## **Bifunctionalization of cotton textiles** by ZnO nanostructures: antimicrobial activity and ultraviolet protection

### Mohammad Shateri-Khalilabad and Mohammad E Yazdanshenas



Textile Research Journal 0(00) 1-12 © The Author(s) 2012 Reprints and permissions: sagepub.co.uk/journalsPermissions.nav DOI: 10.1177/0040517512468812 trj.sagepub.com



#### Abstract

Zinc oxide (ZnO) nanostructures were in situ synthesized on the surface of cotton fabric via a simple wet chemical route for providing antimicrobial activity and ultraviolet (UV) protection. Surface morphology and surface chemistry were characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy. Antibacterial activity was evaluated against Gram-negative Klebsiella pneumonia and Gram-positive Staphylococcus aureus bacteria. UV-blocking ability was investigated by measuring the ultraviolet protection factor (UPF) value in the range of 280-400 nm according to AATCC Test Method 183-2004. SEM images revealed that significant amounts of hierarchical ZnO nanostructures were homogenously formed on the fibers' surface; most of them are bundle/flower-like particles having different sizes. Antibacterial tests showed that the ZnO-coated fabric possesses good bacteriostatic activity against two representative bacteria, demonstrated by the zone of inhibition. However, there was no reduction in the number of bacteria, proving the lack of bactericidal activity. The UPF value of the ZnO-coated fabric was increased to 105.61, which demonstrate its excellent ability to block the UV radiation. The washing durability was also confirmed by performing repeated home laundering.

#### **Keywords**

cotton, ultraviolet blocking, antimicrobial, zinc oxide, nanostructures, functionalization

In recent years, due to the novel properties of semiconductor and metal nanostructures, their application in the field of textile finishes has increased rapidly.<sup>1-18</sup> Textile materials functionalized with these nanostructures have proven to be useful for many applications, such as hydrophobicity,<sup>1–4</sup> antimicrobial,<sup>5–10</sup> ultraviolet (UV) protection<sup>11,12</sup> and self-cleaning.<sup>13–17</sup> substrates. However, more interesting and progressive works in the field of textile finishes are the construction of bifunctional or multifunctional fabrics using various nanostructured materials. The finished fabrics can offer multiple innovative characteristics (antimicrobial, water repellent, self-cleaning, UV blocking, electrical conductivity, etc.) simultaneously, which broadens the practical areas of the final product.<sup>19-24</sup>

ZnO, as one of the multifunctional inorganic nanoparticles, is biosafe, biocompatible and exhibits excellent electrical, optical, chemical and biological properties.<sup>25–30</sup> ZnO nanostructures can be synthesized, with different techniques at certain conditions, into a

variety of morphologies including nanowires, nanorods, tetrapods, nanobelts, nanoflowers, nanoparticles, etc., that makes it suitable for various applications.

There are many reports on the considerable antibacterial activity of ZnO nanostructures.<sup>31-34</sup> The advantage of using this inorganic oxide as an antimicrobial agent is that it contains mineral elements essential to humans and exhibits strong activity. Therefore, the application of ZnO nanoparticles to textile materials

#### **Corresponding author:**

Mohammad Shateri-Khalilabad, Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran. Email: m.shaterikha@iauyazd.ac.ir

Mohammad E. Yazdanshenas, Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran Email: dr.yazdanshenas@iauyazd.ac.ir

Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran

has been the object of several studies aimed for producing antibacterial textiles.<sup>35–38</sup> In addition to antimicrobial activity, it is reported that ZnO-coated textiles have good UV-protection properties.<sup>39–41</sup> For instance, cotton fabric containing micro-sized dumbbell-shaped ZnO particles demonstrated complete UV blocking (280–400 nm) with a unique ultraviolet protection factor (UPF) of 800.<sup>39</sup> The transmission of the treated fabric was about 10% lower than that of non-treated fabric and implied a transparent finishing process.

In situ reduction of metal ions on fibers/fabrics is a promising method that results in a more uniform dispersion of nanoparticles. In this method, metal ions are initially adsorbed onto fiber surfaces by electrostatic or Van der Waals forces and then post-treated with reduction treatment, to reduce metal ions into nanoparticles. By taking advantages of this method, various metal nanoparticles, including Au,<sup>2</sup> Ag,<sup>19,42,43</sup> ZnO<sup>35</sup> and CuO,<sup>10</sup> were successfully synthesized on fibers/fabrics.

In this paper, the potential application of ZnO nanostructures for simultaneous antibacterial and UV-blocking finishes of cotton fabrics has been investigated. ZnO nanostructures were in situ synthesized on the surface of cotton fabric via an efficient wet chemical route, which is simple and straightforward. The applied method offers advantages of being cleanroom free, cost efficient and widely applicable. As-obtained fabrics with a high content of hierarchical ZnO nanoparticles showed good antibacterial activity and excellent UV-blocking properties.

