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침적방법을 이용한 은 카바메이트 전구체의 열환원에 의한 면 섬유/은 복합체의 제조 및 그들의 성질

곽완규 · 김태성 · 공명선†

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Preparation of Cotton Fibers/Silver Composite by a Facile Dipping Method via Thermal Reduction Using Carbamate-type Silver Precursor and Their Properties

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초록: 이 연구의 목적은 신속하고 편리한 방법으로 면 섬유에 열처리에 의하여 안정한 은 나노입자를 형성시키는 방법을 개발하고 면 섬유의 기능을 부가하여 응용성을 증가시키는 것이다. 은의 생성은 은 카바메이트 용액에 면 섬유의 타래를 침적한 후 125 ℃에서 단순히 가열하여 완결할 수 있었다. 면 섬유의 양은 은 이소프로필카바메이트 전구체의 농도를 변화하여 용이하게 조절할 수 있었다. 이렇게 생성된 면 섬유/은 표면의 형태와 정량적인 분석은 전자주사 현미경(SEM)과 에너지 분산형 X선 분석기(EDX)로 결정하였다. 섬유 표면에 생성된 은 나노입자는 30에서 200 nm의 크기를 가지며 조밀하게 생성되었으며, 이것은 125 ℃의 성장 조건에서 은 나노입자의 빠른 성장과 응집에 의한 것이다. 이러한 은 나노입자들은 면 섬유/은을 3회 세척한 후에도 분리되지 않았다. 항균성 시험에서 S. aureus와 E. coli에 대한 우수한 항균 특성을 보여주었으며 은 코팅된 면 섬유는 최고 0.15 kΩ·cm의 전기 저항을 나타내었다.

Abstract: The objective of this study was to develop a rapid and convenient method of producing stable silver nanoparticles (AgNPs) on cotton fibers via a thermal treatment and their application to augment the properties of cotton fibers. Silver deposition was completed by dipping a skein of cotton fiber into silver carbamate precursor solutions, followed by heating at 125 °C. The amount of AgNPs on cotton fibers was controlled by changing the concentration of silver isopropylcarbamate precursor solutions. The surface morphology and quantitative analysis of the silvered cotton fibers were determined by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). The AgNPs between 30-200 nm were seen to be densely deposited on the fiber surface due to rapid growth and aggregation of AgNPs at the 125 °C growing condition. Moreover, the AgNPs did not leach out of the fibers after three laundry cycles. Antibacterial activity was evaluated against S. aureus and E. coli. The cotton fiber/Ag composites imparted high conductivity to the fibers, as evidenced by an electrical resistivity of 0.15 kΩ·cm.

Keywords: silver isopropylcarbamate, thermal reduction, cotton fiber, silver coating, silver nanoparticles.

Introduction

Nanotechnology provides plenty of efficient tools and techniques to produce desirable attributes, mainly by modifying the fiber surface.[1] Modification of textiles and fibers has been a focus of interest due to increasing environmental awareness and to promote a healthy, safe and comfortable lifestyle.[1,2] Conductive textiles and fibers are useful because of their electrical conductivity, electromagnetic shielding, electrostatic discharge, super hydrophobicity, stain resistance and antimicrobial activity, *etc*.[3-7] Electronic textiles (e-textiles) will find use in wearable electronics and smart clothing, which can combine the functionality of smart electronic devices with the comfort and flexibility of stylish clothing.[8] E-textiles[9] not only provide wearing comfort but also can function as pressure sensors,[10] electrocardiogram (ECG),[11] electromyography (EMG),[12] and electroencephalography (EEG) sensors,[13] RFID tags[14] and supercapacitors, *etc*.[15] Recently, an awareness of general sanitation, contact disease transmission, and personal protection

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has led to the development of antibacterial fibers to protect wearers against the spread of bacteria rather than to preserve the quality and durability of the textile itself.[16] Many heavy metals are toxic to microbes at very low concentrations either in its free state or in compounds.[17] Silver has long been used for its antiseptic qualities, which are attributed to the surface oxidation of metallic Ag to Ag^+ and a ligand followed by the generation of a toxic ion (Ag^+). Efforts to exploit this process have led to the widespread incorporation of Ag nanoparticles (AgNPs) into many consumer products as an antimicrobial agent. Various methods have been adopted for coating AgNPs on a textile or fiber surface, such as by generating active groups via plasma[18] or UV irradiation,[19] or sol-gel processing,[20] bioreduction,[21] *in situ* reduction of silver ions to metallic silver on fabric[22-25] and so on. However, conventional surface modification of textiles by AgNPs is not persistent, especially against laundering.[26,27] Thus, an antibacterial resistant to degradation by home laundering is urgently needed.[28] *In situ* synthesis techniques show promise due to their facile nature, efficiency and environmental friendliness, as well as the uniform distribution and stability of the nanomaterials.[29-31] Because of the industrial and medical applications of Ag-loaded multifunctional fibers, we aimed to develop a facile method of producing Ag-loaded cotton fibers. The major advantage of our method is that it provides an easy deposition of AgNPs on cotton fibers by heating at 125 ºC after padding with a solution of silver alkylcarbamate. In addition, the amount of silver loaded on the surface of cotton fiber was simply controlled by changing the concentration of silver alkylcarbamate precursor solution, which would determine the final application in many fields. Silver alkycarbamate produced no residual anions except organic amine and carbon dioxide. The physical adsorption of silver carbamate alcoholic solution onto the surface of cotton fibers enhanced adhesion between AgNPs layer and the cotton fibers.

