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Preparation of silver-coated cotton fabrics using silver carbamate *via* thermal reduction and their properties

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ABSTRACT

In this study, cotton fabric was successfully coated with silver to have both antibacterial and conductive properties through a facile thermal reduction process at a low temperature using silver 2-ethylhexylcarbamate as the starting material. The cotton fabric modified with 3-mercaptopropyltriethoxysilane was padded with a solution of silver 2-ethylhexylcarbamate in methanol and then reduced for the *in situ* generation of Ag nanoparticles by only heating at 130 °C. The silver-coated cotton fabrics (cotton/Ag) were examined by a scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analyses. The morphology of cotton/Ag nanocomposite fabrics conveyed a uniform and continuous layer of silver metal on the cotton surface. The results indicated that the silver nanoparticles were assembled on cotton fibers with a size range from 20 to 100 nm. The cotton/Ag imparts high conductivity to the textiles with electric resistance as low as $3.92 \pm 0.18\ \Omega$. The antibacterial effects of the treated cotton fabric against *Escherichia coli* O157:H7 (ATCC 43889) and *Staphylococcus aureus* (ATCC 25923) were examined and found to be excellent.

1. Introduction

Over the past few decades, the modification of textiles has attracted large attention due to its increasing awareness of human beings toward environmental protection as well as for a healthy, safe and comfortable life (Ashori, Hamzeh, & Amani, 2011; Ashori, Ornelas, Sheshmani, & Cordeiro, 2012; Cordeiro, Ornelas, Ashori, Sheshmani, & Norouzi, 2012; Holme, 2007). Multifunctional textiles could be fabricated through combined treatments using several materials with a specific property of fibers (Xue, Yin, Jia, & Ma, 2011). They can impart the desired properties to the fibers and textiles for their applications. In particular, silver nanoparticle (AgNPs) deposited on textile substrates has been used to produce multifunctional materials with the following properties: antibacterial activity, antistatic finish, electrical conductivity, EMI shielding, ultraviolet (UV) protection, flame retardancy and water repellency (El-Rafie, Shaheen, Mohamed& Hebeish, 2012; Gowri et al., 2010; Jiang, Newton, Yuen, & Kan, 2006; Kelly, & Johnston, 2011; Xue, Chen, Wei, Jia, & Ma, 2012).

In order to assemble nanomaterials on the fabrics, various methods such as the application of UV radiation (Kong, & Jang, 2008), bioreduction (Ravindra, Mohan, Reddy, & Raju, 2010), chemical reduction (Tang et al., 2011) and electron-beam radiation (Chmielewska, & Sartowska, 2012) have been developed. Tollens' procedure, which belongs to green synthetic method, is of outstanding importance these days (Sarkar, Jana, Samanta, & Mostafa, 2007; Sharma, Yngard, & Lin, 2009). The AgNPs were coated directly on the surface of the cotton using a reduction of $[Ag(NH_3)_2]^+$ complex (Montazer, Alimohammadi, Shamei, & Karim Rahimi, 2012) solution. Recently, *in situ* synthesis technique has inspired a great deal of interest due to its facile, efficient and eco-friendly process as well as the uniform distribution and stability of the nanomaterials (Jiang, Liu, & Yao, 2011; Perelshtein et al., 2009; Zhang, & Zheng, 2012). Polypyrrole silver nanocomposite or nano-ZnO were *in situ* fabricated on cotton fabrics by a microwave assistant using pyrrole and silver nitrate, and zinc nitrate and sodium hydroxide, respectively, as the precursors (Li, Hou, & Zou, 2012; Babu, Dhandapani, Maruthamuthu, & Anbu Kulandainathan, 2012). More recently, multifunctional cotton fabric assembled with Ag and ZnO nanoparticles polymer hybrid was fabricated by a one-step *in situ* synthesis method *via* microwave irradiation (Zhang et al., 2013). However, the residual anions derived from silver or zinc oxide precursors should be adequately removed through other processes.

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Carbamic acid is thermally unstable, but is equilibrated with CO_2 and the corresponding amine upon heating (Amico, Calderazzo, Labella, Marchetti, & Pampaloni, 2003; Hampe, & Rudkevich, 2003; McGhee, Riley, Christ, Pan, & Parnas, 1995). However, its silver derivatives were reduced with heating at 130 °C for a few minutes, resulting in its quantitative conversion to silver, carbon dioxide and a corresponding alkyl amine (Jeon, Cho, & Gong, 2009; Lim, Jeon, & Gong, 2009; Park, Lim, Jeon, Kim, & Gong, 2008; Park et al., 2008b). Such reaction occurs because the ionic bond between the silver and carbamate (Ag-OCONHR) is weakened by the coordination of alkyl amine (Park, Shin, Kim, & Gong, 2011). Recently, the controlled thermal reduction of silver carbamate complex in common organic solvents is one of the simplest methods of synthesizing AgNPs. Stable nanopowders and coatings were obtained by a thermal reduction of silver carbamate (Kim, Cha, & Gong, 2013; Kim, Gong, & Park, 2012). This method offers the advantage of producing essentially clean silver particles containing no inorganic ions, except amine and carbon dioxide, even at room temperature. Moreover, the important advantages of the *in situ* synthesis are that no additives (*e.g.*, solvent, surface active agent and reductant) are used, and that the stable silver colloid solution can be directly prepared in high concentration by simply dissolving solid polyvinylpyrrolidone (PVP)/Ag nanocomposites in various organic solvents. Based on the above discussions, in order to realize the immobilization of AgNPs on the cotton with multifunctionality, such as low electrical resistance, antibacterial activity and hydrophobicity, cotton/Ag was prepared only by heating silver 2-ethylhexylcarbamate-absorbed cotton at low temperature. Although this kind of method has been successfully used to prepare AgNPs-coated cottons, it is still desirable to develop fast and efficient routes for the thermal reduction coating. Currently, simple thermal reduction provides a promising method for the preparation of AgNPs because of its characteristics of rapid volumetric heating, high reaction rate, short reaction time and enhanced reaction selectivity. Therefore, this study was aimed at determining the effects of thermal treatment on cotton. We hope that this newly developed metalizing process for fabrics can enhance the textile functionalities; this was evaluated thoroughly in this study. To the best of our knowledge, this approach has not been reported in other similar articles yet. In addition, the amount of silver loaded on the cotton surface was simply controlled by the concentration of silver carbamate precursor solution, which would determine the final application of the treated textile in many fields.

