CELLULOSE CHEMISTRY AND TECHNOLOGY

PREPARATION OF Ag/ZnO-COATED COTTON FABRICS WITH UV-BLOCKING AND ANTIBACTERIAL PROPERTIES

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Cotton fabric was coated with Ag/ZnO nanoparticles (NPs) *via* a facile, low-temperature thermal reduction process to acquire antibacterial activity and ultraviolet-blocking properties. First, cotton fabric modified with (3-mercaptopropyl)triethoxysilane and (3-aminopropyl)triethoxysilane was added to a solution of zinc (II) 2-ethylhexylcarbamate and silver (I) 2-ethylhexylcarbamate in 2-methoxyethanol and reduced for *in situ* generation of Ag/ZnO NPs through heating at 150 °C. The cotton fabrics coated with Ag/ZnO NPs were then examined using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS). High resolution transmission electron microscopy (HR-TEM) showed crystalline metallic Ag on the crystalline wurtzite-type ZnO and a good combination. The nanocomposite fabrics exhibited a uniform and continuous Ag/ZnO layer composed of Ag, ZnO and Ag/ZnO hybrid NPs 20-40 nm in size. UV-visible spectra verified that Ag/ZnO hybrid NPs presented a special two-absorption-region (strong UV-light and weak visible-light at 421 nm). The study demonstrated that the Ag/ZnO NPs can block UV and that the treated cotton fabric exhibited excellent antibacterial performance against *Escherichia coli* (O157:H7, ATCC 43889) and *Staphylococcus aureus* (ATCC 25923).

Keywords: cotton nanocomposite fabric, Ag/ZnO-coating, antibacterial activity, UV blocking

INTRODUCTION

Modern technological advances have driven substantial development of the textile industry. Thus, textiles have been diversified beyond items for the provision of simple clothing, and are now being applied in the healthcare industry.[1-3] As a result, the demand for new materials with beneficial properties is increasing. The development of synthetic fiber has been a significant advance, as this material can be employed in medical treatment through use of advanced technology from various fields. Indeed, synthetic fiber has a broad range of applications relevant to modern society, including applications in the fields of sports, civil engineering, construction, the information industry and environmental preservation.[4] Therefore, multi-functional fibers having various beneficial characteristics are currently being studied or are in development. In particular, increased research attention is being devoted to the development of ultraviolet (UV)-range interception products, in response to the increasing concern regarding the risks posed by UV rays. Notably, wide-ranging research is being conducted on the surface functional areas of fiber-based materials, towards end processing that yields UV-blocking properties.[5-7]

Cotton is the most commonly used fiber in the textile industry;[8] therefore, considerable multidisciplinary research is being focused on the modification of this fiber for enhancing its properties. In particular, fiber research devoted to developing UV-blocking and antibacterial activities of natural fibers has been established in recent years. In such research, TiO_2,[9] ZnO,[10] ZrO_2,[11] SiO_2,[12] CeO_2,[13] or carbon nanotubes (CNTs)[14] are generally used to enhance the properties of natural fibers. Among these materials, ZnO is a semiconductor having a relatively large bandgap of ~3.2 eV at room temperature.[15-17] ZnO typically has a wurtzite structure, where the O ion is located on the hexagonal sites and the Zn ions are located on the tetragonal interstitial sites.[16] Further, ZnO has strong absorption characteristics in the UV region, because of its surface area; thus, treatment with ZnO can enhance the UV-shielding characteristics of a material.[18] In addition, to improve the performance of enhanced fibers, a variety of noble metals have been added to these materials, including Au, Ag, Pt and Pd.[19] Ag is a stable, high-conductivity material, which is non-toxic and exhibits good antibacterial activity. Further, Ag is less expensive than the other noble metals listed above.[20] The antibacterial activity of Ag is related to the amount and rate of Ag-ion release and its ability to inactivate bacteria.[21,39-42]

A variety of preparation techniques have been reported for the synthesis of silver Ag and ZnO NPs; notable examples include photochemical,[22] sol-gel,[23] hydrothermal,[24] spray pyrolysis[25] and electrospinning[26] methods. Recently, the formation of metal NPs for coating fabrics has offered the capacity for multifunctional fabric features, and the use of Ag/ZnO nanocomposites in this manner constitutes a successful biomimetic method for the realization of photocatalytic and antibacterial activity in fabric.[27,38] For example, Ag/ZnO nanocomposites have been phytosynthesized *in situ* on cotton fabrics, resulting in photocatalytic activity, including self-cleaning properties.[28,40-42]

The mechanisms of the antibacterial activities of the Ag/ZnO nanocomposites are as follows: generation of reactive oxygen species (ROS) from the Ag/ZnO NPs, yielding bacterial cell membrane destruction;[29,38] direct interaction of Ag/ZnO nanocomposites with the bacterial cell membrane and release of Ag^+ and Zn^{2+} ions upon surface oxidation.[30,38]

In this paper, the surfaces of cotton fabrics modified with (3-mercaptopropyl)triethoxysilane (MPTES) and (3-aminopropyl)tetraethoxysilane (APTES) were coated with Ag/ZnO NPs, using an alcoholic solution of silver (I) 2-ethylhexylcarbamate and zinc (II) 2-ethylhexylcarbamate *via* heating at 150 °C. Different Ag:ZnO ratios were employed and the morphologies of the resulting fabrics (hereafter, “cotton/Ag/ZnO”) were examined using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and high resolution transmission electron microscopy (HR-TEM). Furthermore, the UV-blocking effect and antibacterial activity against *Escherichia coli* O157:H7 (ATCC 43889) and *Staphylococcus aureus* (ATCC 25923) were examined for each fabric.

