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UV protection finishing of textiles using ZnO nanoparticles

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The synthesis and characterization of nanosized zinc oxide particles and their application on cotton and polyester/cotton fabrics have been studied for the protection against UV radiation. The nanoparticles are produced in different conditions of temperature (90° or 150°C) and reaction medium (water or 1,2-ethanediol). Fourier transform infrared spectroscopy, transmission electron microscopy and X-ray powder diffractometry have been used to characterize the nanoparticles composition as well as their shape, size and crystallinity. The effectiveness of the treatment is assessed using the standardized tests, such as UV–Vis spectrophotometry and the calculation of the ultraviolet protection factor both before and after washing of the treated samples. It is found that the performance of ZnO nanoparticles as UV-absorbers can be efficiently transferred to fabric materials through the application of ZnO nanoparticles. The UV tests indicate a significant improvement in the UV absorbing activity in the ZnO-treated fabrics.

Keywords: Cotton fabrics, Nanoparticles, Polyester/cotton blends, Sun screen, Ultraviolet protection factor

1 Introduction

Nanotechnology creates structures that have excellent properties by controlling atoms and molecules, functional materials, devices and systems on the nanometer scale by involving precise placement of individual atoms of the size around 0.1-100 nm. The unique and new properties of nanomaterials have attracted scientists and researchers of the textile industry also and hence the research interest for the use of nanotechnology in the textile industry has increased rapidly. This is mainly due to the fact that textile is one of the best areas for deploying nanotechnology. Fibres provide optimal substrates where a large surface area is present for a given weight or volume of fabric. The synergy between nanotechnology and textile industry uses this property of large interfacial area and a drastic change in energetics is experienced by macromolecules or supramolecular clusters in the vicinity of a fibre when changing from a wet state to a dry state[1].

The application of nanoparticles to textile materials has been the object of several studies, aimed at producing finished fabrics with different functional performances. For example, nano-Ag has been used for imparting antibacterial properties [2, 3], nano-TiO_2 for UV-blocking and self-cleaning properties[4-6] and ZnO nanoparticles for antibacterial and UV-blocking properties[7-9]. Metal oxide nanoparticles are more preferable than nano-silver because of cost considerations. In fact, zinc oxide and titanium dioxide are non-toxic and chemically stable under exposure to high temperature and are capable of photo-catalytic oxidation. Furthermore, nanoparticles have a large surface area-to-volume ratio that results in a significant increase of the effectiveness in photo-catalytic oxidation activity when compared to bulk materials[10].

Conventional textile finishing methods used to impart different properties, such as water repellency and stain repellency, to the fabrics often do not lead to permanent effects, and lose their functions after laundering or use. Nanoparticles can provide high durability for treated fabrics as they possess large surface area and high surface energy that ensure better affinity for fabrics and lead to an increase in durability of the desired textile functions[11]. Thus, decreasing the size of particles to nano-scale dimensions fundamentally changes the properties of the material. By virtue of its small size and high surface energy, nanoparticles are bound to the fabric surface by Van der Waals forces which give a reasonable wash fastness. In general, as wash fastness is a particular requirement for textiles, it is strongly correlated with the nanoparticles adhesion to the fibres. In order to increase the wash fastness, nanoparticles can be applied by dipping the fabrics in a solution containing a specific binder[7,10]. Wash fastness can be further improved with the formation

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of covalent bonding between nanoparticles and the fabrics surface. In these cases, the excellent functional properties are still maintained after about 55 home launderings[12].

Zinc oxide is widely used in different areas because of its unique photo-catalytic, electrical, electronic, optical, dermatological, and antibacterial properties[13-19]. For these applications, the nano-particles need to be dispersed homogeneously in the different matrices, and a number of new synthetic strategies have been developed in order to prevent particles agglomeration and to increase the stability of ZnO nanoparticles dispersions[20-22]. The wide range of applications is possible as ZnO has three key advantages. First, it is a semiconductor with a direct wide band gap of 3.37 eV and a large excitation binding energy of 60 meV. It is an important functional oxide, exhibiting excellent photo-catalytic activity. Secondly, because of its non-central symmetry, ZnO is piezoelectric, which is a key property in building electromechanical coupled sensors and transducers. Finally, ZnO is bio-safe, biocompatible and can be used for biomedical applications without coating. With these three unique characteristics, ZnO could be one of the most important nanomaterials in future research and applications.