In this study, the AgNPs were coated directly on the surface of the cotton fabric modified with 3-mercaptopropyltriethoxysilane using a transparent alcoholic solution of organometallic silver 2-ethylhexylcarbamate with thermal heating at low temperature 130 °C. The morphology of cotton/Ag nanocomposite fabrics were examined by SEM, XRD, EDX and XPS analyses. Finally, electrical conductivity, silver ion release and antibacterial activity against *Escherichia coli* O157:H7 (ATCC 43889) and *Staphylococcus aureus* (ATCC 25923) were examined.

2. Experimental

2.1. Chemicals and instruments

Silver 2-ethylhexylcarbamate solution was obtained from Inktec Co. Ltd. (Gyeonggi-do, South Korea). The padding medium was a solution of silver 2-ethylhexylcarbamate (26.07 g) in 2-ethylhexylamine (24.14 g) and methanol (49.79 g). 3-Mercaptopropyltriethoxysilane (MPTES, 97%) was obtained from Aldrich Chemical Co. Ltd, USA. All chemicals were of analytic grade and used without further purification. In addition, cotton fabrics (177D, 15 cm × 15 cm, 107.7 g/m^2) were purchased. *Escherichia coli* O157:H7 (ATCC 43889) and *Staphylococcus aureus* (ATCC 25923) were used for the antimicrobial activity of cotton coated with AgNPs. The bacterial strains were cultured in Luria-Bertani (LB) agar or broth at 37 °C.

Surface characterization was carried out by a photoelectron spectrometer (VG Microtech ESCA2000) with an aluminum anode (Kα, λ = 1486.6 eV). Scanning electron microscopy (MIRA LMH, TESCAN, Czech) was used to observe the morphology of the samples. The conductivity of the modified cotton sample was measured using a 4-point probe (SYS-301-6, SIGNATONE, CA). 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).

2.2. Formation of AgNPs on cotton fabric

The procedure for the preparation of AgNPs involves three simple processing steps. In the first step, in order to activate cotton fabric, a piece (15 cm × 15 cm, 3.5 g) of cotton fabric was immersed in 150 mL aqueous solution of a nonionic surfactant (0.5 g) and sonicated for 30 min at room temperature. The fabric was then removed from the solution and rinsed with distilled water several times; then the fabric was dried at room temperature and kept in the dry state until next treatment. In the second step, the samples were then immersed into a 1% MPTES acetone solution at room temperature for 24 h to form a self-assemble monolayer of MPTES on the surface of the fabric. After silanization, the fabrics were baked in an air oven at 70 °C for 30 min. Subsequently, the fabrics were washed in deionized water to remove excess silane molecules. In the third step, the treated fabric was immersed in silver 2-ethylhexylcarbamate solution and sonicated for 10 min. Then, it was removed from the solution and squeezed thoroughly. To form AgNPs, the fabric was transformed into a convection oven maintained at 130 °C for 5 min. The obtained fabric was termed cotton/Ag.

Cotton/Ag fabrics were 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.

2.3. Silver ion release study

In order to study the dynamic release of silver ions, a preweighed quantity of silver-coated cotton fabric (1 cm × 1 cm, 0.02 g) was put into deionized distilled water; then, the silver ion of the solution was measured after 1, 3, 7 and 10 day using an inductive coupled plasma mass spectrometer. In order to attain uniform concentration, the solutions were homogenized by occasional shaking as well as by shaking the flasks just prior to the withdrawal of the analytes for inductive coupled plasma mass spectrometry experiments.

