



Producing multifunctional wool fabrics using nano zinc oxide in presence of natural dye henna

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Received 3 December 2018; revised received and accepted 4 July 2019

Colored wool fabric with special functions, including self-cleaning, anti-bacterial, and ultraviolet (UV) blocking, has been prepared by applying nano ZnO as a photocatalyst and henna as both a natural dye for coloration and an agent capable of modifying the ZnO nanoparticles. Natural dye henna has been used as photo sensitizer to fabricate zinc oxide nanoparticles. Coloration of wool fabrics and surface modification of fabric are performed by adding modified zinc oxide nanoparticles in exhaustion bath. The self-cleaning property of treated wool fabrics is evaluated through discoloring methylene blue dye under sunlight irradiation. The antibacterial activities of the samples against two common pathogenic bacteria, namely *Escherichia coli* and *Staphylococcus aureus* have also been assessed. The results indicate that adding natural dye henna to zinc oxide leads to better self-cleaning properties, even the photocatalytic activity of ZnO has no negative effect on fabric color. Moreover, this process imparts proper antibacterial properties and UV-blocking activity to wool fabrics.

Keywords: Antibacterial, Henna dye, Self-cleaning fabric, UV blocking activity, Wool fabric, Zinc oxide

1 Introduction

In recent years, a variety of nano materials is being widely used for finishing of textiles in commercial forms. Nano structured photocatalysts are used to convert a textile material into a technical textile with functional properties, such as self-cleaning, antibacterial, flame retardancy, UV-blocking, etc.¹⁻⁷. ZnO photocatalyst is one of the most important chemicals used in textile finishing. For instance, Shirgholami *et al.*⁸ synthesized nano-ZnO on wool fabric and obtained self-cleaning fabric with good performance. Mohamadi *et al.*⁹ obtained self-cleaning and antibacterial polyester fabric using nano zinc oxide. Along the same lines, Zhu *et al.*¹⁰ coated cotton fabric with ZnO nanoparticles and showed efficient photocatalytic self-cleaning. Moreover, a chemical coating of cotton fabric with nano-ZnO having self-cleaning and UV-blocking properties was reported by Thi and Lee¹¹. Svetlichnyi *et al.*¹² applied nano ZnO to cotton fabric as an antibacterial agent. Also, Shahidi *et al.*¹³ prepared the antibacterial cotton fabrics through *in situ* synthesis of zinc oxide on cotton fabric.

Although there are numerous advantages for the application of nano photocatalysts such as ZnO for

textile finishing, there are some drawbacks also as listed below. Zinc oxide only shows photocatalytic activities under UV rays. Moreover, the high electron-hole recombination rate causes low efficiency of zinc oxide¹⁴. Attempts to overcome these problems have been mainly focused on the use of a second constituent to combine with nano photocatalysts. For instance, Karimi *et al.*¹⁵ treated cellulose fabrics with Ag/ZnO nanocomposite and reported the significant improvement in self-cleaning and antibacterial properties of the fabric. Along the same lines, Aladpoosh and Montazer¹⁶ applied *in situ* phytosynthesis of Ag/ZnO nanocomposite on cotton fabrics and obtained fabrics with superior photo-activity. Moreover, superior self-cleaning property on wool fabric through adding nano zinc oxide to nano titanium dioxide was reported by Behzadnia and colleagues¹⁷. Also, some studies have focused on the combination of nano photocatalysts with carbonaceous nano materials for producing high performance photocatalytic textiles¹⁸⁻²³.

Recently, several research groups have been working to utilize the natural dyes as sensitizers to improve the efficiency of the photocatalytic process²⁴⁻²⁷. Natural dyes are believed to be safe because of their non-toxic, non-allergic and biodegradable nature^{28, 29}. Henna is a flowering plant and the sole species of

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the *Lawsonia* genus. Chemically, the molecule of lawsone is 2-hydroxy-1,4-naphthoquinone, a red-orange pigment. Industrial classifications also depict lawsone as natural orange 6 and CI 75480³⁰⁻³². In this study, for the first time coloration and functional finishing of wool fabric has been carried out with combination of zinc oxide and natural dye henna. The self-cleaning properties, antibacterial activities and UV-blocking performance of the wool samples, and the synergism effect of ZnO nanoparticles and natural dye henna on these properties are investigated.