In this study, we report a novel one-step thermal reduction of low molecular weight silver isopropylcarbamate to fabricate multifunctional cotton fibers coated with AgNPs aggregates of a pomegranate-shaped structure. The pomegranate-shaped silver NPs grown on the surface of the functionalized fibers mediate considerable antibacterial activity and outstanding electrical conductivity.

Experimental

Materials and Equipment. Chemicals and auxiliary materials of commercial grade were used. Cotton fibers (KCD-40, 130 Denier) were supplied by JV LLC JIZZAX PLASTEKS (Uzbekistan). Silver *n*-propylcarbamate complex solution was prepared by a previously reported method.[32,33] Silver precursor solutions with 1% silver content were prepared by dissolving silver isopropylcarbamate (1.62 g) in methanol (98.38 g). Other silver carbamate precursor solution with 0.5-10% silver content were prepared by dissolving different amount of silver carbamate. The obtained silver carbamate solutions were termed 'Ag (0.1%), Ag (1%), Ag (2%), etc'. All chemicals were of analytical grade and were used without further purification. Cotton fiber/Ag was rinsed in isopropanol/water (50/50) at 20 ºC for 1 h and the solutions were shaken for 15 min before removal. The solutions were then removed from the beaker and excess water was added to wash cleaning alcohol solution. The samples were dried at 50 ºC.

A field-emission SEM (MIRA LMH, Tescan, Brno, Czech Republic) was used to characterize the surface morphology of the coatings. Differential scanning calorimetry (DSC) data were recorded with a DSC (SEIKO Exstar 7020, Tokyo, Japan) instrument. Specimens (~10 mg) were sealed in a DSC Al pan before being placed in the calorimeter, and heated at a rate of 10 ºC/min using a nitrogen atmosphere. Thermogravimetric analysis (TGA) tests were conducted on the samples using Shimadzu TGA 50 (Shimadzu, Tokyo, Japan) equipment at a heating rate of 10 ºC/min and under a nitrogen atmosphere. X-ray diffraction (XRD) patterns of the samples were recorded on a Ultima IV X-ray diffractometer system (Rigaku Corp., Tokyo, Japan) by monitoring the diffraction angle from 10º to 80º (2θ) using monochromatized CuKα (λ=1.54051 Å) radiation. UV-visible (UV-Vis) spectra were determined using a Varian Cary 100 ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Technology, Santa Clara, CA 95051, USA). The samples (1×1 cm, 0.12 mm) were prepared, and air was used as the reference. The spectra were recorded in the range of 200-800 nm. X-ray photoelectron spectroscopy (XPS) (ESCA 2000 Multilab apparatus, VG Microtech) was used to analyze the surface with an Al anode (Kα, hν=1486.6 eV). The chemical composition of the silver coating was determined using an energy-dispersive X-ray spectroscope (EDX) attached to the SEM. The release of the silver ion from the modified cotton sample in water was measured using an inductive coupled plasma mass spectrometer (Perkin-Elmer ELAN 9000/6X00/DRC-e ICP-MS, USA). The conductivity of the silver-modified cotton samples was measured using a LCR-meter (EDC-1630, 0.001 Ω-99 MΩ, ED Lab, Korea). Release of silver ions

from the modified cotton fibers in water was measured by inductively coupled plasma mass spectrometry (ELAN 9000/6X00/DRC-e, Perkin Elmer, Waltham, MA, USA).

Preparation of Silver Isopropylcarbamate. A solution of isopropylammonium isopropylcarbamate (50.0 mmol, 8.12 g) in dry methanol (50 mL) was added to a suspension of silver oxide (24.0 mmol, 5.52 g) in dry methanol (10 mL). The reaction mixture was stirred at room temperature for 24 h until the suspension became transparent. The solution was then evaporated under reduced pressure at 25 °C to concentrate or diluted, and the concentration of silver isopropylcarbamate solution was adjusted to give 1-10 wt% of silver content.

FTIR (KBr, cm^{-1}) 3330 (N-H), 2950-2920 (C-H), 1573-1529 (C=O), 1320-1290 (C-O and C-N). ^{1}H NMR (600 MHz, DMSO-d_6) δ 4.95 (s, 1H, $(CH_3)_2CH$-NH-CO), 3.45 (m, H, -NHC$H(CH_3)_2$), 1.02 (d, 6H, $(CH_3)_2$CHNH-).

Preparation of Cotton Fiber/Ag. A skein of cotton fiber was cleaned using an aqueous solution of a nonionic surfactant (200 mL), *n*-hexadecyl octaethylene glycol ether (10 mmol), and placed in an ultrasonic bath for 20 min at 70 °C. The resulting cleaned fiber was removed from the solution and rinsed with distilled water several times; the fiber was then dried and stored in the dry state until the next step. The resulting cleaned fiber was immersed in a silver isopropylcarbamate solution and sonicated for 10 min. It was then gently squeezed and transferred to a convection oven at 125 °C for 20 min. The silver-coated cotton fiber was rinsed in isopropanol/water (50/50) at 20 °C for 2 h, and the solutions were shaken for 15 min before the fiber was removed. The samples were dried at 50 °C. The resulting fiber was termed "cotton fiber/Ag". Using similar procedures, we prepared other cotton fiber/Ag using different concentrations of the silver precursor solution (Ag (0.5%)-Ag(10%)).

Silver Ion Release Study. The dynamics of ionic silver release were measured by soaking a cleaned cotton fiber/Ag (5 cm) in distilled water. Silver ion in solution was quantified after 1 to 20 days by ICP-MS. To attain uniform concentrations, the solutions were homogenized by occasional shaking as well as by shaking the flasks prior to withdrawal of analyte for spectrometric evaluation.