EXPERIMENTAL

Materials

Silver (I) 2-ethylhexylcarbamate (InkTec Co., Korea), (3-mercaptopropyl)trimethoxysilane (MPTES), (3-aminopropyl)triethoxysilane (APTES), acetone, 2-methoxyethanol (Aldrich Chem. Co., USA), and cotton fabrics (177 denier, 15 cm × 15 cm, 107.7 g/m^2) were used as received. Zinc (II) 2-ethylhexylcarbamate was synthesized using previously reported methods.[31,32] *Escherichia coli* O157:H7 (ATCC 43889) and *Staphylococcus aureus* (ATCC 25923) were used for the antibacterial activity assays of cotton/Ag/ZnO.

Formation of Ag/ZnO NPs on cotton fabric

The cotton/Ag/ZnO NPs were prepared by a three-step process. In the first step, a piece of cotton fabric (5 cm × 5 cm, 0.3 g) was immersed in 250 mL of a non-ionic surfactant aqueous solution (0.5 g) and sonicated for 1 h at room temperature. The cotton fabric was then removed from the solution and rinsed with deionized (DI) water several times. Then, the cotton was dried. Silanization was performed in the second step, with a 3% MPTES and 3% APTES acetone solution being mixed with the cotton at room temperature for 24 h to form a self-assembled MPTES and APTES layer on the cotton surface. The coated cotton was then dried in air atmosphere in an oven at 70 °C for 30 min. In the third step, the treated fabric was immersed into a silver (I) 2-ethylhexylcarbamate and zinc (II) 2-ethylhexylcarbamate solution and sonicated for 10 min. The Ag, ZnO and Ag/ZnO deposition process was performed using Ag and Zn carbamate solution ratios of 3:7 and 5:5 (wt%). Then, the cotton was removed from the solution and squeezed thoroughly. To form Ag, ZnO and Ag/ZnO NPs, the cotton fabric was transferred to a convection oven and maintained at 150 °C for 10 min. As noted above, the resultant fabric is referred to as “cotton/Ag/ZnO.”

The cotton/Ag/ZnO was washed according to AATCC, with a standard detergent without optical brightener. The cotton/Ag/ZnO fabric was cleaned using an aqueous solution of non-ionic surfactant, *n*-hexadecyl octaethylene glycol ether (10 mmol) for 1 h at room temperature. Then, the preparation was washed with DI water. The samples were dried at 50 °C. The procedure was repeated five times for performing the washing durability test.

UV-blocking properties of cotton/Ag/ZnO

The UV-blocking experiment was conducted using a UV/vis transmittance spectrometer. The UV-blocking properties of cotton coated with Ag, ZnO and Ag/ZnO were determined in the UV range of 280-400 nm (UV-A and B) at 0.1 nm intervals. Pristine cotton and cotton/ZnO samples were also examined. The UV-radiation blocking properties were determined using AATCC Test Method 183-2004.[33]

Antibacterial activity of cotton fabric coated with Ag/ZnO nanoparticles

The antibacterial activities of the Ag/ZnO-coated cotton fabrics were examined against *E. coli* and *S. aureus*. These bacterial strains were cultured overnight in a Luria-Bertani (LB) medium with required aeration at 37 °C. In detail, a single colony of each strain was inoculated into 5 mL of an LB broth medium and incubated at 37 °C, with overnight shaking at 180 rpm. The bacterial cultures were then diluted in a ratio of 1:100 in a fresh medium and incubated at 37 °C. The LB-agar medium was poured into Petri plates (1 mL of medium per plate) and cooled. Next, either an *E. coli* or an *S. aureus* colony was streaked onto the agar. Then, pristine cotton, cotton/ZnO and cotton/Ag/ZnO samples cut into 10-mm diameter circles were placed over the colonies and the plates were incubated at 37 °C for 24 h. During this period, care was taken with the agar plates. The decrease in the bacterial growth on the cotton fabrics was evaluated using a standard plating method. The number of bacterial cells was determined *via* measurements conducted with a UV/vis spectrophotometer (UV-1601PC; Shimadzu, Japan).

Characterization

The particle sizes and surface morphologies of the samples were inspected *via* FE-SEM (TESCAN, MIRA LMH, Czech Republic), HR-TEM (JEM-2100F, JEOL Ltd., Japan), and EDS was conducted after analysis of the cotton fabric surface. In addition, the XRD technique (XD-D1; Shimadzu, Japan) was used to characterize the cotton fabrics. The UV-blocking properties of the cotton fabric were evaluated using UV-vis transmittance spectroscopy (UV-1601PC; Shimadzu, Japan).