2.4. Antibacterial test for silver-coated cotton fabrics

The antimicrobial activity of the cotton fiber was evaluated by measuring the inhibition zones and growth of bacteria in LB broth medium containing cotton coated with AgNPs. Zones of inhibition were determined using the agar diffusion method. Then, the LB agar medium was cast into the Petri plates and cooled. Approximately 6×10^8 colony forming units of each bacterium were inoculated; then the fabric, which was cut into 13 mm diameter circles, was carefully placed over the agar plates. Zones of inhibition were measured after 24 h of incubation at 37 °C. The reduction of bacterial growth on the textiles was assessed using the standard plating method. A single colony of each strain was inoculated into a 5 mL of

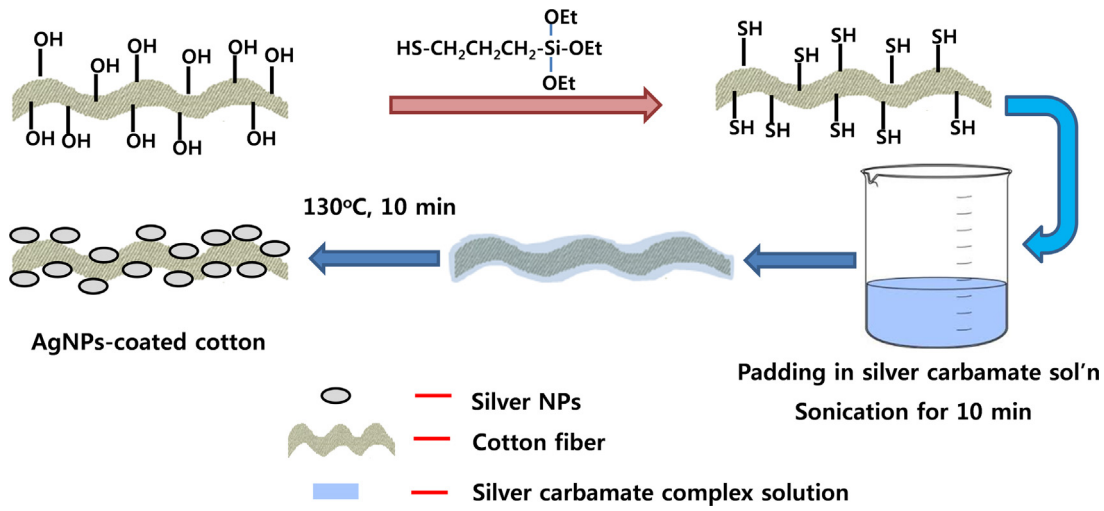

Fig. 1. Schematic diagram of preparation of AgNPs coated cotton by thermolysis using silver carbamate complex.

LB broth medium and incubated at 37 °C with shaking at 180 rpm overnight. The bacterial cultures were diluted 1:100 in a fresh medium and incubated at 37 °C until a late-log phase. Approximately 6×10^8 of each bacterium was inoculated into 1 mL of LB medium containing AgNPs-coated cotton. The number of viable bacterial cells in the supernatant was determined by counting the colony forming units (CFU) on the LB agar plates.

2.5. Resistance measurement

The conductivity of the modified fabrics after silver coating was evaluated by randomly measuring the resistance between two points with 1 cm distance on the textiles for the sake of convenience. The conductive layers of samples are not uniform and therefore, the value of conductivity is taken as an average over the entire area and the standard deviation is a measure of this non-uniformity. All of the resistances were determined by averaging the 5 samples on each sample surface. Further, all measurements were made at room temperature.

3. Results and discussion

The formation of silver nanoparticles 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 130 °C. As is well known, the thermolysis reaction of silver alkylcarbamate may be represented as follows: $2Ag(OCONHC_8H_{17}) \cdot 2C_8H_{17}NH_2 + 2H_2O \rightarrow 2\,Ag + 8\,C_8H_{17}NH_2 + 4CO_2 + O_2$. This reaction indicates that silver 2-ethyhexylcarbamate is reduced to metallic silver simply by thermolysis, and that the reaction is accompanied by the formation of 2-ethylhexylamine and release of carbon dioxide as shown in Fig. 1 and Figures 1S and 2S (Park et al., 2008c).

The MPTES easily reacts with the hydroxyl groups on the cotton fabric to form a self-assembled monolayer. It is confirmed that the MPTMS is formed on the cotton fiber. An XPS analysis of the MPTES-modified cotton fabric was carried out in order to quantify the orientation distribution of the —SH groups on the cotton fiber. The wide scan XPS spectrum of the cotton fabric after MPTMS treatment is shown in Figure 3S. C and O are the most detected species and they occur at 285 and 532 eV, respectively. The presence of silicon (Si 2p) on the surface is detected from their characteristic emission peaks at 102 eV. The binding energy value of the single S 2p line at 163 eV corresponds to the mercapto group on the surface of cotton fabric. The findings indicate the formation of a self-assembled monolayer on the cotton surface.