The present work addresses the synthesis and characterization of ZnO nanoparticles obtained through a homogeneous phase reaction between zinc chloride and sodium hydroxide at high temperature. In order to evaluate the effects of the experimental conditions on the particle size and morphology, the temperature (90° or 150°C) and the reaction medium (water or 1,2-ethanediol) were changed. The particles were then characterized by evaluating their chemical composition through their FTIR spectra, crystallinity using X-ray diffractometry, and shape & size via TEM microscopy. ZnO nanoparticles were then applied on to cotton and polyester/cotton fabrics in order to evaluate the UV protection function in the treated textiles through standardized test procedures.

2 Materials and Methods

2.1 Synthesis of ZnO Nanoparticles

$ZnCl_2$ (min. 98%), NaOH (pellet min. 99%), 1, 2-ethanediol (min. 99.5%), and 2-propanol (min. 99.5%) were used in zinc oxide nanoparticles synthesis. Zinc oxide nanoparticles were synthesized following a procedure reported elsewhere[23]. The synthesis was carried out at a high degree of super saturation in order to achieve a nucleation rate much greater than the growth rate[21]. $ZnCl_2$ (5.5 g) was dissolved in 200 mL of water at 90 °C in an oil bath. Then 16 mL of 5 M NaOH aqueous solution was added drop-wise to the zinc chloride solution with a gentle stirring over a period of 10 min at 90°C. The particles were separated from the supernatant dispersion by sedimentation.

The supernatant solution was discarded and the remaining suspension was washed five times with distilled water to lower the concentration of NaCl below 10^{-6} M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was checked using the solution of $AgNO_3$. The purified particles were then peptized with 2-propanol in an ultrasonic bath for 10 min at room temperature. The peptization process is necessary to disrupt the micro-agglomerates and to release the nanoparticles of zinc oxide[24,25]. The particles were then collected by centrifugation at 6,000 rpm for 15 min. The washing procedure was repeated three times. Thermal treatment of the particles at 250°C for 5 h leads to the formation of ZnO. This method of synthesis of ZnO nanoparticles using water medium is named as synthesis 1 for our reference in this paper. In another method (synthesis 2), ZnO nanoparticles was synthesised using 1, 2 ethanediol (instead of water) medium at 150°C; keeping all other parameters same as described in synthesis 1.

2.2 Fabric Treatment

Four types of fabric samples (cotton and 45:55 polyester/cotton) having both woven and knitted structures were used. These fabrics were made using 100% cotton yarns and 100% Sensura polyester yarns by weaving/knitting. The fabric constructions details for both cotton and 45:55 polyester/cotton fabrics are given below:

(i) woven fabric—structure, plain weave; width, 48 inch; mass, 130g/m^2 ; yarn count (warp + weft), 1/40sNe; ends/inch, 98 (cotton) and 92 (45:55 polyester/cotton); and picks per inch, 72 (cotton) and 78 (45:55 polyester/cotton); and

(ii) knitted fabric—structure, pique; mass, 130g/m^2; yarn count, 34sNe; and gauge, 26 inch.

The two kinds of woven and knitted fabrics with different compositions were then dyed using reactive

blue dye under identical conditions. The yarn counts and constructions were chosen so as to have a uniform mass 130g/ m^2. The construction and the weight of the fabric were chosen so as to keep the fabrics in shirting category.

The fabric samples (130g/ m^2) were conditioned at 21°C and 65% RH. Cotton and 45:55 polyester/cotton blend samples (10 cm × 10 cm) were soaked for 10 min in 2-propanol dispersion of ZnO nanoparticles (5% w/w) under gentle magnetic stirring. The fabrics were then squeezed on a padding mangle to 70% expression to remove the excess dispersion and dried in a oven at 130° C for 15 min under atmospheric pressure (dry heat). In order to evaluate the nanoparticles adhesion to the textile fibres, the treated fabrics were washed five times as per the standard method (UNI EN ISO26330:1996). Electrolux automatic laundry machine (internal drum diameter 51.5 cm, internal drum depth 33.5 cm and heating capacity 5.4 kW) was used, and the washing cycles were performed at 30°C with reference detergent without optical brighteners.