Electrical Resistivity Measurements. The conductivity of the AgNPs-modified cotton fibers was evaluated by randomly measuring the electrical resistivity at two points 2 cm apart. Because the conductive layers of the samples were not uniform, the values are averages of measurements taken over the entire length, and the standard deviation reflects this non-uniformity. Electrical resistivity was determined by averaging five values per sample. All measurements were performed at room temperature.

Antimicrobial Activity. The antimicrobial activity of the cotton fiber/Ag was evaluated by measuring the zones of inhibition of E. coli O157:H7 and S. aureus in Luria-Bertani (LB) broth containing silvered cotton fibers. Zones of inhibition were determined using the agar diffusion method. LB agar was cast into Petri dishes and cooled. Approximately 6×10^8 colony forming units of each bacterium were inoculated. Then, 15 mm fibers were placed on the agar plates. Zones of inhibition were measured after 24 h of incubation at 37 °C.

Results and Discussion

Preparation of Silver Isopropylcarbamate. Silver isopropylcarbamate (Ag-IPCB) is prepared by the reaction of isopropylammonium isopropylcarbamate with silver oxide powders. After 24 h, the reaction mixtures changed from gray black slurry to transparent solution, indicating formation of silver isopropylcarbamate, which was confirmed by ^{1}H NMR spectroscopy.

TGA using isothermal aging method after an incremental temperature increase from 28 to 110 °C showed a 13.9% residual weight after 20 min as shown in Figure 1. Therefore, the silver carbamate complex can be decomposed to silver metal after aging at 110 °C within 20 min.[32]

The formation of silver may be explained as follows. It has been shown that silver carbamate complex can be decomposed to form silver metal by only heat treatment at temperatures in

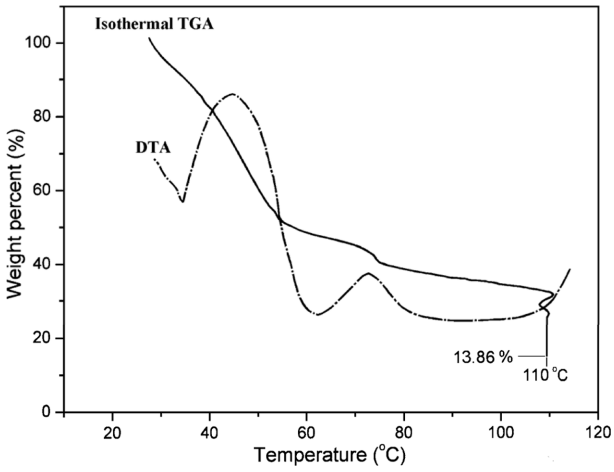

Figure 1. DSC and TGA thermograms of Ag-IPCB complex solution using isothermal aging up to 110 °C.

the range of 70 to 130 °C. This reaction indicates that Ag-IPCB is reduced to metallic silver simply by heating, and that the reaction is accompanied by the formation of *n*-propylamine and release of carbon dioxide.

Preparation of Ag-loaded Cotton Fiber. Prior to thermal reduction, the cotton fiber was first irradiated ultrasound by a high intensity ultrasonic horn. The ultrasound irradiation did not generate new bonds between the silver and the hydroxyl groups of the cotton. In fact, silver coating is a physical adsorption of AgNPs on the cotton fiber as a result of the sonication. When the microscopic cavitation bubbles collapse near the surface of the fiber, they generate powerful shock wave microjets that cause effective stirring and mixing of the adjusted layer of the silver precursor solution. The after-effects of the cavitation are several hundred times greater in heterogeneous systems than in homogeneous systems.[33,34] This may be the reason why the particles strongly adhere to the fabric's surface.

The alcoholic solution of silver precursor affords control over deposition on the hydrophilic surface of cotton fibers. Silver-coated cotton fibers were produced by deposition of AgNPs via thermal reduction of silver carbamate as reported previously:[35,36] $2Ag_2(OCONHC_3H_7)_2 + 2H_2O \rightarrow 4Ag + 4C_3H_7NH_2 + 4CO_2 + O_2$.

During the silvering process, the clear silver isopropylcarbamate-coated cotton fibers turn immediately brown and then the metallic gray of AgNPs after heating at 125 °C. Cotton fibers have a negative zeta potential due to acidic groups in their chemical structure such as carboxyl or hydroxyl groups.[37] Silver ions with positive charges can adsorb and diffuse into the micro fibrils of cotton fiber due to the electrostatic interaction of negative charge groups and positive charge of silver ions. Thus, silver ions can be converted to silver atoms and nanoparticles by thermal reduction and cotton fiber acts as a template and controls the growth of AgNPs.[2] The process is shown schematically in Figure 2.

Visual Observation. Visual observations can determine whether cotton fibers have been successfully loaded with AgNPs. In the chemical reduction system, concentration of reducing agent was adjusted more than the silver ions concentration on the cotton fiber, while all the absorbed Ag^+ into cotton fiber was reduced to Ag atom in thermal reduction system. Moreover, the higher concentrations of silver carbamate precursor create higher nuclei which lead to larger AgNPs due to growth of AgNPs during thermal reduction at 125 °C for 20 min. Synthesizing silver nanoparticles on cotton fiber changes the color of cotton fiber from yellow to metallic color.

