materials: (a) **7**, 200x; (b) **12**, 200x; (c) **7**, 1000x; (d) **10**, 1000x; (e) **8**, 1000x; (f) **11**, 1000x; (g) **9**, 1000x; (h) **12**, 1000x.

2.5 Surface Analysis of cotton fibers

The chemical composition on the surface of different cottons would become different after being modified by carbenes, functionalized by sulfides, as well as binding Ag NPs. X-ray photoelectron spectroscopy (XPS) was carried out to explore the difference between these modified samples (Figure 3). Comparing the survey spectra of pure cotton (Figure 3(a)) with modified cotton (Figure 3(b)), the characteristic peaks of nitrogen (N 1s) at 398.97 eV confirmed the success of surface modification by carbene 6. Similarly, the peak of fluorine (F 1s) at 687.97 eV and the peak of sulfur (S 2p) at 163.97 eV proved that the amidation was succeeded (Figure 3(c)). As the result, the subsequent loading of Ag NPs on the surface (determined from the silver (Ag 3p) peak at 368.08 eV) was greatly enhanced and followed the sequence of **12** (Figure 3(f)) > **11** (Figure 3(e)) > **10** (Figure 3(d)). This is consistent with better binding of Ag NPs with sulfide-functionalized cotton **9** than with amino-modified cotton **8**, and there was nearly no binding force of Ag NPs with hydroxyls on the surface of pure cotton **7**. It was noteworthy that the loading of Ag NPs on the surface of **12** was so large that signals of other elements was much reduced (Figure 3(f)).

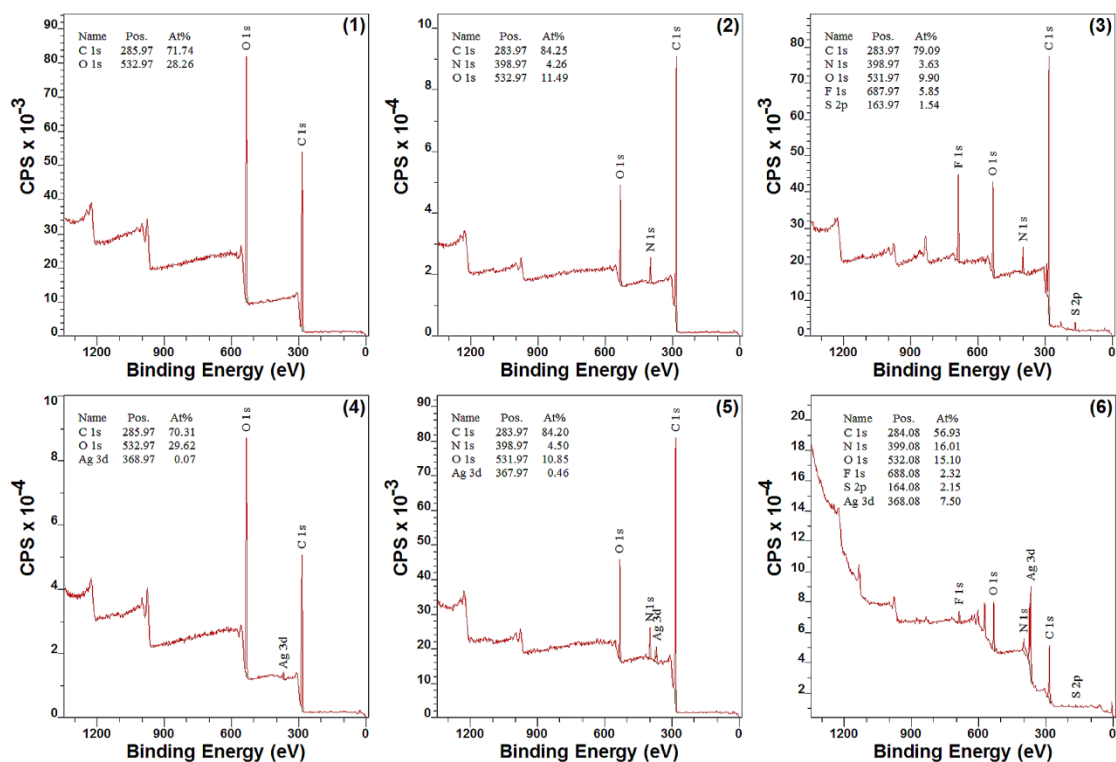


Figure 3 XPS spectra of different cottons: (a) survey of **7**; (b) survey of **8**; (c) survey of **9**; (d) survey of **10**; (e) survey of **11**; (f) survey of **12**

The detailed data of XPS are shown in Table 1. For comparison, these samples were characterized by EDX (correct abbreviation?) to show the amounts of all elements in the bulk (Table 2). It was found that the content of silver in **12** is obviously higher than other samples, which indicated that the introduction of sulfide onto the surface of cotton fibers greatly increased the loading of silver.