RESULTS AND DISCUSSION

Preparation of cotton/Ag/ZnO

The synthesis mechanism of Ag/ZnO NPs is as follows. The cotton was added to a silane and amine coupling reaction to form a self-assembled monolayer using MPTES and APTES. The hydroxyl groups on the cotton surface changed to –SH and –NH_2 groups. Thereafter, the modified cotton was immersed into the Ag and Zn carbamate solution. The ratios of Ag:ZnO = 1:0, 5:5, 3:7 and 0:1 were employed, as noted above, and the Ag and Zn ions were transformed into Ag/ZnO NPs *via* thermal reduction. The decomposition reaction of Ag and Zn carbamate proceeded according to:

$$2\ Ag(OCONHC_8H_{17}) \bullet 2C_8H_{17}NH_2 + 2H_2O \rightarrow 2\ Ag + C_8H_{17} + 4\ CO_2 + O_2$$

$$Zn(OCONHC_8H_{17})_2 + H_2O \rightarrow ZnO + 2C_8H_{17}NH_2 + 2\ CO_2.$$

This reaction indicates that the Ag carbamate and Zn carbamate were decomposed to Ag and ZnO simply by heating and this reaction was accompanied by the formation of 2-ethylhexylamine and the release of CO_2, the presence of which was later confirmed on the cotton surface. A schematic diagram of the process used to prepare Ag and ZnO on the cotton fabric is given in Figure 1.

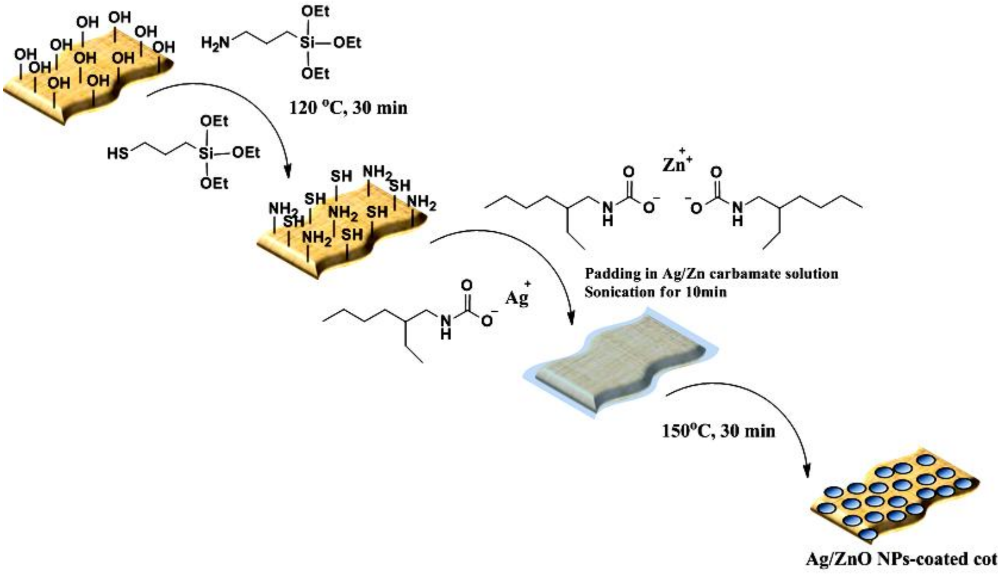


Figure 1: Schematic diagram of preparation process for Ag/ZnO-NP-coated cotton *via* thermolysis using Ag and ZnO carbamate complex

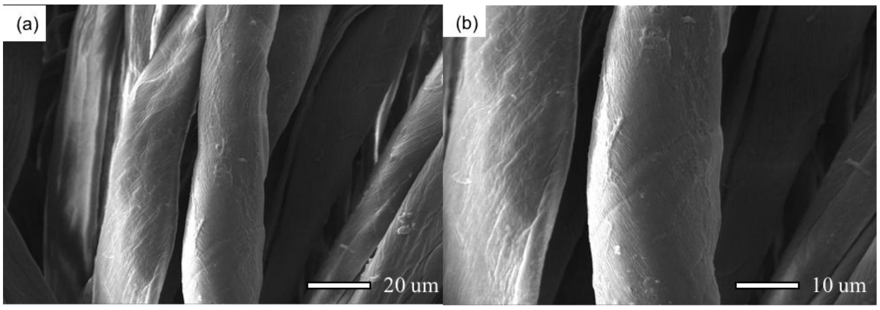


Figure 2: SEM images of pristine cotton at magnifications of (a) 3000× and (b) 5000×