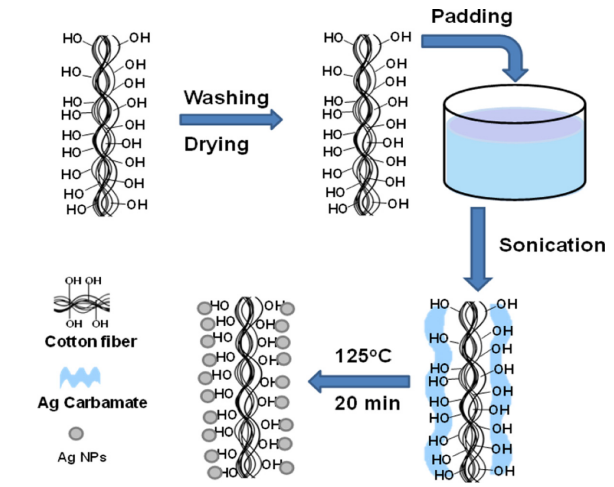

Figure 2. Illustration of the processes involved in the coating of cotton fibers with AgNPs using silver isopropylcarbamate.

Figure 3. Optical images of cotton threads prepared with different loadings of AgNPs.

A yellow color of various shades from dark yellow to brown is generated on cotton fibers treated with Ag(0.5%), Ag(1%), Ag(2%) and Ag(5%) silver precursor solutions as shown in Figure 3.[38,39] This was evident as a white thread was employed. Cotton fiber treated with Ag(7%) and Ag(10%) exhibited a metallic silver color.

SEM Images. SEM was used to assess the surface morphology of the cotton fibers before and after coating with AgNPs. On micron-level image of the original cotton fiber (Figure 4(a)), smooth and neat surface with grooves and fibrils were evident. Figure 4(b) shows SEM images of AgNPs on cotton fiber after thermal reduction of Ag(2%) precursor solu-

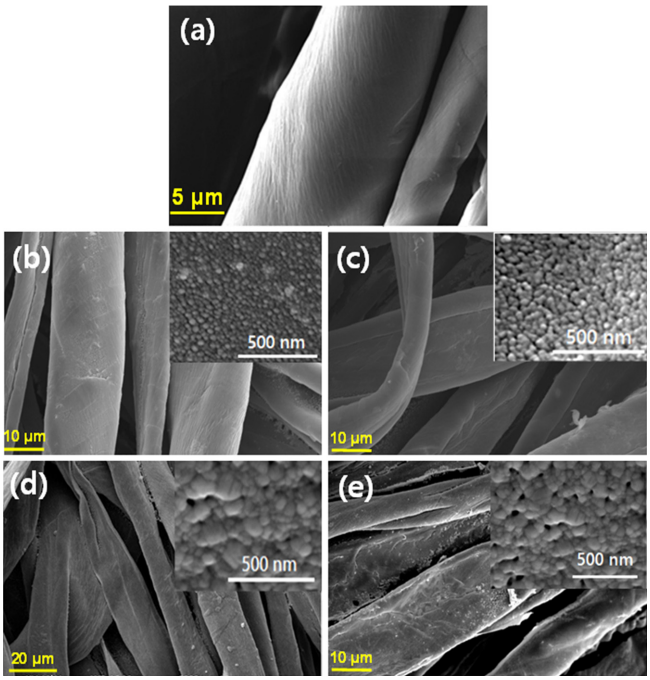

Figure 4. SEM images of (a) pristine cotton fiber; (b) cotton/Ag(2%); (c) cotton/Ag(5%); (d) cotton/Ag(7%); (e) cotton/Ag (10%); inset figure was captured with a magnification setting of 100 kx.

tion-treated cotton fibers. The cotton fibers were covered homogeneously with AgNPs. SEM image of silver-coated cotton fibers using Ag(5%) silver carbamate solution is shown in Figure 4(c). The size of AgNPs on the cotton fibers was in the 30-100 nm range due to rapid growth and aggregation of AgNPs at 125 °C growing condition. From Figure 4(d), AgNPs coated on the fiber using Ag(7%) precursor solution were in the range 50-150 nm, which is consistent with previous reports.[40] Figure 4(e) displays SEM images of cotton fibers treated with Ag(10%) precursor solution at 30 kx and 100 kx magnifications, respectively. Compact and dense AgNPs with 50-200 nm in size on the fiber surface were evident after treatment with such a high silver concentration. Thermally reduced AgNPs were grown into silver layers composed of grains with large AgNPs through condensation. Thermal reduction of silver carbamate is an alternative method, simple and cost effective to obtain AgNP thin layer on the substrates such as film, fiber and textile.

XPS Measurement. To verify the presence of AgNPs on the cotton fibers, XPS analysis was performed (Figure 5). In the wide scan spectrum, peaks of O1s and C1s are evident. The appearance of Ag3d indicated the presence of silver in the cotton fiber. The narrow scan spectrum of Ag3d exhibited two

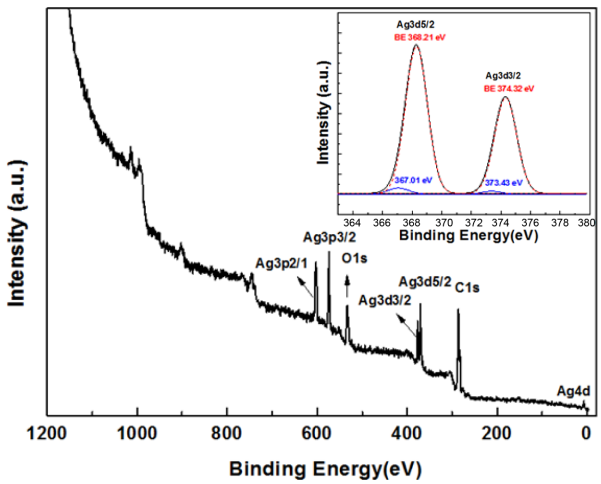

Figure 5. XPS spectra of Ag coated cotton fiber. Inset figure: deconvoluted Ag3d XPS spectra of cotton fiber surface.