Table 1 XPS data of different cotton samples

XPS	C(%)	O(%)	N(%)	F(%)	S(%)	Ag(%)
7	71.74	28.26	/	/	/	/
8	84.25	11.49	4.26	/	/	/
9	79.09	9.90	3.63	5.85	1.54	/
10	70.31	29.62				0.07
11	84.20	10.85	4.50	/	/	0.46
12	56.93	15.10	16.01	2.32	2.15	7.50

Table 2 EDX data of different cotton samples

EDX	C(%)	O(%)	N(%)	F(%)	S(%)	Ag(%)
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7	55.15	44.85	/	/	/	/
8	57.88	37.27	4.86	/	/	/
9	58.98	55.5	3.39	2.88	1.25	/
10	56.47	43.48				0.05
11	57.54	37.66	4.4	/	/	0.39
12	59.94	31.75	0.3	0.52	0.94	6.54

The spectra from reflectance UV also showed the attachment of organics and Ag NPs to the surface of cotton fibers (Figure 4). As expected, there is no aryl group in pure cotton **7**, so there is no peak in UV spectra. After being modified with diaryl carbene to give **8** and then reaction with aryl chloride to give **9**, an obvious peak at the wavelength of 230 nm appeared, which was attributed to the newly introduced benzene rings. The subsequent coordination with Ag NPs in Ag NPs - loaded cottons **12** gave a weaker absorption, possibly because the benzene rings on the surface of cotton were partially covered by silver.

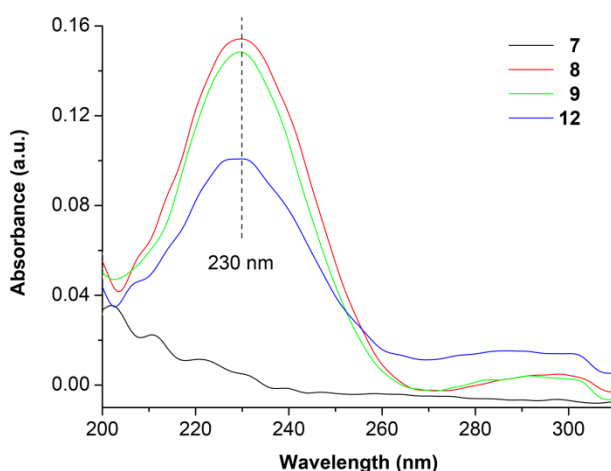


Figure 4 The reflectance UV spectra of cottons and cotton/Ag NPs materials

2.6 Thermal analysis of cotton fibers

The thermal behavior was measured by thermogravimetric analysis (TGA), which showed the mass loss of various cotton fibers. From Figure 5, All the samples showed good thermal stability until 300°C, followed by the maximum decomposition at about 350°C. Although the maximum decomposition temperature was lowered slightly after the amidation reaction (sample **9**) and silver nanoparticles deposition (sample **12**), it was very

similar for all the samples, which indicated that the bulk property of cotton fibers were well maintained. Compared with the sulfide-functionalized cotton **9**, the residual percent of silver-loaded cotton **12** greatly increased from 47.3% to 56.0%. Thus, the loading of Ag NPs on the surface of cotton was calculated to be 8.7%, which demonstrated that the present methodology successfully incorporated significant amounts of silver nanoparticles on cotton fibers.

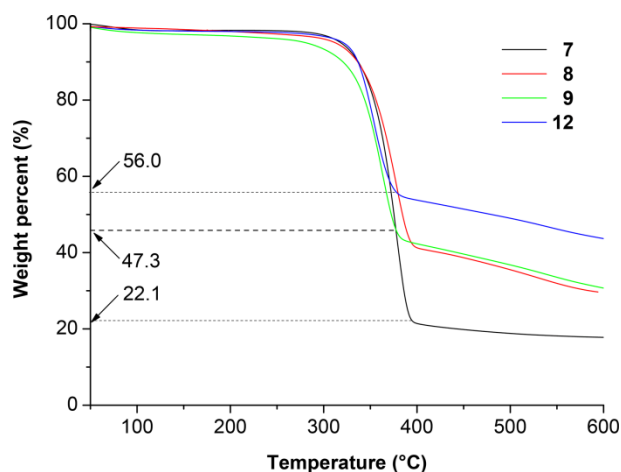


Figure 5 TGA curves of different cotton fibers and cotton/Ag NPs materials (20 °C·min⁻¹, air).