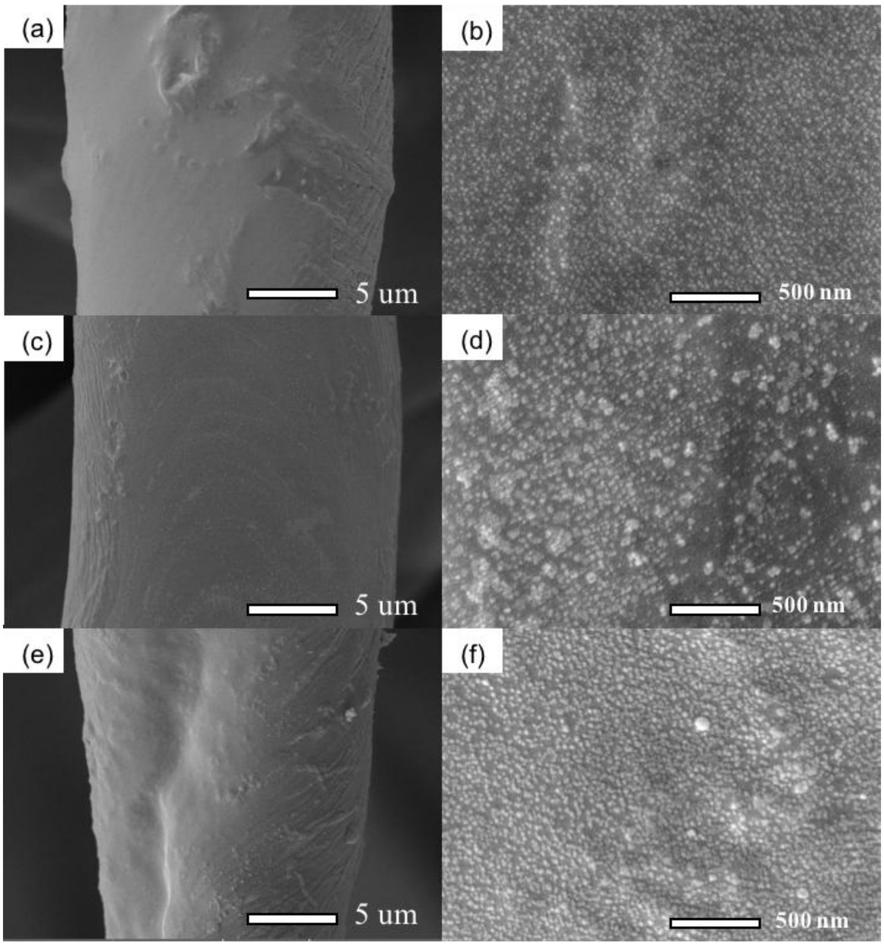


Figure 3: SEM images of cotton/ZnO at magnifications of (a) 10,000×, (b) 100,000×; cotton/Ag/ZnO (3:7) at magnifications of (c) 10,000×, (d) 100,000×; and cotton/Ag/ZnO (5:5) at magnifications of (e) 10,000×, (f) 100,000×

SEM images of cotton/Ag/ZnO

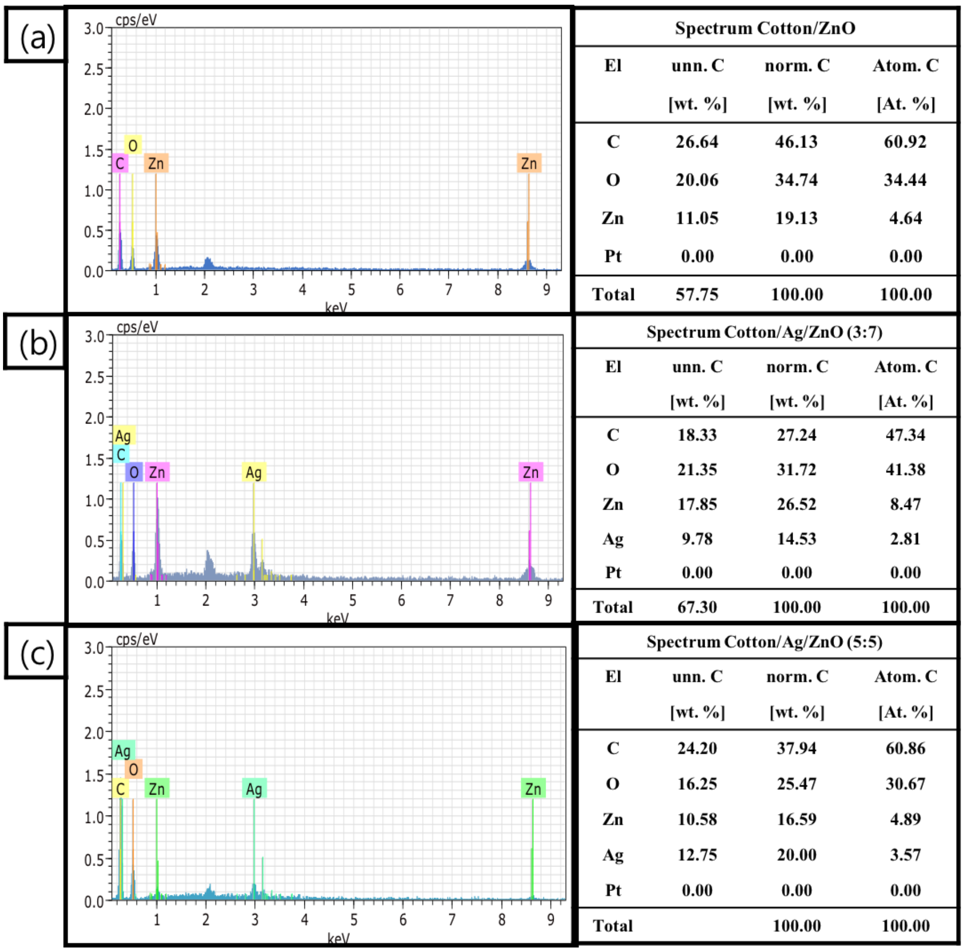
SEM analysis was conducted to compare the pristine cotton with the Ag, ZnO and Ag/ZnO-coated cotton. Figure 2 shows the smooth surface of the pristine cotton, as observed at magnifications of 3000× and 5000×. Further, SEM images of the cotton fabrics coated with Ag/ZnO are shown in Figure 3. Figures 3a and 3b show images of cotton fabric coated with ZnO NPs only, whereas Figures 3c-f show images of the cotton/Ag/ZnO with Ag:ZnO ratios of 3:7 (c, d) and 5:5 (e, f). A higher content of Ag with Ag/ZnO ratio of 5:5 leads to Ag/ZnO NPs with an average grain size of 45 nm, and these particles are evenly distributed on the fibrous surface. SEM analysis indicates that cotton fabric was coated with Ag/ZnO particles with sizes of 28-49 nm. A high deposition density is obtained for the Ag/ZnO NPs on the cotton fabric using the Ag and Zn carbamate solution. Further, larger Ag/ZnO NPs were obtained for Ag:ZnO = 3:7 (Figs. 3c and d). The particle sizes are similar to that of Ag:ZnO = 5:5 (Figs. 3e and f), although several larger and agglomerated Ag/ZnO NPs are present.