peaks at 368.23 and 374.24 eV with 6.01 eV separations, corresponding to Ag3d5/2 and Ag3d3/2 binding energy of Ag^0, respectively. Therefore, the nanoparticles on the cotton fibers were AgNPs. It is reported that the metallic silver shows an anomalous negative shift in the binding energy (BE) upon oxidation to silver oxides, that is, the Ag3d peaks shift to lower BE values for oxidized form of silver. The Ag3d XPS peaks were deconvoluted into two component peaks, 368.21 eV (97%) and 367.01 eV (3%) and, which correspond to two different states of silver, namely metallic silver (Ag^0) and silver oxide (Ag^+), respectively.[41]

EDX and XRD Analysis. The chemical composition of the Ag-coated cotton samples is analyzed with EDX (Figure 6). EDX analysis show that Ag, C and O are present. The pres-

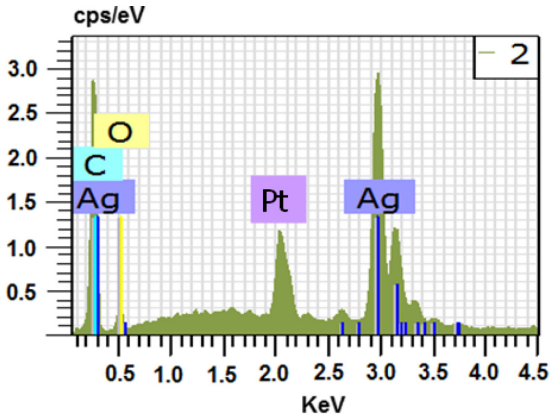

Figure 6. EDX analysis patterns of Ag coated cotton fiber treated with 5% silver carbamate complex.

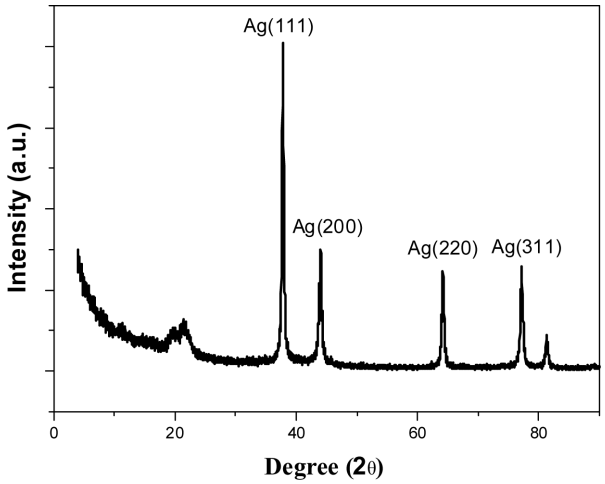

Figure 7. XRD patterns of cotton fibers coated with silver nanoparticles.

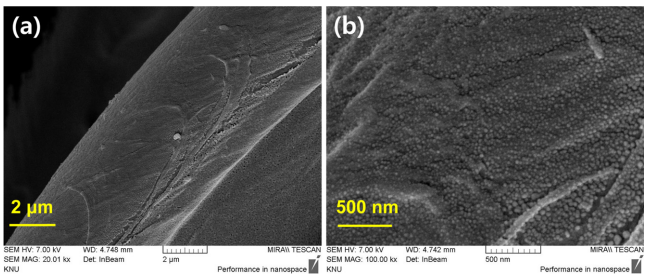

Figure 8. SEM images of washed silvered cotton fiber at magnification (a) 20 kx; (b) 100 kx.

ence of Ag atoms in the coated cotton fibers suggests successful deposition of AgNPs. The results were reported as both weight percentages (C, 17.84%; O, 6.65%; Ag, 75.71%) and atomic percentages (C, 57.10; O, 15.98; Ag, 26.92%) of detected elements. The elemental weight and atomic level were increased to a level greater than that reported previously.[42,43] This confirmed the presence of silver in the cotton fibers.

The XRD pattern of the Ag-coated cotton fiber reveals the presence of crystalline silver. The diffraction peaks match with the JCPDS silver file No. 04-0783. Four reflection peaks were distinguishable at 2θ values of 37.5, 44.3, 64.4, and 77.6 degrees, assigned to the (111), (200), (220), and (311) reflection lines of face-centered cubic (fcc) crystal structures, respectively (Figure 7). Thus, silver nanoparticles were deposited directly on the cotton fiber surface and cotton fiber/Ag nanocomposites were prepared using silver carbamate by heating at 125 °C.

Washing Properties. During washing, unbound AgNPs are lost. SEM images of cotton fiber/Ag washed three times show

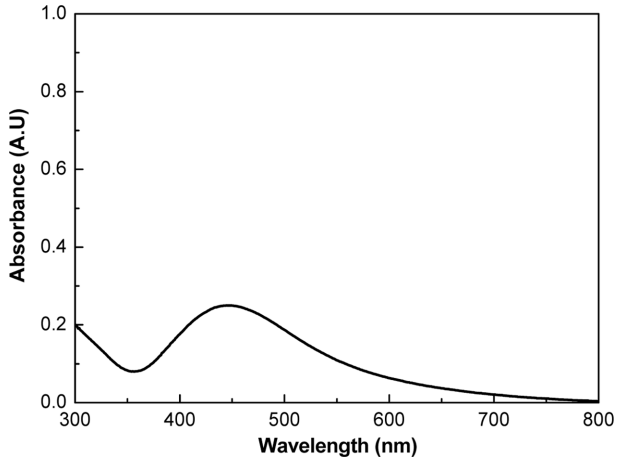

Figure 9. UV-visible spectrum of AgNPs-dispersed colloidal solution obtained after washing of cotton fiber/AgNPs.