#### **Experimental details**

#### Materials

All the reagents, including zinc nitrate (Zn  $(NO_3)_2.6H_2O$ , ammonium chloride  $(NH_4Cl)$ , urea and 25 wt.% aqueous ammonia solution, were supplied by Merck and were used as received. Desized, scoured and bleached plain woven cotton fabric was supplied from Yazd Baf Co. Ltd, Iran. Before being used, the fabric was washed in warm water using a non-ionic detergent to ensure removal of residual chemicals. After washing, the fabric was rinsed with warm water three times, thoroughly with cold water and then oven at  $75^{\circ}$ C for 60 min. Deionized dried water  $(18.2 M\Omega cm)$  from a TLA GenPure ultrapure water system (Germany) was used in all experiments.

# In situ synthesis of ZnO nanostructures on cotton fabrics

ZnO nanostructures were prepared based on the method of Wu et al.<sup>44</sup> with some modifications.

One gram of fabric was transferred into a 100 mL aquewhich ous solution. contained 0.005 mol Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. After 15 min, 0.02 mol NH<sub>4</sub>Cl, 0.01 mol urea and 5mL ammonia solution were added to the reaction vessel. The system was rapidly heated (10°C/ min) to 90°C and kept for 60 min. The pH value of whole system was maintained at  $10 \pm 0.5$  and the reaction was carried out under magnetic stirrer (300 rpm). After reaction, the fabric was removed, rinsed by distilled water several times, then air-dried for 60 min and finally oven cured at 150°C for 10 min to ensure particles' adhesion to the fibers' surface.

#### Scanning electron microscopy

Microscopic investigations on specimens were carried out on an AIS-2100 or a KYKY-EM 3200 scanning electron microscope. Specimens were mounted on conductive carbon adhesive tabs and examined after gold sputter coating. To determine the elemental composition of the fabric surface, an energy-dispersive X-ray spectroscopy (EDS) detector was used with the AIS-2100 scanning electron microscope. Digital images taken from a scanning electron microscope were analyzed by Microstructure Measurement software for measuring the size of the particles.

#### ZnO content

An inductively coupled plasma-optical emission spectrometry (ICP-OES) simultaneous charge-coupled device (CCD) was used on Varian Vista Pro, Australia, to measure the quantity of ZnO concentration on the fabric samples.

#### Antimicrobial assessment

Antimicrobial activity of the ZnO-coated fabrics was studied using two different standard methods: ISO 20645-2004 (Agar diffusion plate method) and AATCC 100-2004 (modified colony counting method). The former method shows bacteriostatic activity, whereas the latter method demonstrates bactericidal activity. Klebsiella pneumoniae (K. pneumoniae, ATCC 10031, Gram-negative bacterium) and Staphylococcus aureus (S. aureus, ATCC 25923, Gram-positive bacterium) were used as model challenge microorganisms. The tests were performed under dark and UV lighting ( $\lambda = 254$  nm; 20 W) conditions. In this agar diffusion method, two-layered agar plates were prepared. The lower agar layer consisted of 10 mL of ordinary agar, whereas the upper layer consisted of  $5 \pm 1 \text{ mL}$  agar inoculated with bacteria, whereby 1 mLof bacteria working solution with a concentration of  $1^{-5} \times 10^8$  colony forming units per milliliter (CFU/mL) was added per 150 mL of agar. Circular cotton specimens, diameter about 18 mm, were uniformly pressed on the agar and incubated for 24 h at  $37 \pm 1^{\circ}$ C. After incubation, the antibacterial effect of the fabrics was assessed by evaluating different parameters: the growth of the bacteria underneath and the presence of at least 1 mm of inhibition zone around the specimen. Ideally, no bacterial growth should be observed on the fabric. Thus a "no growth" category represents "ideal" antibacterial efficacy; that is, no bacterial growth on the cotton. The average width of a zone of inhibition around the test specimen was calculated using the following equation:

$$H = \frac{D-d}{2} \tag{1}$$

where *H* is the width of clear zone of inhibition in mm. D is the total diameter of the fabric specimen and zone of inhibition in mm and d is the diameter of the fabric specimen in mm. In the modified colony counting method, a diluted bacteria suspension with about  $1^{-3} \times 10^5$  CFU/mL concentration was used. A 50  $\mu$ L bacteria suspension was loaded onto the specimen  $(1 \text{ cm} \times 2 \text{ cm})$  surface, and the inoculated specimen was placed in a sterilized glass jar. As soon as possible after inoculation, 5 mL nutrient broth was added to the jar, the cap was tightened and the jar was shaken. After incubation at 37°C for 24 h, the bacteria were eluted from the swatches by shaking them in 10 ml of nutrient broth for 1 min. Serial dilutions of the liquid were made in sterilized water. Dilutions of  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  and  $10^{-6}$  were used for the colony counting method. Of each dilution, 1 mL was spread on to the agar plate. The plates were then incubated at 37°C for 24 h. After incubation, bacterial colonies were counted. The reduction percent of bacteria was calculated using the following formula:

$$R(\%) = \frac{B-A}{B} \times 100 \tag{2}$$

where *B* is the number of bacteria recovered from the inoculated treated test specimen swatches after inoculation (at "0" contact time) and *A* is the number of bacteria recovered from the inoculated treated test specimen swatches after 24 h.<sup>45</sup>

#### UV-protection measurement

The UPF rating system measures the UV protection provided by fabric. The UPF is defined as the ratio of

the average effective irradiance calculated for skin to the average UV irradiance calculated for skin protected by the test fabric. UV-blocking properties of the cotton fabrics were evaluated according to AATCC Test Method 183-2004 (Transmittance or blocking of erythemally weighted UV radiation through fabrics) with a Lambda 35 UV-visible spectrophotometer. The UPF was calculated using mean percentage transmission in the UVA region (315–400 nm) and mean percentage transmission in the UVB region (280–315 nm) according to the following equation:

$$UPF = \frac{\sum_{280nm}^{400nm} E_{\lambda} \times S_{\lambda} \times \Delta_{\lambda}}{\sum_{280nm}^{400nm} E_{\lambda} \times S_{\lambda} \times T_{\lambda} \times \Delta_{\lambda}}$$
(3)

where  $E_{\lambda}$  is the relative erythemal spectral effectiveness,  $S_{\lambda}$  is the solar spectral irradiance,  $T_{\lambda}$  is the average spectral transmission of the specimen and  $\Delta_{\lambda}$  is the measured wavelength interval (nm).

#### Laundering durability

Laundering durability was performed to evaluate the stability of antibacterial and UV-protection properties of the fabrics in analogy to the ISO 105-C02:1989(E) method. In order to get sufficient rubbing and reflect true laundering durability under normal conditions, the ZnO-coated fabrics were washed with other loading cotton fabrics. The ZnO-coated and non-treated (control) fabrics (each one gram) were immersed into an aqueous solution containing 5 g/L Triton X-100 nonionic detergent, at liquor ratio 50:1. The bath was thermostatically adjusted to 50°C. The test was run for 45 min at 750 rpm. The samples were then removed, rinsed in cold distilled water and held under cold tap water for 10 min and dried at room temperature. The cotton samples were subjected to laundering for one and five cycles.

#### Colorimetric measurements

Color measurements were performed on a Lambda 35 UV-visible spectrophotometer using the CIE L\* a\* b\* color space at D65/10°. The color difference ( $\Delta E$ ) between the control and the ZnO-coated samples was calculated using the Equation (1):

$$\Delta E = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}$$
(4)

1.

#### **Results and discussion**

#### Surface morphology and surface chemistry

The coating process involves the in situ generation of ZnO nanoparticles on the fabrics' surface in a one-step reaction. ZnO nanoparticles are formed according to the following reactions:

$$Zn^{2}+2OH^{-} \rightarrow Zn(OH)_{2}$$
$$Zn(OH)_{2} \rightarrow ZnO + H_{2}O$$
(5)

Morphological changes of the cotton fabric treated by solution of zinc nitrate can be clearly seen from the scanning electron microscopy (SEM) images (Figure 1). Compared to the SEM images of the control cotton (Figure 1(a)), the presence of ZnO nanostructures on fibers' surface is clearly distinguished. Hierarchical ZnO nanostructures are formed and distributed on the surface. Particles are in two different structures: bundle-like (Figure 1(b)) and flower-like (Figure 1(c)). Bundle-like particles are composed of a few rods with the length of 2-4 µm and the width of 200-800 nm, adhered together with different forms, whereas flowerlike particles are consist of many single rods aligned in a radial way from a center and having the length of 1- $2\,\mu\text{m}$  and the width of 50–300 nm. The reason for the formation of the two different morphologies is not clear for us and an intensive investigation of this aspect is needed and is still ongoing in our research group. Therefore, a more detailed study concerning this topic will be discussed in a later publication.