EDS analysis of cotton/Ag/ZnO

The presence of Ag and ZnO NPs coating on the cotton fabric surface was confirmed using EDS analysis (Fig. 4). As shown in Figure 4, Zn, O, Ag and C, which are all components of cotton fabric, and Ag/ZnO were detected on the cotton fabrics. Both the weights and atomic percentages of the elements detected on the ZnO and metal-coated cotton are shown to be C, Ag, Zn and O, which are major elements of the cotton fabrics coated with ZnO and Ag/ZnO. Based on these EDS results, no other elements were detected and the thermal reduction process yielded efficient coating of the cotton surface by the ZnO and Ag/ZnO NPs.

XRD analysis of cotton/Ag/ZnO

Figure 5 shows the XRD patterns of the pristine cotton and cotton/Ag/ZnO (3:7). The peaks at $2\theta=$ 14.2, 17.0 and 23.1° are related to the cotton fabric structure (the trendline labeled (b) in Fig. 5). The peaks at 38.5, 43.8 and 63.7° in the trendline labeled (a) in Figure 5 conform to the (111), (200) and (220) planes of Ag NPs with face-centered cubic (FCC) structure (JCPDS:04-0783).[34,35] In addition, the peaks at 32.8, 35.1, 36.5, 47.3 and 56.9° in the same figure correspond to the (100), (002), (101), (102) and (110) planes of the ZnO NPs with hexagonal wurtzite structure (JCPDS:36-1451) located on the cotton fabric surface. The crystallite size of the NPs present on the cotton fabric surface was calculated using Scherer's equation according to the full width at half-maximum (FWHM).



Spectrum Cotton/ZnO			
El	unn. C [wt. %]	norm. C [wt. %]	Atom. C [At. %]
C	26.64	46.13	60.92
O	20.06	34.74	34.44
Zn	11.05	19.13	4.64
Pt	0.00	0.00	0.00
Total	57.75	100.00	100.00

Spectrum Cotton/Ag/ZnO (3:7)			
El	unn. C [wt. %]	norm. C [wt. %]	Atom. C [At. %]
C	18.33	27.24	47.34
O	21.35	31.72	41.38
Zn	17.85	26.52	8.47
Ag	9.78	14.53	2.81
Pt	0.00	0.00	0.00
Total	67.30	100.00	100.00

Spectrum Cotton/Ag/ZnO (5:5)			
El	unn. C [wt. %]	norm. C [wt. %]	Atom. C [At. %]
C	24.20	37.94	60.86
O	16.25	25.47	30.67
Zn	10.58	16.59	4.89
Ag	12.75	20.00	3.57
Pt	0.00	0.00	0.00
Total		100.00	100.00

Figure 4: EDS spectra and analysis data for (a) cotton/ZnO, (b) cotton/Ag/ZnO (3:7), and (c) cotton/Ag/ZnO (5:5)