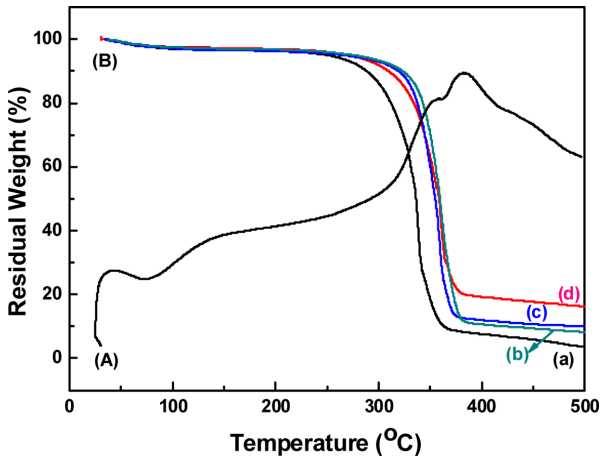

Figure 10. (A) DSC; (B) TGA analysis of cotton/Ag fibers with different silver content fibers.

that most particles remained on the surface of the cotton fibers, as the silver nanoparticles were effectively bound (Figure 8). After the washing solution was collected three times and concentrated, UV-Vis spectra analysis revealed a small plasmon resonance peak around 450 nm due to release of silver nanoparticles after three washing cycle as shown in Figure 9. This confirms that the cotton fiber surface enabled binding of the AgNPs.

Thermal Properties. The thermal properties of pure cotton and Ag-cotton fibers were investigated. Figure 10(A) shows the DSC curves of pristine cotton fibers and cotton fiber/Ag. Two endothermic peaks appear in the DSC curves-peak I at 78 °C (control sample) and peak II at 366 °C (control sample). The first peak can be attributed to loss of moisture from the

Table 1. Composition of Silver Precursor Solutions with Various Content of Silver and the Electrical Property of Cotton Fibers

Cotton/Ag[a]	Ag content[b] (%)	Electrical resistivity (kΩ·cm)[d]		
		10-ply	20-ply	30-ply
Pristine cotton	0 (2.49)[c]		-	
Cotton/Ag(2%)	4.23		-	
Cotton/Ag(5%)	6.48	12.76	4.31	1.26
Cotton/Ag(7%)	8.57	5.38	1.96	0.98
Cotton/Ag(10%)	14.32	1.17	0.38	0.15

[a]Cotton fiber treated with various concentration of silver carbamate precursor solution. [b]Ag content in cotton fiber coated with silver measured by residual weight at 600 °C. [c]Residual weight of pristine cotton at 600 °C. [d]Cotton fibers with 130 denier were joined together by twisting.

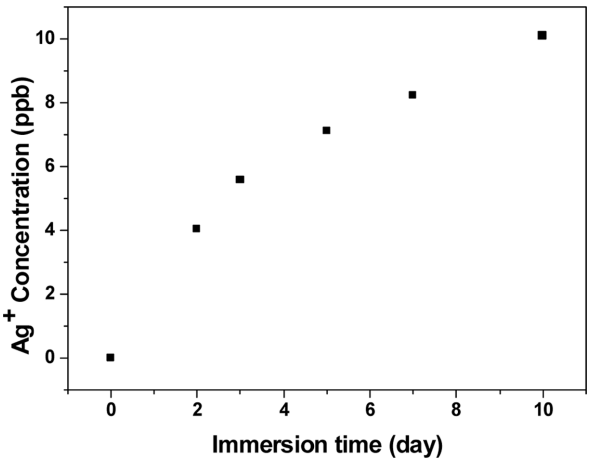

Figure 11. Silver ion (Ag+) release of cotton fiber/Ag after immersing sample in water.

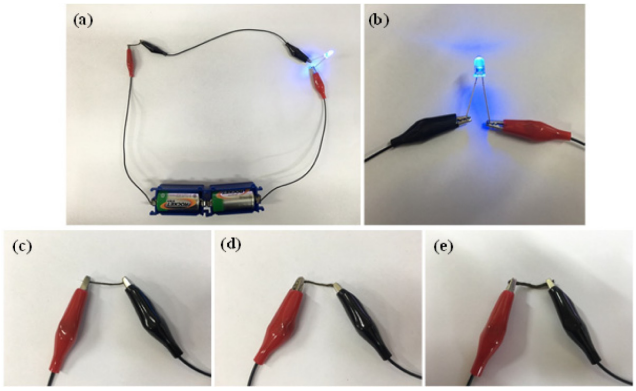

Figure 12. Conductive silver coated cotton fibers ties into a simple circuit: (a) knotting one end to a battery and the other to an LED; (b) lighted LED lamp and tied with (c) 10-ply; (d) 20-ply and (e) 30-ply of AgNPs-coated cotton fiber.

cotton material and the AgNPs. For silvered cotton fibers this peak shifts to higher temperatures. The second peak corresponds to the temperature of cellulose degradation.[44] Figure 10(B) shows thermograms of unmodified and silvered cotton fibers. Pristine cotton fibers showed good thermal stability up to 250 °C, and maximum decomposition occurred at 330 °C. The amount of residual silver on the cotton fiber surface was determined by TGA analysis to be 4.23 and 14.32% for samples treated with Ag(2%) and Ag(10%) silver precursor solutions (Table 1). The decomposition onset temperature of silvered cotton fibers increased by more than 20 °C compared to that of pristine cotton fiber. However, the maximum decomposition temperature decreased slightly for the cotton fibers with highest silver concentration, but the overall thermal stability of the cotton fiber/Ag improved.