The drying step was carried out on a horizontal flat surface. The fabric specimens were tested before and after the washing cycles using TEM and UV spectrophotometry.

2.3 UV Absorption Properties

The UV-screen properties of the treated fabrics were investigated by absorption spectroscopy using a UV–Vis spectrophotometer (Perkin-Elmer Lambda 35 equipped with a 60mm integrating sphere). The blank reference was air. The UV profiles of the untreated samples were compared with the spectra collected from the same fabrics treated with ZnO nanoparticles, and the effectiveness in shielding UV radiation was evaluated by measuring the UV absorption, transmission and reflection. Each measurement is the average of four scans obtained by rotating the sample by 90º. The transmission data were used to calculate the ultraviolet protection factor (UPF) and the per cent UV transmission, using the following equations[26,27]:

$$\mathrm{UPF} = \frac{\int_{\lambda 1}^{\lambda 2} E(\lambda)S(\lambda) * d\lambda}{\int_{\lambda 1}^{\lambda 2} E(\lambda)S(\lambda) * Td(\lambda)} \quad \ldots (1)$$

$$\text{UV transmission}(\%) = \frac{\sum_{\lambda 1}^{\lambda 2} T(\lambda)}{\lambda 2 - \lambda 1} \quad \ldots (2)$$

where $E(\lambda)$ is the relative erythemal spectral effectiveness; $S(\lambda)$, the solar spectral irradiance in W m^{-2} nm^{-1} ; and $T(\lambda)$, the spectral transmission of the specimen obtained from UV spectrophotometric experiments. The values of $E(\lambda)$ and $S(\lambda)$ were obtained from the National Oceanic and Atmospheric Administration database (NOAA). The UPF values were calculated both for UV-A (315–400 nm) and for UV-B (295 - 315 nm). The per cent UV transmission, obtained from Eq.(2), was determined for UV-A and UV-B radiations from the transmission spectra of the fabric samples.

2.4 Physical and Physico-chemical Characterization

The chemical composition of the synthesized materials was evaluated using FTIR spectroscopy Biorad FTS-40 spectrometer. The crystallinity was determined by XRD using a Bruker D8 advance Xrays diffractometer equipped with a Cu Kα (k = 1.54 Å) source, maintaining applied voltage at 40 kV and current at 40 mA. About 0.5 g of the dried particles were deposited as a randomly oriented powder onto a plexiglass sample container, and the XRD patterns were recorded between 20° and 80° angles, with a scan rate of 1.5°/min. The crystallite domain diameter (D) was obtained from XRD peaks using the following Scherrer's equation[28]:

$$D = \frac{0.89 * \lambda}{\Delta W * \cos\theta}$$

where λ is the wavelength of the incident X-ray beam; θ, the Bragg's diffraction angle; and ΔW, the width of the X-ray pattern line at half peak-height in radians. The shape and size of the particles were obtained through TEM, using a Philips EM201C apparatus operating at 80 kV. For TEM measurements, the samples were placed on carbon coated copper grids. These samples were prepared from much diluted dispersions of the particles in 2-propanol. The ZnO-treated fabrics were analyzed through scanning electron microscopy (SEM), using a Stereoscan S360 (Oxford, Cambridge). The samples were previously coated with a thin layer of gold deposited by sputtering under vacuum.

3 Results and Discussion

3.1 FTIR and XRD Study

Figure 1 shows the FTIR spectra of the synthesized nanomaterials. The spectrum of the material obtained from Synthesis 1 clearly shows the ZnO absorption band near 430 cm^{-1}. The peaks at 3450 and 2350 cm^{-1} indicate the presence of –OH and C=O residues, probably due to atmospheric moisture and CO_2 respectively. The same spectrum was obtained from the nanomaterial produced via Synthesis 2. TEM images of the ZnO nanoparticles are shown in Fig. 2. Nanoparticles are nearly spherical and quite monodisperse. However, there are some larger aggregates in the sample obtained from Synthesis 1 (Fig. 2a), because of the high surface energy of ZnO nanoparticles that results in aggregation, especially when the synthesis is carried out in an aqueous medium. Particles obtained from Synthesis 2 are more monodisperse and isolated than those obtained from Synthesis 1. This result indicates a larger peptization yield for Synthesis 2 in comparison to synthesis 1. Figure 2b shows some halos surrounding the particles due to the retention of some diol that remains adsorbed on the ZnO nanoparticles, and produces the tiny peaks at 2850–2920 cm^{-1} in the FTIR spectrum (Fig. 1b).

