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-textiles9 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 tags14 and supercapacitors, etc.15 Recently, an awareness of general sanitation, contact disease transmission, and personal protection
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. Many heavy metals are toxic to microbes at very low concentrations either in its free state or in compounds. 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 (Ag²⁺). 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 or UV irradiation, or sol-gel processing. Bioreduction, in situ reduction of silver ions to metallic silver on fabric and so on. However, conventional surface modification of textiles by AgNPs is not persistent, especially against laundering. Thus, an antibacterial resistant to degradation by home laundering is urgently needed. 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. 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 °C 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 alkylcarbamate 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 HIZZAX PLASTEKS (Uzbekistan). Silver n-propylcarbamate complex solution was prepared by a previously reported method. 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 °C 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 °C.

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 °C/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 °C/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 10° to 80° with a 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 spectroscopy (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).

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 6×10⁴ 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 ¹H 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
the range of 70 to 130 °C. This reaction indicates that Ag-IPC
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 son-
ication. 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. Sil-
ver-coated cotton fibers were produced by deposition of AgNPs
via thermal reduction of silver carbamate as reported previ-
ously:35,36

\[
2 \text{Ag}_2(\text{OCONHC}_3\text{H}_7)_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + 4\text{C}_3\text{H}_7\text{NH}_2 + 4\text{CO}_2 + \text{O}_2.
\]

During the silvering process, the clear silver isopropylcar-
bamate-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 inter-
action 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 con-
centration on the cotton fiber, while all the absorbed Ag⁺ into
cotton fiber was reduced to Ag atom in thermal reduction sys-
tem. 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.

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 mor-
phology 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-
Preparation of Cotton Fibers/silver Composite by a Facile Dipping Method

Solution-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. 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 peaks at 368.23 and 374.24 eV with 6.01 eV separations, corresponding to Ag3d5/2 and Ag3d3/2 binding energy of Ag⁰, 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 (Ag⁰) and silver oxide (Ag⁺), respectively.

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 presence of Ag3d indicated the presence of silver in the cotton fiber. The narrow scan spectrum of Ag3d exhibited two peaks at 368.23 and 374.24 eV with 6.01 eV separations, corresponding to Ag3d5/2 and Ag3d3/2 binding energy of Ag⁰, 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 (Ag⁰) and silver oxide (Ag⁺), respectively.

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.

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

Figure 6. EDX analysis patterns of Ag coated cotton fiber treated with 5% silver carbamate complex.
The presence 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. 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 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 cycles 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
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.\textsuperscript{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.

\textbf{Silver Ion Release.} Positively charged silver ions (Ag\textsuperscript{+}) 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.\textsuperscript{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\textsuperscript{+} 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\textsuperscript{+}), 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\textsuperscript{+} 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.

\textbf{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-

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

<table>
<thead>
<tr>
<th>Cotton/Ag\textsuperscript{a}</th>
<th>Ag content\textsuperscript{b} (%)</th>
<th>Electrical resistivity (kΩ·cm)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10-ply</td>
</tr>
<tr>
<td>Pristine cotton</td>
<td>0 (2.49)\textsuperscript{c}</td>
<td>-</td>
</tr>
<tr>
<td>Cotton/Ag(2%)</td>
<td>4.23</td>
<td>-</td>
</tr>
<tr>
<td>Cotton/Ag(5%)</td>
<td>6.48</td>
<td>12.76</td>
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<tr>
<td>Cotton/Ag(7%)</td>
<td>8.57</td>
<td>5.38</td>
</tr>
<tr>
<td>Cotton/Ag(10%)</td>
<td>14.32</td>
<td>1.17</td>
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\textsuperscript{a}Cotton fiber treated with various concentration of silver carbamate precursor solution. \textsuperscript{b}Ag content in cotton fiber coated with silver measured by residual weight at 600 °C. \textsuperscript{c}Residual weight of pristine cotton at 600 °C. \textsuperscript{d}Cotton fibers with 130 denier were joined together by twisting.
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(10%) silver precursor solution yielded 22.0 and 17.5 mm, respectively (Figure 13A). In contrast, fibers created using Ag(10%) silver carbamate solution resulted in zones of inhibition of 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 alkylcarbamate 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**