EDS measurements were carried out for chemical characterization of the fabric surface. The representative EDS patterns are shown in Figure 2. Peaks at about 0.5 keV are characteristic for oxygen and Zn signals are located at about 1.0, 8.6 and 9.6 keV. The peaks of Au were observed at about 2 keV, which are from the gold coating. The EDS results reveal that the prepared nanostructures are certainly composed of Zn and O. The concentration of Zn element was 99.38 wt.% and the ZnO quantity was 133.7 g/kg. which was measured by EDS and ICP-OES methods, respectively. It should be noted that the ZnO content determined by EDS is always different from the actual amounts on materials. This discrepancy is experienced because although the penetration depth of EDS is about 500 nm, most ZnO particles are localized on the outer surface of cotton fibers.<sup>9</sup>

#### Antibacterial properties

Antibacterial properties of the ZnO-coated fabrics were evaluated against Gram-negative *K. pneumonia* and Gram-positive *S. aureus* bacteria. The agar diffusion



**Figure 1.** Scanning electron microscopy images of the control fabric (a) and the ZnO-coated fabric at different surface positions (b) and (c). The high-magnification image of the ZnO particle is shown in (d).

technique was used to probe the bactericidal effect of the fabrics toward bacteria. Cotton substrates were placed on bacteria-inoculated agar plates and were visualized for antibacterial activity (Figures 3 and 4). The antibacterial activity was assessed by evaluating different parameters: the growth of the bacteria underneath and over the fabric and the presence of at least 1 mm of inhibition zone around the fabric (Table 1). Control samples exhibited no zone of inhibition for either strain. In addition, the growth of bacteria was observed underneath the specimens, which demonstrates the lack of antibacterial effect. A distinct zone of inhibition (areas with no bacterial growth, larger than 1 mm) was observed around the ZnO-coated fabric in contact with *K. pneumonia* and *S. aureus*, indicating complete inhibition of the bacterial growth. Nearly the same inhibition zone was observed for the samples in the dark and the samples exposed to UV



Figure 2. Energy-dispersive X-ray spectroscopy spectra of the control (a) and the ZnO-coated (b) fabrics.



**Figure 3.** Antibacterial activities of the control fabric (top), the ZnO-coated fabric (right), the ZnO-coated fabric after one cycle of washing (bottom) and the ZnO-coated fabric after five cycles of washing (left), placed on the agar plate inoculated with *K. pneumonia*. The image on the right is for the same samples under ultraviolet radiation.



**Figure 4.** Antibacterial activities of the control fabric (top), the ZnO-coated fabric (right), the ZnO-coated fabric after one cycle of washing (bottom) and the ZnO-coated fabric after five cycles of washing (left), placed on the agar plate inoculated with *S. aureus*. The image on the right is for the same samples under UV radiation.

**Table 1.** Tested response of *S. aureus* and *K. pneumonia* strains to the control and the ZnO-coated fabrics, before and after one and five cycles of washing

Sample	S. aureus	K. pneumonia
Control fabric	+	+
ZnO-coated fabric	++++	++++
ZnO-coated fabric after one cycle of washing	++++	++++
ZnO-coated fabric after five cycles of washing	++++	++++

+ indicates the growth underneath of the fabric, and ++++ indicates the presence of a significant (at least I mm) inhibition zone around the textile.

light, which shows the effectiveness of synthesized ZnO particles in the incidence of antimicrobial effect, even without the presence of light. The difference in the inhibition zone diameter suggests that the ZnO-coated fabrics have better antibacterial effects against *S. aureus* and Gram-positive bacteria than *K. pneumonia* and Gram-negative bacteria. The reason for the greater sensitivity of Gram-positive bacteria to ZnO than Gram-negatives is probably due to the difference in their cell walls and is fully described by Tayel et al.<sup>46</sup> The cell wall of the Gram-negative bacteria consists of lipids, proteins and lipopolysaccharides that provide effective protection against biocides, whereas that of the

Gram-positive bacteria does not consists of lipopolysaccharides.

The antibacterial effect of ZnO particles can be explained by several mechanisms, including the production of reactive oxygen species as reported by Applerot et al.<sup>47</sup> The probable production of free radicals under dark conditions or other toxicity mechanisms additional to reactive oxygen species production is proposed by performing the entire assay steps under dark conditions to avoid the possible effects of released reactive oxygen species from ZnO nanoparticles.<sup>46</sup>

Ouantitative evaluation was performed according to AATCC 100-2006 standard method under dark and UV lighting. As expected, no reduction of S. aureus and K. pneumonia was found on the control cotton fabric. Moreover, there was actually an increase in the number of bacteria recovered from the inoculated sample after 24 h of incubation compared to the sample at "0" contact time, indicating that bacteria can use pure cotton as a substrate.<sup>45</sup> Also, for the ZnO-coated fabric, an increase in the number of both strains compared to the sample at "0" contact time was observed, which shows a lack of bactericidal activity. It should be noted that the growth of bacteria was higher in the case of control cotton as compared to the ZnO-coated fabric. These results demonstrate that the antibacterial activity of the formed ZnO particles is limited to the biostatic, rather than the biocidal. They inhibit the growth of bacteria, but do not kill them.