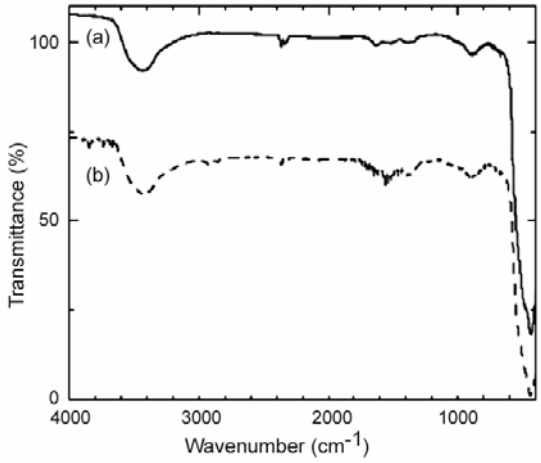

Fig. 1—FTIR spectrum of ZnO nanoparticles obtained from (a) Synthesis 1 and (b) Synthesis 2

Figure 3 shows the XRD spectra of the ZnO nanomaterials. The spectra show well-defined peaks typical of ZnO in the crystal structure of zincite. This indicates crystallinity of the synthesized solids. Traditionally, the broadening of the peaks in the XRD patterns of solids is attributed to particle size effects[24]. The mean crystallite size of a powder sample was estimated from the full width at half-maximum of the diffraction peak (ΔW) according to the Scherrer's equation. The ΔW values for Syntheses 1 and 2 are 0.0087 and 0.017 radians respectively. Thus, using the Scherrer's equation, the average sizes of the nanoparticles synthesized by Syntheses 1 and 2 are 20 ± 5nm and 10 ± 1 nm respectively. The important feature of the XRD patterns is that the peaks from Synthesis 2 (Fig. 3b) are broader than the peaks from Synthesis 1 (Fig. 3a). This result suggests that the particles obtained from Synthesis 2 are smaller than the particles obtained from Synthesis 1, as confirmed by TEM micrographs (Fig. 2), and reflects the effects due to the experimental conditions on the nucleation and growth of the crystal nuclei. The particles sizes calculated on the basis of Scherrer's equation agree quite well with the value obtained through TEM micrographs. The results also indicate that the experimental conditions greatly affect the morphology and size of the particles. In fact, the increase in reaction temperature from 90°C in water to 150°C in 1,2-ethanediol results in a significant lowering of the nanoparticle size from 20 nm to 9 nm.

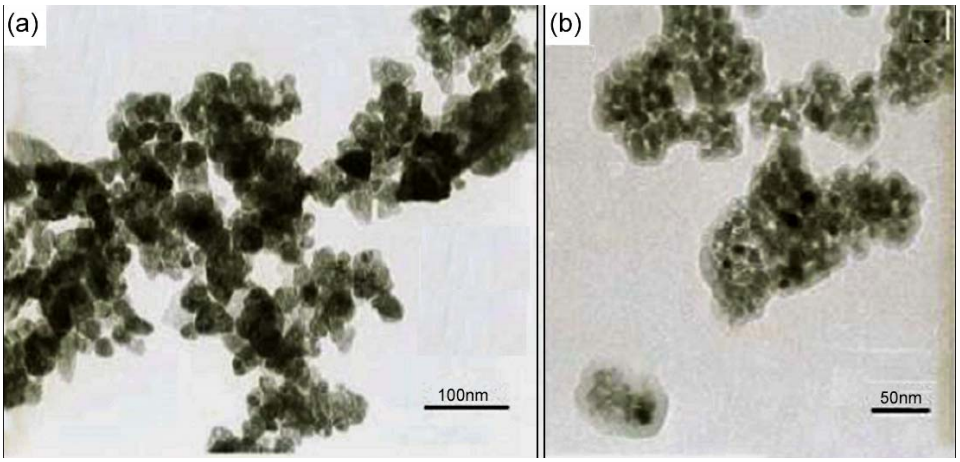

Fig. 2—TEM micrographs of the materials obtained from (a) Synthesis 1 and (b) Synthesis 2 after three peptizations

3.2 Electron Microscopy

The surface of the treated fabrics was observed by scanning electron microscopy. In Fig. 4, the nanoscaled ZnO particles are observed on polyester/cotton samples. The nanoparticles are well dispersed on the fibre surface in both the cases, although some aggregated nanoparticles are still visible. The particles size plays a primary role in determining their adhesion to the fibres. It is reasonable to expect that the largest particle agglomerates will be easily removed from the fibre surface, while the smaller particles will penetrate deeper and adhere strongly into the fabric matrix. SEM image (Fig. 4b) confirms that most of the large agglomerates are removed from the textile surface after washing.