2.7 Antibacterial activity of Ag NPs - loaded cottons

Escherichia coli (*E. coli*) and *Staphylococcus aureus* (*S. Aureus*) were selected to investigate the antibacterial property of the Ag NPs - loaded cottons **11**–**12**. In order to give a comparison of silver-loaded cotton with other materials, Penicillin G potassium salt in aq. solution was chosen for calibration, giving log(nmole per well) versus diameter of inhibition zone as a straight line³⁶. Using this calibration curve, the equivalent concentration of Penicillin G potassium salt for **11**–**12** could be determined from the diameter of their inhibition zones (Figure 6). It was shown that the Ag NPs - loaded cotton **12** had much better antibacterial activity than the Ag NPs - loaded cotton **11**, consistent with a higher level of silver nanoparticles in the Ag NPs - loaded cotton **12**, which was in accordance with the data of XPS, EDS, and TGA. It was noteworthy that the Ag NPs - loaded cotton **10** prepared by physical absorption showed no antibacterial activity under the test conditions, which suggested that the Ag NPs - loaded cottons **11**–**12** would expand application of these materials as antibacterial agents, and this method could

supplement other antiseptic treatments³⁶.

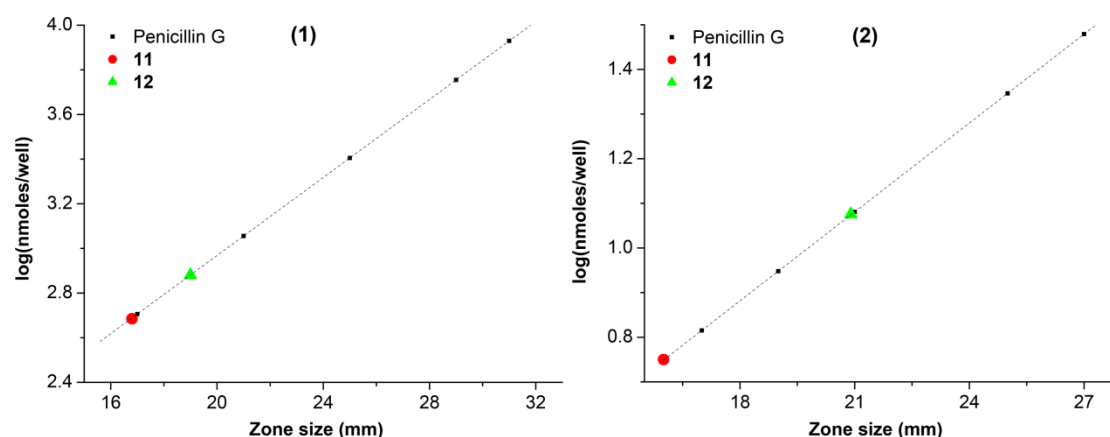


Figure 6 Log(nmole/well) versus diameter plot for Penicillin G and the equivalent of Penicillin G for cotton/Ag NPs materials: (1) *S. Aureus*; (2) *E. Coli*

3 Conclusions

An amino-bis(aryldiazomethane) was synthesized, and used to modify cotton fibers by carbene insertion reaction, which was showed to be successful by XPS spectra (N 1s). The amino-modified cotton fibers were subsequently amidated to introduce sulfide groups on the surface, which was further confirmed by XPS spectra (F 1s and S 2p). These two cottons were used to bind Ag NPs and the surface loadings determined by XPS, EDS, and TGA, and the derived materials exhibited significant antibacterial activity. The development of this modification process opens a new horizon for preparing not only antibacterial cotton fibers, but also synthetic materials and surfaces to give excellent antibacterial activity.

4 Experimental part

4.1 Materials and characterization

Cotton fibers were purchased from Aladdin Co. as the grade of biochemical reagent. The other chemicals (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received. Two bacterial strains, *E.coli* and *S.aureus*, were purchased from J&K Scientific Ltd.

Scanning electron microscope (SEM) photographs were taken on a SUPRA™ 55 thermal field emission Scanning Electron Microscopy (Zeiss Co., Germany) with energy dispersive x-ray spectroscopy (EDX) after the samples were coated with gold (~20 nm thickness).