In order to determine the washing fastness of the ZnO-coated fabric, fabrics were washed according to the *Experimental details* section. Images of the zone of inhibition of the washed fabrics are shown in Figures 3 and 4. As compared to the samples before washing, the bacteriostatic activity of the fabrics was not reduced even after five cycles washing. Moreover, the larger inhibition zone was formed on the agar inoculated by the *S. aureus*. For the washed samples, again, similar results were obtained under dark and UV

radiation. In order to understand the observed results of the inhibition zone, SEM images of the washed samples was taken and also the amount of ZnO content was determined. From the SEM images of the washed samples (Figure 5), it is obvious that some of the micronsize agglomerated particles are removed from the one cycle washed sample, whereas the removal of these agglomerates is nearly complete in the case of five cycles washed sample. However, high resolution image of the five cycles washed sample demonstrate that the high number of individual and aggregates polvgonal particles having the nanometer size (less than 100 nm) are still exist on the fiber surface. ZnO content of the fabrics were measured to be reduced from 133.7 to 95.0 and 30.4 g/kg, after one and five cycles washing, respectively. This shows the removal of about 29% (one cycle of washing) and 77% (five cycles of washing) of ZnO particles from the ZnO-coated fabric. So, from the results of the inhibition zone and the ZnO content, it can be concluded that the antibacterial activity of the samples comes from the nanoparticles rather than microparticles. Quantitative assessment was also performed. Increase of the bacteria colonies for both strains was observed to be the same as before washing, which demonstrates the lack of bactericidal activity.

#### UV protection

To quantify the protective effect of textiles, the SPF was determined. The SPF is the ratio of the potential erythemal effect to the actual erythemal effect transmitted through the fabric by the radiation and it can be calculated from spectroscopic measurements. The larger the SPF, the more protective the fabric is to UV radiation.<sup>48</sup> Unlike the sun protection factor (SPF), which traditionally uses human sunburn testing in a laboratory environment, UPF measures both UVA and UVB radiation transmittance using a laboratory instrument (Spectrophotometer) and an artificial light source and



Figure 5. Scanning electron microscopy images of the ZnO-coated fabric after one (a) and five (b) cycles washing. Image (c) shows the higher-magnification of (b).

translates these results using a mathematical expression based upon the sunburn action spectrum (Erythema action spectrum) integrated over the UV spectrum. Typically, a fabric with an UPF of >40 is considered to provide excellent protection against UV radiation.<sup>49</sup> The results of the UPF and transmittance of light in the ranges of UV (UVB, UVA and UVR) for the control and the ZnO-coated samples are presented in Table 2. Initial investigations regarding the UVprotection property of the control cotton fabric

**Table 2.** UV (ultraviolet)-blocking properties of the control and the ZnO-coated fabrics, before and after one and five cycles of washing

Sample	Percentage of transr			
	UVR 280–400 nm	UVA 315–400 nm	UVB 280–315 nm	UPF value
Control fabric	14.58	6.33	17.98	10.81
ZnO-coated fabric	2.42	3.12	0.71	105.61
ZnO-coated fabric after one cycle of washing	1.34	1.68	0.50	161.74
ZnO-coated fabric after five cycle of washing	4.06	5.14	1.40	54.67

UPF: ultraviolet protection factor



**Figure 6.** Ultraviolet-blocking spectra of the control fabric (blue line), the ZnO-coated fabric (red line), the ZnO-coated fabric after one cycle washing (green line) and the ZnO-coated fabric after five cycles washing (pink line). (Color online only.).

showed that the fabric afforded poor protection against UV radiation. The UPF value of the control fabric was 10.81. An UPF value <15 indicates no protection against transmittance of UV radiation through fabric and onto skin (standard AS/NZS 4399, 1996). As reflected from the data, ZnO nanostructures significantly improved the UV-protection property of the cotton fabric. The UV transmittance decreased significantly (percentage of transmittance in the UVB is lower than UVA) and the UPF value increased to 105.61 for the ZnO-coated fabric.