Surface morphology of the reference cottons before and after coating with Ag-carbamate was investigated *via* SEM, as shown in Fig. 2. The untreated cotton depicts a smooth longitudinal fibril structure without any contaminating particles on their surfaces (Figs. 2a and 3b), whereas AgNPs with high surface coverage were formed on the silver carbamate-treated fabric. Many particles can be found dispersed on the surface of the treated ones (Fig. 2c and d) at a magnification of 30k×. From the SEM image of treated cotton fiber at high magnification (100k×), it is obvious that the particles dispersed on the surface of cotton fiber are sphere- and polygon-like in shape (Fig. 2e). The size of the particles is approximately from 20 to 150 nm, as determined by SEM. Some of the AgNPs were agglomerated and therefore caused the formation of large nanoparticles. The small AgNPs were adsorbed on silver-coated fibers and larger aggregated particles. SEM pictures show that the most of the particles are embedded in the cotton matrix. After the samples were washed in the water several times, the cotton fiber surfaces still show a compact and uniform covering of silver nanoparticles, as shown in Fig. 2f and g. The shapes of the silver nanoparticles are irregular with particle size ranging from 20 to 150 nm. The cotton modified with MPTES can efficiently absorb silver atoms, which would result in fast crystal nucleation and growth. The migration and aggregation of silver particles are probably driven largely by the instability of silver atoms because of their high surface-free energy. Their aggregation would produce thermodynamically stable particles with bigger sizes.

XRD patterns of the pristine cotton and cotton/Ag samples are shown in Fig. 3a. Compared to the pristine fabric, four new peaks at 2θ values of 38.4°, 44.6°, 64.7° and 77.5° were detected, which were attributed to the diffraction peaks of the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of silver, respectively, with the face centered cubic structure (crystalline lattice, 0.4090 nm) reported in JCPDS file No. 004-0783 card on the cotton/Ag sample. Fig. 3b shows that the crystalline peaks at 2θ values of 15.0°, 16.7°, 23.1° and 34.1° were attributed to the diffraction peaks of the (1 1 0), (1 1 0), (2 0 0) and (0 0 4) planes of pristine cotton, respectively. No other characteristic peaks were observed for other impurities, such as AgO. The XRD pattern clearly indicates that AgNPs were deposited directly on the cotton surface and cotton/Ag nanocomposites were successfully prepared using silver carbamate simply by heating.

EDX analysis of a treated sample confirming the existence of the Ag element on the surface of the cotton fabric treated with silver carbamate. It was observed that Ag was the only element on the treated cotton samples. The results were reported based on both the weight percentages (C, 18.88%; O, 14.75%; Ag, 66.37%) and