Silver Ion Release. Positively charged silver ions (Ag^+) are released from the surface of silver layer and exert an antibacterial effect in the presence of atmospheric oxygen and moisture from the metallic silver surface.[45] The silver ion release analysis was more significant than the other tests in showing the effect of AgNPs on the silvered cotton fibers. The Ag^+ release was observed as increasing with time using ICP-MS measurements as shown in Figure 11. AgNPs on cotton fibers were oxidized and then released from the cotton/Ag composites. Silver ion (Ag^+), which is a versatile antimicrobial species, was released in a steady and prolonged manner from silver-coated cotton fibers.

The observed finding may be explained on the basis of the fact that Ag^+ ions, which were oxidized and subsequently released from the internal part of the cotton fiber/Ag, are released slowly into the surrounding fluid. The cotton/Ag surfaces still show a compact and uniform covering of AgNPs.

Electrical Conductivity. The advantages of silvered cotton fiber in contrast to metal wire are its flexibility, considerable elasticity, and deformability. Table 1 shows the influence of silver precursor concentration on the electrical resistivity of silvered cotton fiber.

The amount of silver embedded on the fiber surface increased with increasing silver carbamate concentration. The thick silver coating on the material resulted in a low level of electrical resistivity. This indicates that the silver particles are in close proximity to one another and form an even layer. The electrical resistivity of cotton fiber treated with Ag(5%) and Ag(10%) was 12.7 and 0.15 kΩ·cm depending on the precursor solution concentration. The conductivity of the silver-

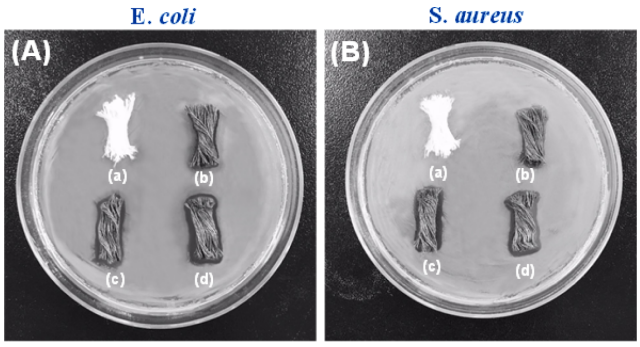

Figure 13. Antimicrobial activity of AgNPs coated cotton. (A) Zones of inhibition of E. coli O157:H7 and (B) S. aureus with AgNPs coated cotton. Growth rate of E. coli O157:H7 and S. aureus incubated with cotton fiber coated with AgNPs using silver carbamate precursor: (a) pristine cotton fibers (negative control); (b) cotton/Ag(0.1%); (c) cotton/Ag(1%); (d) cotton/Ag(2%).

treated cotton fibers was evaluated by making a simple circuit, attaching one end to a battery and the other to an LED (Figure 12).

Antimicrobial Activity. The antimicrobial activity against E. coli O157:H7 and S. aureus of the cotton fiber/Ag samples was evaluated (Figure 13). The cotton fiber/Ag produced using Ag (5%) silver carbamate solution resulted in zones of inhibition against E. coli O157:H7 and S. aureus of diameters 17.3 and 17.5 mm, respectively (Figure 13A). In contrast, fibers created using Ag(10%) silver precursor solution yielded 22.0 and 21.2 mm zones of inhibition against E. coli O157:H7 and S. aureus, respectively. Normal cotton fiber exhibited no antimicrobial activity. These results indicated that silver ions were released from AgNP-coated cotton fiber upon contact with moisture, and exerted antimicrobial activity against E. coli O157:H7 and S. aureus.

Conclusions

Multifunctional silvered cotton fibers were prepared by *in situ* silvering with AgNPs using silver alkylcarbamate by treatment at 125 °C. The amount of silver loaded on the cotton surface was simply controlled by changing the concentration of silver alkycarbamate precursor solution, which would determine the final application from antibacterial to conductive properties in many fields. The morphologies of silver nanoparticles assembled on cotton fiber were unaffected by washing three times, suggesting strong binding to the surface. Electrical conductivity was enhanced by formation of a uniform silver layer on the surface of cotton fibers. The electrical resistivity changed from 12.76 to 0.15 kΩ·cm, depending on the silver concentration. The silver coating also imparted antibacterial activity. The silvered cotton fibers had reasonably good fastness to washing, which will facilitate further multifunctionalization using AgNPs in the fiber industry.