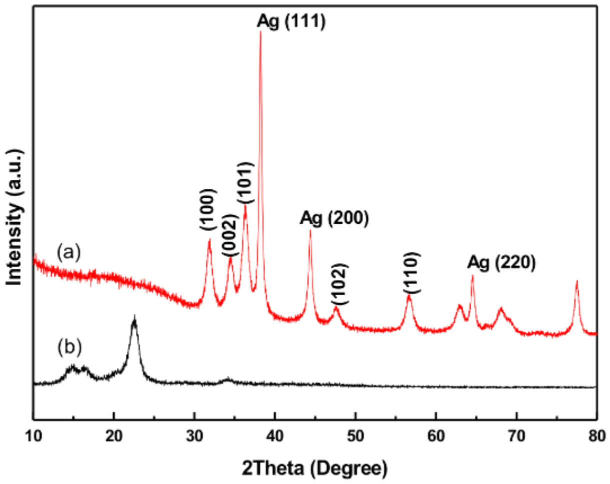


Figure 5: XRD patterns of (a) cotton/Ag/ZnO (3:7) and (b) pristine cotton

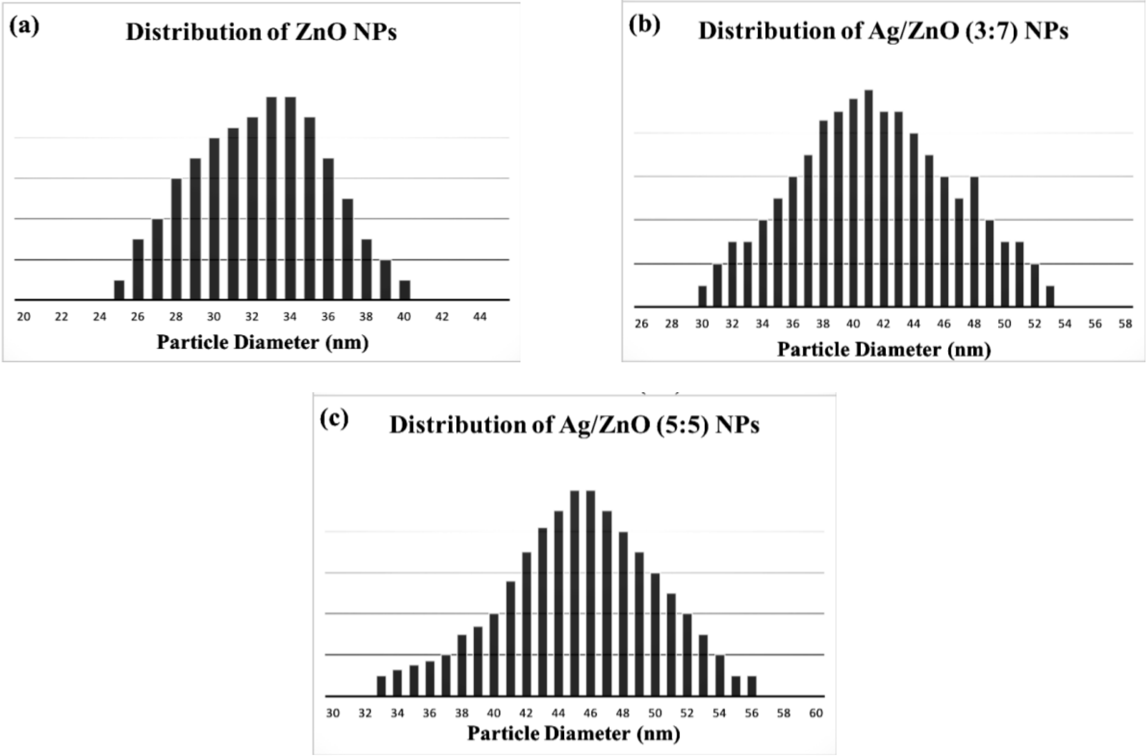


Figure 6: Particle size distribution of (a) ZnO NPs, (b) Ag/ZnO (3:7) NPs, and (c) Ag/ZnO (5:5) NPs

The results indicate that the ZnO and Ag/ZnO NPs had sizes of approximately 48 and 32 nm, respectively. However, it is difficult to obtain the crystallite size from XRD data, because silver and zinc are combined or hybrid nanoparticles. Figure 6 shows the distribution of ZnO, Ag/ZnO (3:7) and Ag/ZnO (5:5) NPs, respectively. As a result, it was confirmed that the ZnO, Ag/ZnO and Ag/ZnO (3:7) (5:5) NPs with average sizes of 34, 41 and 45 nm were obtained, respectively.

HR-TEM study of Ag/ZnO

Figure 7a shows the high resolution TEM image of the Ag/ZnO (5:5) nanocomposite, which presents the lattice fringes of the Ag/ZnO nanocomposite, from which the interplanar spacing is found to be 0.25 nm and 0.23 nm, for ZnO and Ag (111) planes, respectively. The corresponding SAED pattern (Fig. 7b) exhibits the diffraction patterns for both Ag and ZnO. This study indicates the formation of Ag/ZnO combined or hybrid nanocomposites with intermixing. The structural evolution of the Ag/ZnO nanocomposite has also been examined from the XRD spectra, as shown in Figure 5a. The spectra clearly reveal the formation of a well-crystalline hexagonal wurtzite phase ZnO combined with Ag metal. The XRD result is consistent with the HR-TEM measurements.

UV blocking property

Figure 8 shows the UV diffuse reflectance spectroscopy results for pristine cotton, cotton/ZnO and cotton/Ag/ZnO (3:7 and 5:5). The ultraviolet protection factor (UPF) value of the pristine cotton was 8.57. Typically, cotton with a UPF of >50 is considered to provide excellent protection against UV radiation. The UPF values of the cotton/ZnO and cotton/Ag/ZnO (3:7, 5:5) were increased to 237.37, 633.93 and 1899.68, respectively. Hence, it was confirmed that the transmittance of the Ag/ZnO-NP-coated cotton was lower than that of the pristine cotton in the UV region; this behavior was observed because the Ag/ZnO NPs effectively coated the cotton, as confirmed above. Moreover, these results verify that lower transmittance is obtained for higher Ag concentration. The results clearly indicate that the coating of cotton with Ag/ZnO NPs can effectively block UV irradiation.[36] The light transmittance results in the UV ranges (UV-R, UV-A and UV-B) and the UPF values of the pristine cotton, cotton/ZnO, cotton/Ag and cotton/Ag/ZnO (3:7, 5:5) are listed in Table 1. Typically, cotton fabrics with an UPF value of more than 50 are considered as providing excellent protection against UV radiation. Also, silver provides better UV protection than zinc oxide, it is judged by the UPF index, which increased as the silver content was increased.[37]