Figure 6 shows the UV-blocking spectra of the cotton samples, which are in accordance with their UPF values. The blue line represents the UV transmittance curve of the control fabric, indicating that a high percentage of the UVA and UVB light can penetrate the cotton. The UV-blocking ability of the control

fabric is higher in the UVB region. The red line represents the UV transmittance curve of the ZnO-coated fabric, indicating that it can block almost all of the UVB and a high percentage of the UVA radiation. UV transmittance after 370 nm increased, and the lowest blocking is in the range of 370-400 nm. Since the actual damage to human skin from UV radiation is a function of the wavelength of the incident radiation, with the most damage done by radiation in the 300-320 nm range, then textiles must demonstrate effectiveness in this range.48 Obtained results reveal that the ZnO-coated fabric can provide excellent UV blocking to the cotton textiles in the mentioned range. The UV absorption properties of ZnO are due to its intrinsic optical band gap energy, which is around 3.3 eV (~370 nm).<sup>50</sup> The ZnO particles can absorb light with the energy of hv that matches or exceeds



Figure 7. Visible spectra of the control fabric (blue line), the ZnO-coated fabric (red line), the ZnO-coated fabric after one cycle washing (green line) and the ZnO-coated fabric after five cycles washing (pink line). (Color online only.).

**Table 3.** Color coordinates (CIE L\* a\* b\*) and color differences  $(\Delta E)$  of the control and the ZnO-coated fabrics, before and after one and five cycles of washing

Sample	L*	a*	b*	$\Delta E$
Control fabric	85.68	-0.06	1.14	-
ZnO-coated fabric	88.07	-0.47	2.88	3.00
ZnO-coated fabric after one cycle of washing	88.72	-0.63	3.20	3.72
ZnO-coated fabric after five cycles of washing	85.5 I	-0.18	2.09	0.97

their band gap energy. The band gap energy of ZnO lies in the UV range of the solar spectrum, and therefore ZnO particles block UV radiation.<sup>39</sup>

Washing durability in regard to UV protection was evaluated, too. It can be seen from Figure 6 (green line) that the UV-blocking efficiency of the ZnO-coated fabric increased after one cycle of washing. Also, the results of UV transmittance and UPF measurements (Table 2) demonstrated that transmittance in the full range of UVR decreased. This observation is consistent with the results of previous works that demonstrated laundering significantly increases the UPF of the cotton fabric due to reduction in fabric porosity associated with shrinkage.<sup>50–52</sup>

However, after five cycles of washing, the UV-blocking efficiency decreased with the UPF value of 54.67. The reason for this is that most of the ZnO particles are removed from the fabric as determined by measuring the ZnO content in previous sections. However, the UPF value is higher than 40, which demonstrates excellent ability to block UV radiation.

#### Reflectance spectra and color coordinates

The impact of the treatment of cotton fabrics with ZnO nanostructures on the color of the samples was investigated by reflectance spectrophotometry. The reflectance spectra of the control and the ZnO-coated fabrics, before and after one/five cycles of washing, are shown in Figure 7. The obtained spectra show that the reflectance percentages of the coated samples were affected. For both ZnO-coated and one-cycle washed samples, the reflectance percentage increased, whereas after five cycles of washing, it decreased and reached near the control sample. The results of color differences are given in Table 3. The  $\Delta E$  value between the control and the ZnO-coated fabric is 3.0 and after one cycle washing, it increased and reached 3.72. However, after five cycles of washing,  $\Delta E$  decreased to 0.97, due to removing the high amount of ZnO particles proved by the ICP results. Therefore, these results show little effect of the formed ZnO nanostructures on the color change of the cotton fabric.

#### Conclusions

ZnO nanostructures were in situ synthesized on the surface of cotton fabric thorough a simple and efficient wet chemical method. The ZnO-coated fabric showed bacteriostatic activity against both Gram-positive *S. aureus* and Gram-negative *K. pneumonia* bacteria, as demonstrated by the zone of inhibition formed around the fabric surface. However, bactericidal activity was not found. Excellent UV-blocking ability of the finished fabric, particularly in the region of the UVB (280– 315 nm), was confirmed. The ZnO-coated fabric preserved very good durability in regard to antibacterial activity and UV protection, even after five cycles of washing. It is expected that these ZnO-functionalized cotton fabrics have a high potential for the preparation of advanced multifunctional textiles.

#### Funding

This research received no specific grant from any funding agency in the public, commercial or not-for-profit sectors.