References

1. E. R. Saad and N. M. Hafez, *Inter. Design J.*, **4**, 33 (2014).
2. T. Liu, D. Li, D. Yang, and M. Jiang, *Mater. Lett.*, **65**, 628 (2011).
3. M. H. El-Rafie, T. I. Shaheen, A. A. Mohamed, and A. Hebeish. *Carbohydr. Polym.*, **90**, 915 (2012).
4. S. Gowri, L. Almeida, T. Amorim, N. Carneiro, A. Pedro Souto, and M. F. Esteves, *Text. Res. J.*, **80**, 1290 (2010).
5. S. Q. Jiang, E. Newton, C. W. M. Yuen, and C. W. J. Kan, *J. Appl. Polym. Sci.*, **100**, 4383 (2006).
6. F. M. Kelly and J. H. Johnston, *ACS Appl. Mater. Interf.*, **3**, 1083 (2011).
7. C. H. Xue, J. Chen, Y. N. Wei, S. T. Jia, and J. Z. Ma, *Appl. Surf. Sci.*, **258**, 2468 (2012).
8. L. M. Castano and A. B Flatau, *Smart Mater. Struct.*, **23**, 053001 (2014).
9. S. Liu, M. Hu, and J. Yang, *J. Mater. Chem. C*, **4**, 1320 (2016).
10. J. Lee, H. Kwon, J. Seo, S. Shin, J. H. Koo, C. Pang, S. Son, J. H. Kim, Y. H. Jang, D. E. Kim, and T. Lee, *Adv. Mater.*, **27**, 2433 (2015).
11. J. Coosemans, B. Hermans, and R. Puers, *Sens. Actuat. A*, **130**, 48 (2006).
12. T. Linz, L. Gourmelon, and G. Langereis, *Proceedings of the 4th international workshop on wearable and implantable body sensor networks*, vol **13**, p 29 (2007).
13. J. Löfhede, F. Seoane, and M. T. Thordstein, *Sensors*, **12**, 16907 (2012).
14. L. Ukkonen, L. Sydänheimo, Y. Rahmat-Samii, *Antennas and propagation (EUCAP), 2012 6th European conference on*, IEEE, p 3450 (2012).
15. K. Jost, D. Stenger, C. R. Perez, J. K. McDonough, K. Lian, Y. Gogotsi, and G. Dion, *Energy Environ. Sci.*, **6**, 2698 (2013).
16. D. T. W. Chun and G. R. Gamble, *J. Cotton Sci.*, **11**, 154 (2007).
17. S. Shahidi, A. Rashidi, M. Ghoranneviss, A. Anvari, M. K. Rahimi, M. M. Bameni, and J. Wiener, *Cellulose*, **17**, 627 (2010).
18. N. K. Vu, A. Zille, F. R. Oliveira, N. Carneiro, and A. P. Souto, *Plasma Proc. Polym.*, **10**, 285 (2013).
19. T. Yuranova *et al*. *J. Photochem. Photobiol. A*, **161**, 27 (2003).
20. B. Mahltig, H. Haufe, and H. Böttcher, *J. Mater. Chem.*, **15**, 4385 (2005).
21. K. Anuradha, P. Bangal, and S. S. Madhavendra, *Macromol. Res.*, **24**, 152 (2016).
22. J. He, T. Kunitake, and A. Nakao, *Chem. Mater.*, **15**, 4401 (2003).
23. P. Potiyaraj, P. Kumlangdudsana, and S. T. Dubas, *Mater. Lett.*, **61**, 2464 (2007).

24. I. Perelshtein, G. Applerot, N. Perkas, G. Guibert, S. Mikhailov, and A. Gedanken, *Nanotechnol*., **19**, 245705 (2008).
25. I. Osório, R. Igreja, R. Franco, and J. Cortez, *Mater. Lett*., **75**, 200 (2012).
26. C. A. Impellitteri, T. M. Tolaymat, and K. G. Scheckel, *J. Environ. Qual*., **38**, 1528 (2009).
27. C. Lorenz, L. Windler, N. von Goetz, R. P. Lehmann, M. Schuppler, K. Hungerbúhler, M. Heuberger, and B. Nowack, *Chemosphere*, **89**, 817 (2012).
28. H. Liu, M. Lv, B. Deng, J. Li, M. Yu, Q. Huang, and C. Fan, *Scientific Report*, **4**, 1 (2014).
29. T. Jiang, L. Liu, and J. Yao, *Fibers Polym*., **12**, 620 (2011).
30. I. Perelshtein, G. Applerot, N. Perkas, E. Wehrschetz-Sigl, A. Hasmann, G. M. Guebitz, and A. Gedanken, *ACS Appl. Mater. Interf*., **1**, 361 (2009).
31. H. Zhang and J. Y. J. Zheng, *J. Appl. Polym. Sci*., **125**, 3770 (2012).
32. H. K. Hong, C. K. Park, and M. S. Gong, *Bull. Korean Chem. Soc*., **31**, 1252 (2010).
33. R. D. Alessio, B. Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, and P. Strasser, *Helv. Chim. Acta*, **81**, 219 (1998).
34. K. S. Suslick, *Sci. Am*., **260**, 80 (1989).
35. K. A. Kim, J. R. Cha, and M. S. Gong, *Bull. Korean Chem. Soc*., **34**, 505 (2013).
36. K. Y. Kim, M. S. Gong, and C. K. Park, *Bull. Korean Chem. Soc*., **33**, 3987 (2012).
37. Y. Sood, R. Tyagi, S. Tyagi, P. Pande, and R. Tondon, *J. Sci. Ind. Res*., **69**, 300 (2010).
38. J. M. Gorham, R. I. MacCuspie, K. L. Klein, D. H. Fairbrother, and R. D. Holbrook, *J. Nanopart. Res*., **14**, 1139 (2012).
39. J. M. Gorham, A. B. Rohlfing, K. A. Lippa, R. I. MacCuspie, A. Hemmati, and R. D. Holbrook, *J. Nanopart. Res*., **16**, 2339 (2014).
40. W. K. Kwak, M. H. Oh, and M. S. Gong, *Carbohydr. Polym*., **115**, 317 (2015).
41. V. Kumar, C. Jolivalt, J. Pulpytel, R. Jafari, and F. K. Arefi-Khonsari, *J. Biomed. Mater. Res. A*, **101**, 1121 (2013).
42. W. K. Kwak, M. H. Oh, and M. S. Gong, *Macromol. Res.*, **23**, 509 (2015).
43. W. K. Kwak, J. R. Cha, and M. S. Gong, *Fibers Polym.*, **17**, 1146 (2016).
44. P. Rantuch and T. Chebert, *Cellulose Chem. Tech*., **48**, 461 (2014).
45. S. Agnihotri, S. Mukherji, and S. Mukherji, *Nanoscale*, **5**, 7328 (2013).