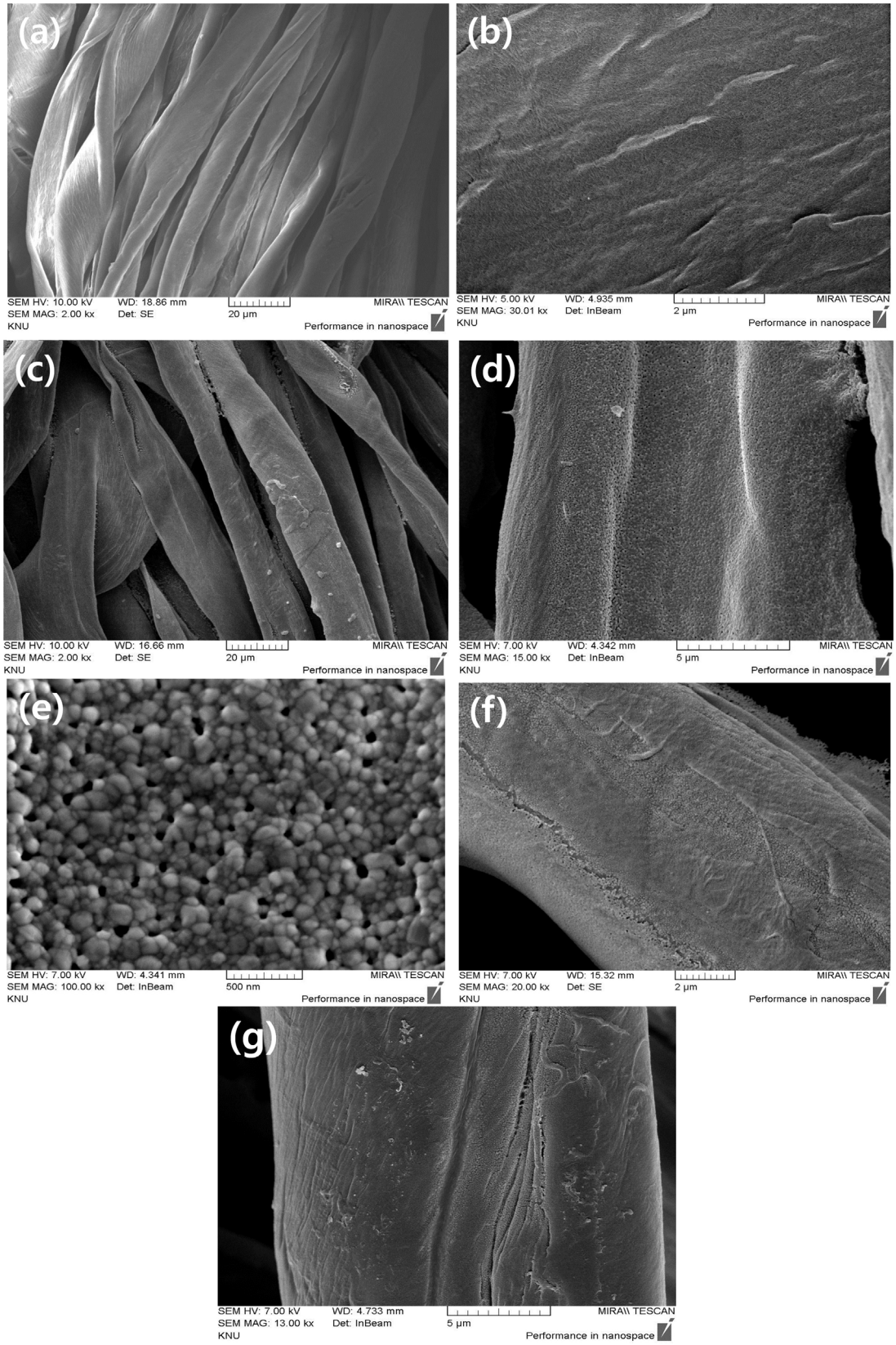

Fig. 2. SEM images of (a) pristine cotton, (b) pristine cotton at magnification 30k×, cotton/Ag at magnification (c) 2k×, (d) 10k×, and (e) 100k×, (f) 20k× after washing and (g) 13k× after washing.

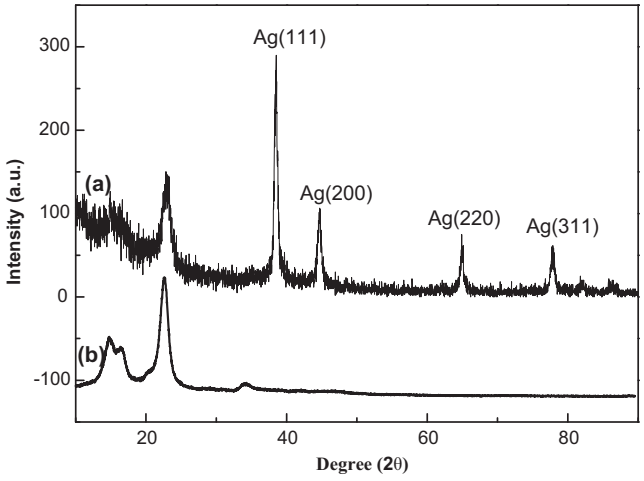

Fig. 3. XRD patterns of (a) cotton fabric coated with silver nanoparticles and (b) pristine cotton fabrics.

atomic percentages (C, 50.56; O, 29.65; Ag, 19.79%) of the detected elements. Higher silver content was observed for the samples using silver carbamate, indicating that silver was effectively formed by the thermal reduction of silver carbamate.

Fig. 4 shows the TGA spectrum of the reference cotton and cotton/Ag coated with silver particles. It is clear that pristine cotton fabric begins to undergo a thermal decomposition at 290 °C while silver-coated cotton has an initial decomposition temperature of nearly 271 °C. The total weight losses, suffered by the two samples, up to 600 °C are nearly 100% and 84.16%, respectively. However, the slightly lower weight loss of pristine cotton fabric compared to silver-coated fabric is simply due to the presence of the highly and thermally stable silver metal in the fabric. Therefore, the overall conclusion is that the attachment of silver onto cotton fabric enhances the thermal stability of the resultant fabric. The initial decomposition temperature of silver-coated cotton is slightly higher than the original one, implying that the silver coating has a minor effect on the heat-resistant or flame retardant property of cotton fabric. The amount of Ag finally retained at the cotton surface was provided by TGA analysis and was about 15.84%.

Fig. 5 conveys the high resolution spectra of the reference cotton and silver-coated cotton. The XPS spectrum of the C1s core-level obtained for the two samples are deconvoluted to three peaks with

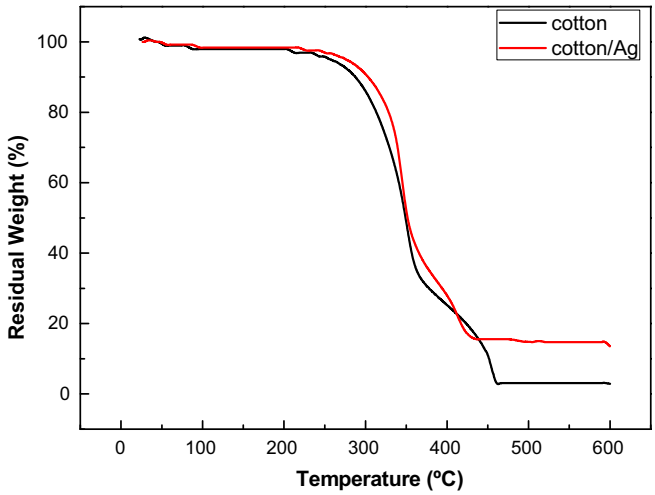

Fig. 4. TGA analysis of (a) cotton, (b) cotton/Ag treated with 26.07% silver carbamate solution.