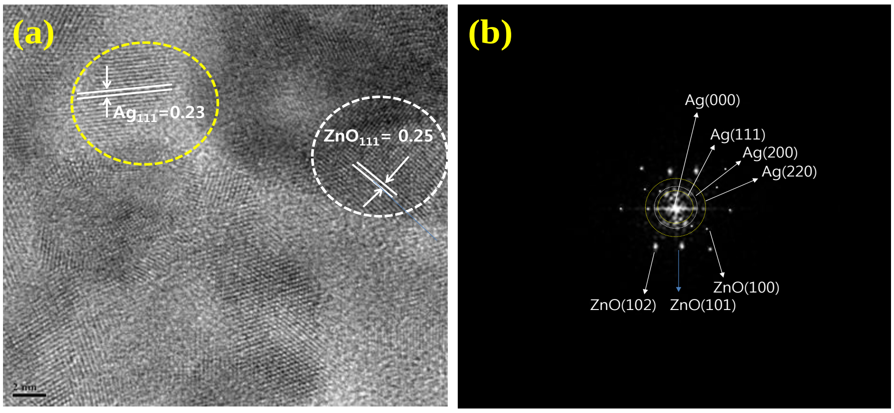


Figure 7: (a) HR-TEM image of Ag-ZnO nanocomposite showing the lattice fringes of Ag and ZnO and (b) combined SAED pattern of Ag/ZnO (5:5) nanocomposite

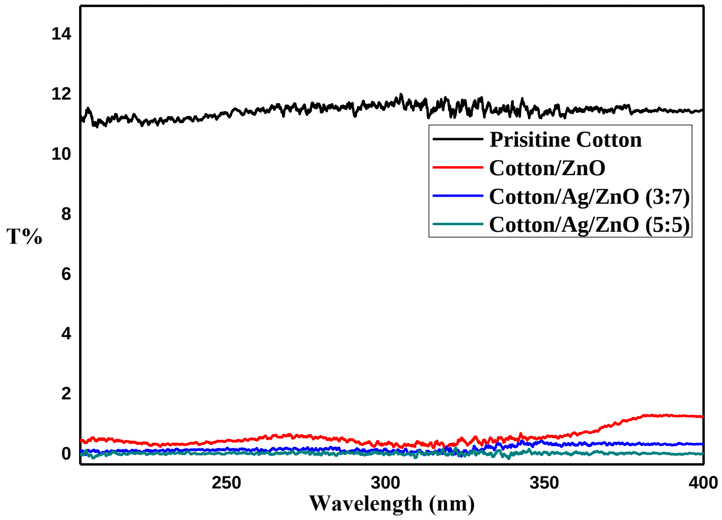


Figure 8: UV-vis transmittance spectra of pristine cotton, cotton/ZnO, cotton/Ag/ZnO (3:7) and cotton/Ag/ZnO (5:5)

Table 1
UV-blocking properties of pristine cotton, cotton/ZnO, cotton/Ag/ZnO (3:7) and cotton/Ag/ZnO (5:5)

Sample	Transmittance percentage (%)			UPF value
	UV-R 280-400 nm	UV-A 315-400 nm	UV-B 280-315 nm	
Pristine	11.57	11.55	11.64	8.57
Cotton/ZnO[a]	0.71	0.82	0.43	237.37
Cotton/Ag[b]	0.12	0.12	0.13	452.25
Cotton/Ag/ZnO (3:7)[a]	0.27	0.32	0.14	633.93
Cotton/Ag/ZnO (5:5)[a]	0.06	0.07	0.04	1899.68

[a,c]Total solution concentrations of Ag and Zn carbamate were 2 wt%; [b]Cotton/Ag was obtained from 1 wt% solution of Ag carbamate

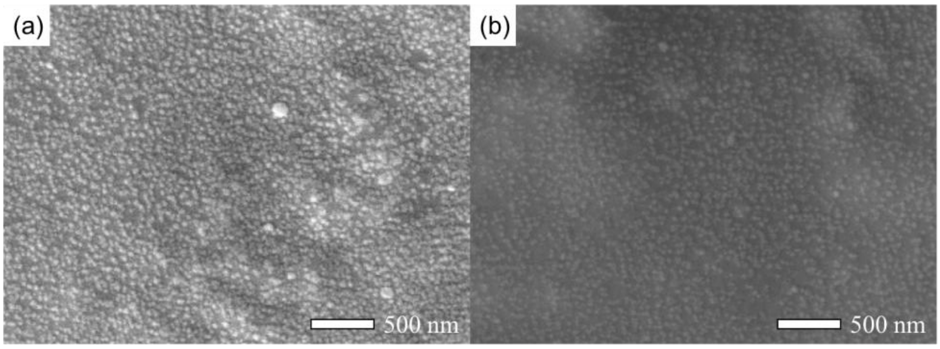


Figure 9: SEM images of cotton/ZnO (5:5) (a) before washing of cotton/ZnO and (b) after washing of cotton/ZnO

Washing durability properties

One of the most important characteristics of Ag/ZnO-coated cotton fabric is its durability during repeated washings. In Figure 9, cotton fabric coated with Ag:ZnO = 5:5 was washed with detergent (AATCC standard detergent without optical brightener) 5 times to study the washing durability. The results confirmed that the Ag/ZnO NPs do not fall off the coated cotton, even after 5 washing cycles. The cotton modified with MPTES and APTES can efficiently absorb Ag and ZnO atoms, which results in fast crystal nucleation and growth. The amount of loaded Ag/ZnO still remained almost unchanged after up to five washing cycles, suggesting that it is possible to obtain almost permanent adhesion of the Ag/ZnO NPs on the thiol- and amino-treated cotton surface for a real application, including for disinfection purposes.