#### References

- Roe R and Zhang X. Durable hydrophobic textile fabric finishing using silica nanoparticles and mixed silanes. *Textil Res J* 2009; 79: 1115–1122.
- Wang T, Hu X and Dong S. A general route to transform normal hydrophilic cloths into superhydrophobic surfaces. *Chem Commun* 2007; 18: 1849–1851.
- Shirgholami MA, Shateri Khalil-Abad M, Khajavi R, et al. Fabrication of superhydrophobic polymethylsilsesquioxane nanostructures on cotton textiles by a solution– immersion process. *J Colloid Interface Sci* 2011; 359: 530–535.
- Shirgholami MA, Shateri-Khalilabad M and Yazdanshenas ME. Effect of reaction duration in the formation of superhydrophobic polymethylsilasesquioxane nanostructures on cotton fabric. *Textil Res J* 2013; in press.
- Gorensek M, Gorjanc M, Bukosek V, et al. Functionalization of PET fabrics by corona and nano silver. *Textil Res J* 2010; 80: 253–262.
- Shateri Khalil-Abad M, Yazdanshenas ME and Nateghi MR. Effect of cationization on adsorption of silver nanoparticles on cotton surfaces and its antibacterial activity. *Cellulose* 2009; 16: 1147–1157.
- Chen CC, Wang CC and Yeh JT. Improvement of odor elimination and anti-bacterial activity of polyester fabrics finished with composite emulsions of nanometer titanium dioxide-silver particles-water-borne polyurethane. *Textil Res J* 2010; 80: 291–300.
- 8. Tomsic B, Simoncic B, Orel B, et al. Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohyd Polym* 2009; 72: 618–626.

- Damerchely R, Yazdanshenas ME, Rashidi A, et al. Morphology and mechanical properties of antibacterial nylon 6/nano-silver nano-composite multifilament yarns. *Textil Res J* 2011; 81: 1694–1701.
- Perelshtein I, Applerot G, Perkas N, et al. CuO–cotton nanocomposite: Formation, morphology, and antibacterial activity. *Surf Coating Technol* 2009; 204: 54–57.
- Paul R, Bautista L, De la Varga M, et al. Nano-cotton fabrics with high ultraviolet protection. *Textil Res J* 2010; 80: 454–462.
- Fei B, Deng Z, Xin JH, et al. Room temperature synthesis of rutile nanorods and their applications on cloth. Nanotechnology 2006; 17: 1927–1931.
- Qi K, Chen X, Liu Y, et al. Facile preparation of anatase/ SiO<sub>2</sub> spherical nanocomposites and their application in self-cleaning textiles. *J Mater Chem* 2007; 17: 3504–3508.
- Wang R, Wang X and Xin JH. Advanced visible-lightdriven self-cleaning cotton by Au/TiO<sub>2</sub>/SiO<sub>2</sub> photocatalysts. ACS Appl Mater Interface 2010; 2: 82–85.
- Qi K, Daoud WA, Xin JH, et al. Self-cleaning cotton. J Mater Chem 2006; 16: 4567–4574.
- Qi K, Wang X and Xin JH. Photocatalytic self-cleaning textiles based on nanocrystalline titanium dioxide. *Textil Res J* 2011; 81: 101–110.
- Veronovski N, Sfiligoj-Smole M and Viota JL. Characterization of TiO<sub>2</sub>/TiO<sub>2</sub>–SiO<sub>2</sub> coated cellulose textiles. *Textil Res J* 2009; 80: 55–62.
- Mahltig B and Textor T. Nanosols and textiles, 1st ed. Singapore: World Scientific, 2009.
- Shateri Khalil-Abad M and Yazdanshenas ME. Superhydrophobic antibacterial cotton textiles. J Colloid Interface Sci 2010; 351: 293–298.
- Abidi N, Cabrales L and Hequet E. Functionalization of a cotton fabric surface with titania nanosols: applications for self-cleaning and UV-protection properties. ACS Appl Mater Interface 2009; 1: 2141–2146.
- Xue CH, Yin W, Jia ST, et al. UV-durable superhydrophobic textiles with UV-shielding properties by coating fibers with ZnO/SiO<sub>2</sub> core/shell particles. *Nanotechnology* 2011; 22: 415603.
- Shyr TW, Lien CH and Lin AJ. Coexisting antistatic and water-repellent properties of polyester fabric. *Textil Res J* 2011; 81: 254–263.
- Gowri S, Almeida L, Amorim T, et al. Polymer nanocomposites for multifunctional finishing of textiles-a review. *Textil Res J* 2010; 80: 1290–1306.
- Bayer I, Fragouli D, Attanasio A, et al. Water repellent cellulose fiber networks with multifunctional properties. *ACS Appl Mater Interface* 2011; 3: 4024–4031.
- 25. Cheng HM, Chiu WH, Lee CH, et al. Formation of branched ZnO nanowires from solvothermal method and dye-sensitized solar cells applications. *J Phys Chem C* 2008; 112: 16359–16364.
- Su YK, Peng SM, Ji LW, et al. Ultraviolet ZnO nanorod photosensors. *Langmuir* 2010; 26: 603–606.
- Gonzalez-Valls I and Lira-Cantu M. Vertically-aligned nanostructures of ZnO for excitonic solar cells: a review. *Energy Environ Sci* 2009; 2: 19–34.
- 28. Manekkathodi A, Lu MY, Wang CW, et al. Direct growth of aligned zinc oxide nanorods on paper

substrates for low-cost flexible electronics. *Adv Mater* 2010; 22: 4059–4063.