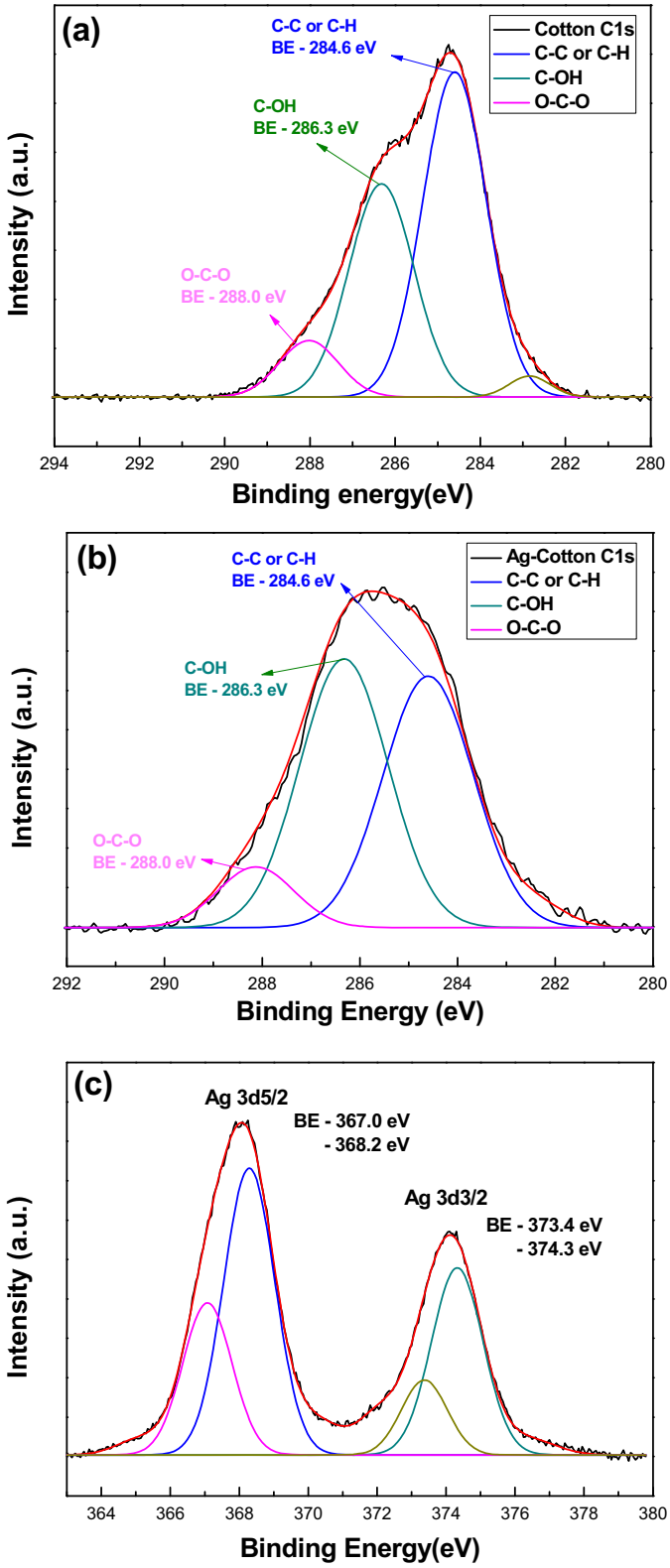

Fig. 5. Deconvoluted XPS spectra of (a) cotton C1s, (b) cotton/Ag C1s, and (c) cotton/Ag Ag 3d.

a binding energy of 284.6 eV (C—C or C—H), 286.3 (C—OH) and 288.0 (O—C—O), as shown in Fig. 5a. The high resolution XPS of the C1s core-level obtained for cotton/Ag is also decomposed to three peaks with a binding energy (BE) of same values, as shown in Fig. 5b. The high resolution spectra of Ag3d of the Ag modified cellulose

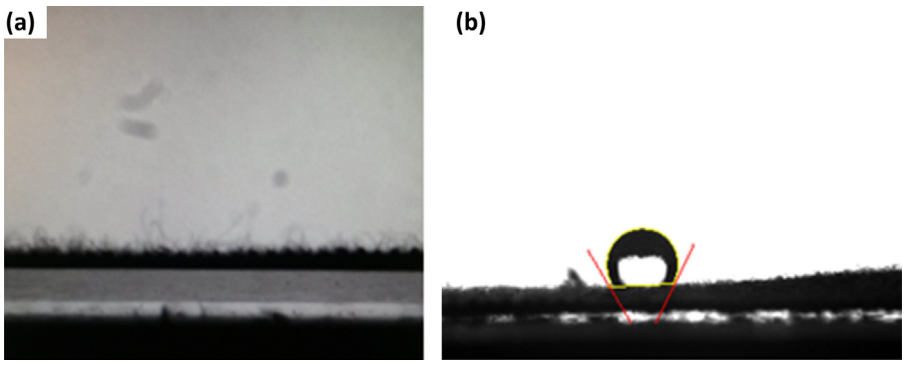

Fig. 6. Contact angle image of (a) pristine cotton and (b) cotton/Ag.

shows two XPS signals at BE of 368 and 374 eV with 6.0 eV separations, corresponding to Ag3d5/2 and Ag3d3/2 binding energy of Ag^0, respectively (Fig. 5c). Ag3d5/2 decomposed into two peaks with a binding energy of 367.0 and 368.2 eV. In addition, Ag3d3/2 decomposed into two peaks with a binding energy of 373.4 and 374.3 eV. Therefore, it is clearly evident that silver ions are reduced to silver nanoparticles in the presence of cotton.