Antibacterial activities of cotton/Ag/ZnO

Both Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria were used in the antibacterial activity test (Fig. 10). Pristine cotton, cotton/ZnO and cotton/Ag/ZnO (3:7 and 5:5) samples were placed on bacteria-inoculated agar plates. Pristine cotton was used as a control, for which no antibacterial activity was confirmed.

A zone of inhibition was observed surrounding the cotton coated with ZnO, Ag/ZnO (3:7) and Ag/ZnO (5:5) carbamate solution for both *E. coli* and *S. aureus*. The antibacterial effect of the Ag/ZnO-NP-coated cotton in the LB broth medium was also evaluated, as shown in Figure 11. Generally, bacterial growth was observed on the cotton fabric. However, this growth was restrained on the cotton coated with Ag/ZnO NPs. In other words, the presence of Ag/ZnO NPs on the cotton fabric suppresses bacterial growth, the treated cotton fabric exhibiting significantly higher antibacterial activity than the untreated cotton fabric. Therefore, the Ag/ZnO-NP-coated cotton appears to have strong antibacterial activity against *E. coli* and *S. aureus*.

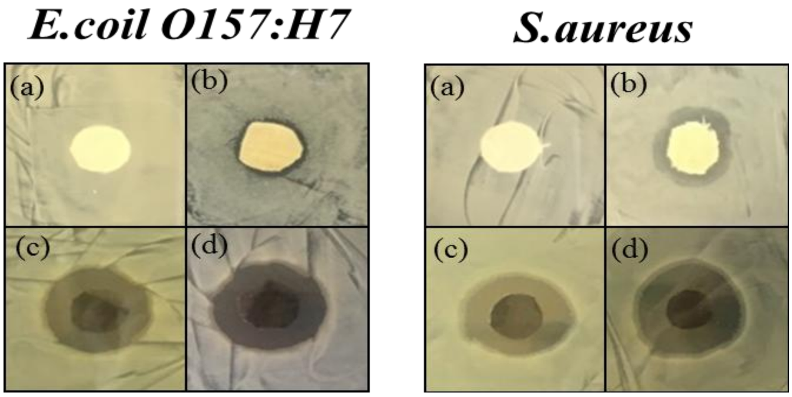


Figure 10: Antibacterial activities of (a) pristine cotton, (b) cotton/ZnO, (c) cotton/Ag/ZnO (3:7) and (d) cotton/Ag/ZnO (5:5); showing the zones of inhibition of *E. coli* O157:H7 and *S. aureus* for Ag/ZnO-NP-coated cotton

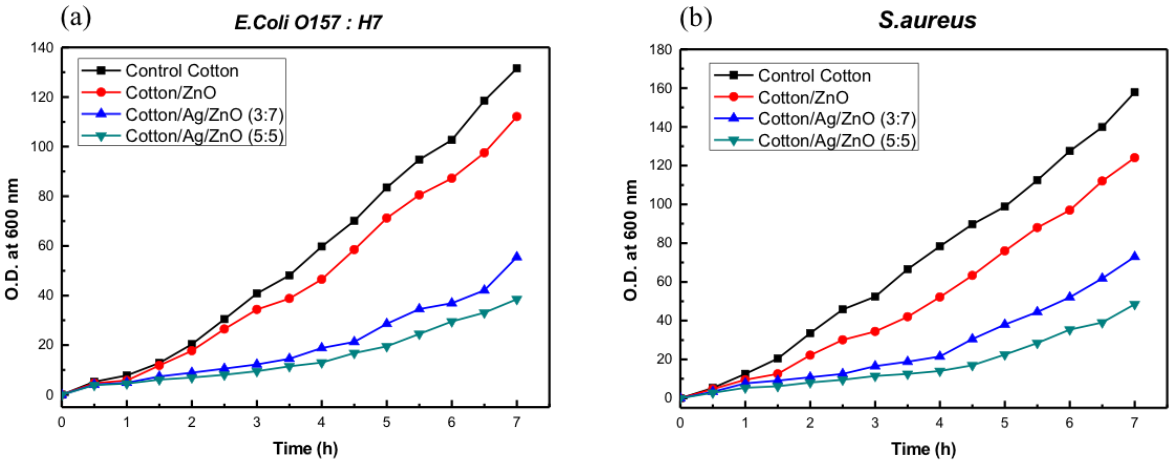


Figure 11: Growth curves of (a) *E. coli* and (b) *S. aureus* bacteria with time evolution on pristine cotton, cotton/ZnO, cotton/Ag/ZnO (3:7) and cotton/Ag/ZnO (5:5) under visible light (600 nm)

CONCLUSION

In summary, cotton fabric with UV-blocking and antibacterial properties was successfully prepared *via in situ* coating of cotton fabrics with Ag/ZnO NPs; this was achieved using a solution comprising organometallic Ag-2-ethylhexylcarbamate and Zn-2-ethylbexylcarbamate and by simple thermal reduction at 150 °C. The successful thermal reduction of the Ag/ZnO nanocomposites on the cotton fabric was confirmed by XRD, SEM and EDS analyses. Excellent antibacterial activity against both *E. coli* and *S. aureus* was observed for the cotton coated with the Ag and ZnO NPs. In addition, cotton fabrics samples coated with the Ag/ZnO NPs exhibited excellent UV-blocking in the UV range. This treatment method, which provides fabric based on a single material with multifunctional properties, has considerable potential application in the textile industry.

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