XPS analysis was performed with a VG – Escalab X-ray Photo-electron Spectrometer VGX900 using Al K α radiation at an operating pressure less than 1×10^{-8} mBar. Casa XPS peak fitting software was used to analyze spectra and a reference charge correction of 284 eV for C 1s was used. The area under the elemental peaks and standard sensitivity factors (C, 1.00; O, 2.93; N, 1.80; F, 4.43; S, 1.68; Ag, 18.04) were used to calculate relative chemical composition within the surface and near-surface sampling depth. UV spectra was recorded on an UV-2600 instrument with an integrating sphere manufactured by Shimadzu.

TGA experiments were performed on a NETZSCH TG 209 instrument with a linear heating rate of 20 °C·min⁻¹ from room temperature to 600 °C under air atmosphere.

4.2 Synthesis of bis(aryldiazomethane)s

4-Trifluoroformamidobenzophenone (**2**), 4-(4'-trifluoroformamidodiphenyl ether)-1,3-diphenone (**3**), 4-(4'-trifluoroformamido diphenyl ether)-1,3-diphenone hydrozone (**4**), 4-(4'-trifluoroformamido diphenyl ether)-1,3-di(phenyl diazomethane) (**5**) were synthesized according to the literature ³⁶.

4.3 Modification and amidation of cotton fibers

Compound **5** (0.30 g, 0.25 mmol) was dissolved in dichloromethane (10 mL). Cotton fibers (1.2 g) were added to the solution and stirred for a few minutes. The solvent was carefully evaporated under vacuum so that the compound **5** was absorbed evenly on the surface of cotton fibers. The mixture was heated to 120 °C until the color changed from purple to light yellow (about 20 min) without stirring. The modified cotton was washed by dichloromethane (20 mL \times 3) under ultrasonic irradiation and dried to yield the modified cotton fibers **8**.

Cotton fibers **8** (0.17 g), potassium carbonate (0.15 g, 0.94 mmol), and dichloromethane (10 mL) were placed into a round bottom flask. To this was added triethylamine (5 drops) and the solution stirred at 0 °C for 10 min. A solution of 4-(trifluoromethylthio)benzoyl chloride (0.15 g, 0.62 mmol) in dichloromethane (2 mL) was added drop wise to the flask. The mixture was stirred at room temperature for 24 h. The cotton was washed with sodium bicarbonate aq. solution (0.2 M, 20 mL \times 3) and DCM (20 mL \times 3) to give the

cotton fibers **9**.

4.4 Preparation of silver nanoparticles (AgNPs)

A glycol solution (49.8 mL) containing PVP (10.5 g, $M=58000$, $K=27\sim32$) was heated to 60°C . AgNO_3 (1.5 g, 8.83 mmol) was added to the solution and heated at 120°C for 1.5 h. The AgNPs solution was obtained after the reaction was cooled to room temperature.

4.5 Preparation of the cotton/Ag NPs materials

AgNPs were dispersed in DMF with ultrasonic irradiation for a few minutes before the cotton fibers **7~9** were added. The amount of AgNPs and cotton fibers was 1:5 (mass/mass??). The mixture was stirred at 120°C for 1 h, washed with EtOH (20 mL \times 3), water (20 mL \times 3), DCM (20 mL \times 3) to give cotton/Ag NPs materials.

4.6 Bioassay

S. aureus and *E. coli* were chosen to quantify the antibacterial activity of cotton fibers **10~12**. The specific bacterial solution was diluted to 1:50 with sterile water and added to cool molten agar in a 1:100 ratio (bacterial solution (1:50) : agar, v/v). The inoculated agar (25 mL) was pipetted into empty Petri dishes (90 mm), which were then swirled to ensure even thickness of agar. The Petri dishes were allowed to store in the refrigerator for use.

According to a sterile method, 15 mm-diameter circles were punched in the bacteria-seeded agar plate, and the inner agar was removed to produce an empty well. The required cotton (20 mg) and water (300 μL) were added to pre-punched wells of the seeded agar plates. The well was then sealed with some molten agar so that a uniform layer of agar was produced. The agar plates were covered and incubated for 24 h to encourage bacterial growth. The diameter of the antimicrobial zones around each material was measured and recorded. Blank samples were taken as a reference. Did you run these in duplicate?

An aq.solution of Penicillin G potassium salt was used to calibrate the antibacterial activity. The concentration of Penicillin G was 1.0 mg mL^{-1} and the dosage in each well was 50 μL , 100 μL , 150 μL , 200 μL , 250 μL , and 300 μL . After the solution was added to pre-punched wells of the seeded agar plates, the well was fulfilled to 300 μL with distilled water. The agar plates were covered and incubated for 24 h to encourage bacterial growth.

The diameter of the inhibition zones around each well was measured and recorded.

Acknowledgments

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