Wetting properties of the fabrics were analyzed by measuring the water droplet contact. As shown in Fig. 6, the pristine cotton fabric was completely wetted by water *via* rapid spreading of the water droplet due to the presence of abundant hydroxyl groups on the surface of cotton cellulose. On the other hand, the cotton/Ag sample showed a slow spreading of water droplet so that the water droplet was gently adsorbed on its surface, demonstrating that coating with AgNPs changed the wetting properties of the fabric because the cotton surface turned hydrophobic with the coated silver. The contact angle of the water droplet on the silver-coated cotton was 118.7° for a 5 μL.

The antimicrobial activity of silver is dependent on the silver cation Ag^+, which binds strongly to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen (Kumar, & Münstedt, 2005). Hence, the cotton/Ag has to release the Ag^+ to a pathogenic environment in order to be effective. The oxidation of the metallic silver to the active species Ag^+ is possible through an interaction of the silver with the water molecules. Silver ion (Ag^+), which is a versatile antimicrobial species, was released in a steady and prolonged manner from silver-coated cotton fabrics. The Ag^+ release was observed as increasing with time as shown in Fig. 7. It can be seen that after an initial increase the rate of release

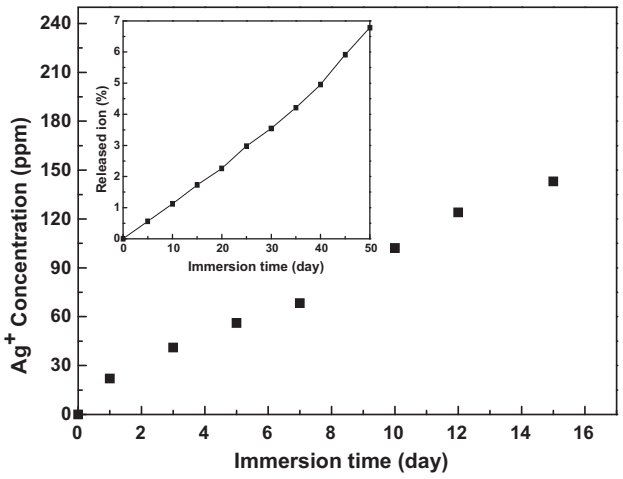

Fig. 7. Silver ion (Ag^+) release after immersing sample in water; the total Ag content of the cotton/Ag sample for 50 days is shown in inset figure.

shows a minimum toward the fifteenth day. The initial release of silver ions (for 1 day) must be from those AgNPs, which are incompletely aggregated within the surface layers of the cotton/Ag sample. After the cotton/Ag sample was washed in the aqueous isopropanol solution, the cotton/Ag, percent of released ions related to the total Ag content of the cotton/Ag sample was about 17 wt% for 50 days as shown in inset figure of Fig. 7. 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/Ag composite, are released slowly into the surrounding fluid. The cotton/Ag surfaces still show a compact and uniform covering of AgNPs.

Conductive fabrics have the potential advantages to solve the problem of interconnecting electronic equipment on textile fabrics. The cotton/Ag is composed of silver crystals only and no other compounds exist, thereby imparting high conductivity to the textiles with electric resistance as low as $3.81 \pm 0.21\ \Omega$ measured using a multimeter, which is comparable to the value of the silver-coated cotton obtained from $[Ag(NH_3)_2]^+$ (Xue et al., 2012). After the cotton/Ag sample was washed in the aqueous isopropanol solution, the resistance value with $3.92 \pm 0.18\ \Omega$ is slightly greater than that of the unwashed sample. The cotton/Ag fabric still retain a low resistance value, indicating that with the conducting layer is not scraped and damaged after washing in water.

The antimicrobial activity of washed cotton/Ag samples was determined by the inhibition zones formed on an agar medium and a direct plating method after the incubation of *E. coli* O157:H7 and *S. aureus*, along with the textiles coated with AgNPs at incubation times as indicated (Fig. 8). The cotton/Ag placed on the agar medium killed the bacteria around the textiles (Fig. 8A). The average diameters of the zone inhibition of *E.coli* O157:H7 and *S. aureus* were 17.3 mm and 17.5 mm, respectively, with cotton coated with a 13.04% silver carbamate solution. When the textiles coated with a 26.07% silver precursor solution were applied on the agar medium, the average zones of inhibition were increased to 22.0 mm and 21.2 mm against *E. coli* O157:H7 and *S. aureus*, respectively. However, the normal and silver particles that simply loaded on the cotton, which were used as a negative and a positive control, respectively, did not show any antimicrobial activity or only slightly killed both bacteria. The effects of the cotton coated with AgNPs on the antimicrobial activity in LB broth medium were also assessed (Fig. 8B). 6×10^8 CFU of each bacterium were inoculated into 1 mL of LB medium containing cotton coated with a 26.07% silver precursor solution. During the first 20 min of incubation after bacterial inoculation, the bacterial growth was slightly reduced by AgNPs-coated cotton. However, after 20 min of incubation, when compared to the growth of the bacteria incubated with normal cotton or silver particles simply loaded on the cotton, the growth of the bacteria incubated with AgNPs-coated cotton was significantly reduced in an incubation-time dependent manner. In particular,