- Zhang Q, Dandeneau CS, Zhou X, et al. ZnO nanostructures for dye-sensitized solar cells. *Adv Mater* 2009; 21: 4087–4108.
- Du X, Mei Z, Liu Z, et al. Controlled growth of highquality ZnO-based films and fabrication of visible-blind and solar-blind ultra-violet detectors. *Adv Mater* 2009; 21: 4625–4630.
- Wang X, Yang F, Yangab W, et al. A study on the antibacterial activity of one-dimensional ZnO nanowire arrays: effects of the orientation and plane surface. *Chem Commun* 2007; 4419–4421.
- Padmavathy N and Vijayaraghavan R. Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study. *Sci Technol Adv Mater* 2008; 9: 035004.
- Liu Y, He L, Mustapha A, et al. Antibacterial activities of zinc oxide nanoparticles against Escherichia coli O157:H7. J Appl Microbiol 2009; 107: 1193–1201.
- Jones N, Ray B, Ranjit KT, et al. Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. *FEMS Microbiol Lett* 2008; 279: 71–76.
- 35. Perelshtein I, Applerot G, Perkas N, et al. Antibacterial properties of an in situ generated and simultaneously deposited nanocrystalline ZnO on fabrics. *ACS Appl Mater Interface* 2010; 2: 361–366.
- Ghule K, Vithal Ghule A, Chen BJ, et al. Preparation and characterization of ZnO nanoparticles coated paper and its antibacterial activity study. *Green Chem* 2006; 8: 1034–1041.
- El Shafei A, Shaarawy S and Hebeish A. Application of reactive cyclodextrin poly butyl acrylate preformed polymers containing nano-ZnO to cotton fabrics and their impact on fabric performance. *Carbohyd Polym* 2010; 79: 852–857.
- Sivakumar PM, Balaji S, Prabhawathi V, et al. Effective antibacterial adhesive coating on cotton fabric using ZnO nanorods and chalcone. *Carbohyd Polym* 2010; 79: 717–723.
- Wang RH, Xin JH and Tao XM. UV-Blocking property of dumbbell-shaped ZnO crystallites on cotton fabrics. *Inorg Chem* 2005; 44: 3926–3930.
- Mao Z, Shi Q, Zhang L, et al. The formation and UVblocking property of needle-shaped ZnO nanorod on cotton fabric. *Thin Solid Films* 2009; 517: 2681–2686.
- Xue CH, Wang RL, Zhang J, et al. Growth of ZnO nanorod forests and characterization of ZnO-coated nylon fibers. *Mater Lett* 2010; 64: 327–330.
- 42. Onggar T, Cheng T, Hund H, et al. Metallization of inert polyethylene terephthalate textile materials: wet-chemical silvering with natural and synthetic polyamine, part I. *Textil Res J* 2011; 81: 2017–2032.
- Onggar T, Cheng T, Hund H, et al. Silvering of inert polyethylene terephthalate textile materials: the factors of adjustment on silver release, part II. *Textil Res J* 2011; 81: 1940–1948.
- 44. Wu X, Zheng L and Wu D. Fabrication of superhydrophobic surfaces from microstructured ZnO-based surfaces via a wet-chemical route. *Langmuir* 2005; 21: 2665–2667.

- 45. AATCC Test Method 100-2004. Antibacterial finishes on textile materials: Assessment of. American association of textile chemists and colorists, 2006.
- Tayel AA, El-Tras WF, Moussa S, et al. Antibacterial action of zinc oxide nanoparticles against foodborne pathogens. *J Food Saf* 2011; 31: 211–218.
- Applerot G, Lipovsky A, Dror R, et al. Enhanced antibacterial activity of nanocrystalline ZnO due to increased ROS-mediated cell injury. *Adv Funct Mater* 2009; 19: 842–852.
- 48. Schindler WD and Hauser PJ. *Chemical finishing of textiles*. Cambridge: Woodhead, 2004.

- 49. AS/NZS 4399. Sun protective clothing-evaluation and classification. Australian/New Zealand Standard, 1996.
- 50. Gorensek M, Urbas R, Strnad S, et al. The evaluation of a natural pigment in cotton as a UV absorber. *AATCC Rev* 2007; 7: 50–55.
- Wang Q and Hauser PJ. Developing a novel UV protection process for cotton based on layer-by-layer selfassembly. *Carbohyd Polym* 2010; 81: 491–496.
- Hustvedt G and Cox Crews P. The ultraviolet protection factor of naturally-pigmented cotton. *J Cotton Sci* 2005; 9: 47–55.