3.3 Sunscreen Activity of Fabrics

The solar UV radiation is actually composed of UV-A (400–315 nm), UV-B (315–290 nm) and UV-C (290–200 nm). These radiations are present in natural terrestrial sunlight in different amounts due to the filtering activity of the upper atmosphere and local conditions (latitude, altitude and clouds). UV-C and most of UV-B are filtered by the ozone layer. UV spectra were recorded for untreated and treated fabrics by measuring the absorbance, transmission and reflection. Untreated cotton does not absorb UV radiation while untreated polyester strongly absorbs UV radiations in the UV region between 200 nm and 300 nm. The application of nanosized ZnO particles on the cotton and polyester/cotton blended fabrics increases the absorption of UV light over the entire investigated UV spectrum.

The UPF values and the per cent of UV transmission for UV-A and UV-B ranges were calculated according to Eqs (1) and (2) respectively and are given in Table 1. The data reflect the higher

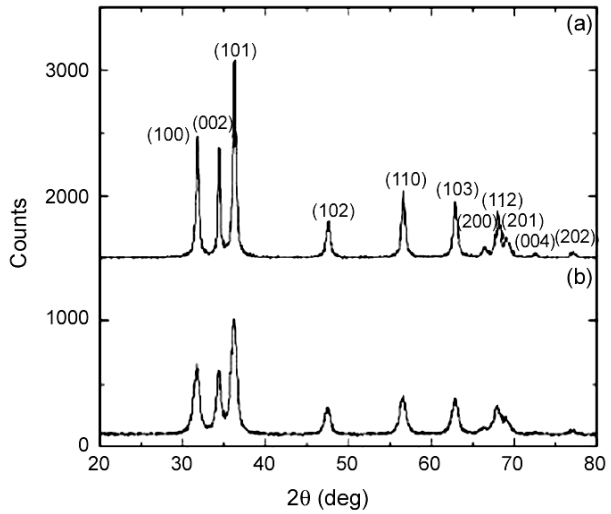

Fig. 3—XRD patterns of the material obtained from (a) Synthesis 1 and (b) Synthesis 2

Table 1—UPF values of different samples for UV-A (315–400 nm) and UV-B (295–315 nm) radiations

Sample	UPF value	
	UV-A	UV-B
Untreated		
Cotton (woven)	1.05	1.07
Cotton (knitted)	0.98	1.00
P/C blend (woven)	2.30	5.50
P/C blend (knitted)	1.80	4.40
Treated		
Cotton (woven) with Z_1	4.92	5.23
Cotton (woven) with Z_2	8.45	10.29
Cotton (knitted) with Z_1	4.00	4.70
Cotton (knitted) with Z_2	8.80	9.50
P/C blend (woven) with Z_1	10.23	15.76
P/C blend (woven) with Z_2	11.80	16.20
P/C blend (knitted) with Z_1	9.62	14.53
P/C blend (knitted) with Z_2	11.10	15.87

Z_1—ZnO nanoparticles synthesized through Synthesis 1.
Z_2—ZnO nanoparticles synthesized through Synthesis 2.