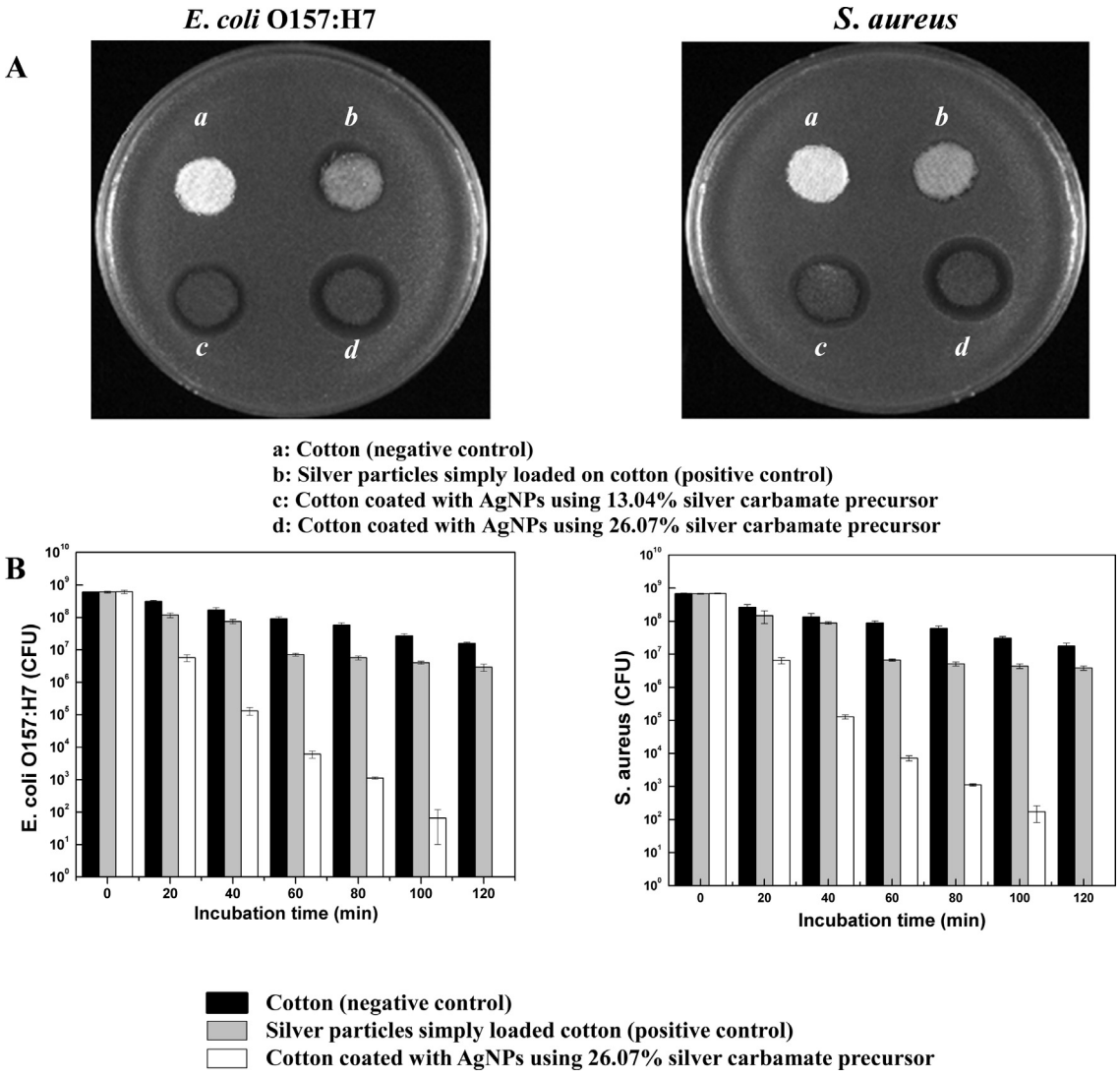

Fig. 8. Antimicrobial activity of AgNPs coated cotton. (A) Zones of inhibition of *E. coli* O157:H7 and *S. aureus* with AgNPs coated cotton. (B) Growth rate of *E. coli* O157:H7 and *S. aureus* incubated with cotton coated with AgNPs using 26.07% silver carbamate precursor. The number of bacterial cells in supernatant was determined by counting CFU on LB agar plates at time intervals as indicated. Data are means ± SEM from three independent experiments.

viable colonies of both bacteria on agar plates were not observed after 120 min of incubation. These results indicated that silver ions might be effectively released from AgNPs-coated cotton on contact with moisture, and AgNPs-coated cotton has a powerful antimicrobial activity against both Gram negative *E. coli* O157:H7 and Gram positive *S. aureus*.

4. Conclusions

Conductive cotton textiles with antibacterial property were fabricated successfully by *in situ* coating cotton fabrics with AgNPs using a transparent alcoholic solution of organometallic silver 2-ethylhexylcarbamate by simple thermal at low temperature 130 °C. The silver nanoparticle roughening effect of the fiber surface favors the construction of hydrophobic surfaces, whereas the compact coating of silver imparts not only the metallic feature to the fibers rendering the textiles conductive, but also the antibacterial property to the cottons. This method of multifunctionalizing conventional fabrics with one material is useful in the fabric industry. Hence, this strategy is expected to become a powerful platform for the fabrication of multifunctional materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.070.

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