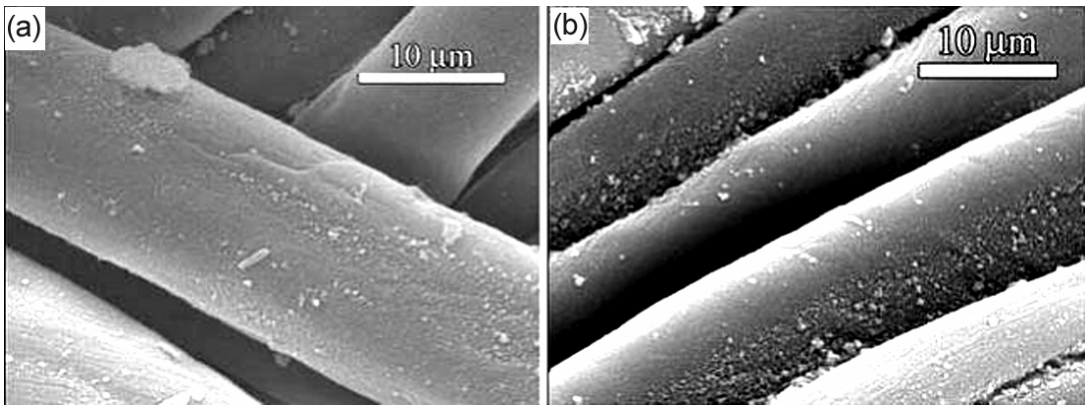

Fig. 4—SEM images of ZnO nanoparticles obtained from Synthesis 1 on (a) polyester/cotton before washing and (b) cotton after washing

protection against UV radiation provided by the ZnO-treated fabrics, particularly for the cotton samples loaded with zinc oxide nanoparticles synthesized according to the procedure Synthesis 2, while in the case of polyester/cotton blends the nanoparticles produced with the two different methodologies give comparable results.

Although for 100% cotton fabrics, the calculated UPF is significantly lower than the standard values required for classifying the clothing as excellent in UV-shielding, these results confirm the protection against UV radiation by using the treatment with nanosized ZnO on the fabrics. Higher values of UV absorbance are obtained when ZnO nanoparticles produced from Synthesis 2 were applied both on 100% cotton and polyester/cotton blends. It can be seen that in all the cases, the woven fabrics showed better UV blocking properties than the knitted fabrics for both 100% cotton and polyester/cotton blends. Polyester/cotton blends show better UV absorption characteristics than 100% cotton samples because of the better UV absorption characteristics of the polyester component in the blend. All these findings are in confirmation with the results reported by the other researchers[7,10]. It is clearly evident that the application of nanosized ZnO on polyester/cotton blended fabric increases UV light absorbance in the region between 300 nm and 400 nm. The results imply that the effectiveness in shielding UV radiation is due to the UV absorption capacity of ZnO nanoparticles on the fabrics surface. However, this effect can be further enhanced by using a different procedure for the application of nanoparticles on to the fabric surface. When the process of padding is used for applying the nanoparticles on to the fabric, the nanoparticles get applied not only on the surface alone but also penetrate into the interstices of the yarns and the fabric, i.e. some portion of the nanoparticles may get penetrated into the fabric structure. Such nanoparticles which do not stay on the surface may not be very effective in shielding the UV rays. It is worthwhile to note that only the right (face) side of the fabric gets exposed to the rays and therefore, this surface alone needs to be covered with the nanoparticles for better UV protection. Spraying (using compressed air and spray gun) the fabric surface with the nanoparticles can be an alternate method of applying the nanoparticles.

The interesting aspect of the nanoparticles treatment is their wash fastness. The treated fabric was tested after 25 washes again and no significant change in its sunscreen activity was observed. This clearly indicates that the nanoparticles are well bound to the fabric surface even without the use of a binder. However, when a higher level of wash fastness is required, a binder may be used.

4 Conclusions

The reaction with 1,2-ethanediol at 150ºC results in the formation of smaller nanoparticles with respect to the reaction carried out in water at 90ºC. In both the cases, the nanoparticles appear to be nearly spherical and with a quite narrow size range. The homogeneous phase reaction processes offer a valid alternative for an industrial-scale production of ZnO nanoparticles for many applications.

The performance of ZnO nanoparticles as UV-absorbers can be efficiently transferred to fabric materials through the application of ZnO nanoparticles on the surface of cotton and polyester/cotton blended fabrics. The UV tests indicate a significant improvement of the UV absorbing activity of the ZnO-treated fabrics. Such results can be exploited for the protection of the body against solar radiation and for other technological applications.

Industrial Importance: The ZnO nanoparticles finishing on fabrics not only imparts the UV absorption characteristic to the treated materials but also adds two more functions, viz. antibacterial activity and self cleaning. Thus, finishing of textiles with ZnO nanoparticles opens up the possibility of multifunctional finishing of textiles with a single treatment.

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