2 Materials and Methods

2.1 Materials

A plain wool fabric composed of 100% wool yarn (48/2 Nm) with a warp and weft density of 17 ends/cm was used. Zinc acetate dihydrate [(CH₃COO)₂Zn.2H₂O] as reagent for producing nano-ZnO and ammonia (NH₃, 25%) were procured from Merck. Methylene blue (CI 52015) was provided by Uhao Co. (China). The natural dye henna was purchased from Iranian traditional natural dyers.

2.2 Instruments

The surface morphology and energy dispersive X-ray spectroscopy (EDS) studies were performed using a field emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN, Czech). X-ray diffraction (XRD) patterns of the wool fabrics were recorded by an X-ray diffractometer (EQuinox 3000, INEL, France). Ultraviolet-Visible (UV-vis) spectra were measured on a Perkin-Elmer Lambda 35 spectrometer, USA. An ultrasonic bath Euronda Eurosonic[®] 4D, 350 W, 50/60 Hz (Italy) for synthesis processing and a 400 W UV lamp (HPA, Philips, Belgium) as the source of irradiation were used.

2.3 Syntheses

The natural dye aqueous extract prepared by soaking 100 g of dried powder in 1000 mL of distilled water and kept for 24h. The mixture was filtered to obtain brown solution for synthesis. To synthesize modified zinc oxide nanoparticles, diverse amounts of zinc acetate were used. Zinc acetate was dissolved in 100 mL natural dye solution at room temperature (28 °C) using ultrasound bath. The solution was then kept under ultrasonic irradiation to completely dissolve zinc acetate. Synthesis was carried out from ambient temperature to 45-50 °C with rate of 1 °C/min by controlled drop-wise of ammonia into the solution (pH9) under ultrasound irradiation. Finally, for fabric finishing, the wool fabrics were immersed in the aqueous suspension of nano-ZnO with various concentrations and heated for 40 min at 70 °C. Then, for fixation of coatings, the fabric was kept in an oven at 80 °C for 30 min. For comparison, wool fabrics were treated with zinc oxide nanoparticles under the same conditions without natural dye henna. The exact formation and tests results for each sample examined in this study are summarized in Table 1.

2.4 Test Methods

The photocatalytic activities of treated wool fabrics were estimated by decolorization of the methylene blue solution under sunlight irradiation. The concentration of dye in the solution was estimated by Varian Cary 300 UV-Vis spectrophotometer using calibration curve. The treated wool fabrics (4 × 6 cm²) were added into 100 mL of the dye solution (10 mg/L). Firstly, the solution was stirred for 15 min without irradiation in order to get equilibrium of dye adsorption. Then the solution was irradiated with sunlight (Yazd, Iran) for 3 consecutive days under

Table 1 — Experimental conditions and tests results

Natural dye	Zinc acetate, g	Zinc oxide (owf), %	Color coordinates			Fastness against photoactivity (ΔE^*) \pm SD
			<i>L</i> *	<i>a</i> *	<i>b</i> *	
Nil	0	-	70.55	2.22	12.17	-
	1	-	74.31	2.45	11.59	-
	2	-	77.34	2.32	12.08	-
	3	-	78.86	2.42	12.43	-
	4	-	79.88	2.11	11.87	-
Henna	5	-	84.98	2.82	11.45	-
	0	0	36.33	7.86	11.32	1.23 \pm 0.1
	1	0.58	39.59	8.23	11.78	1.33 \pm 0.1
	2	1.32	42.87	8.88	12.32	1.62 \pm 0.2
	3	2.24	45.65	8.75	11.54	1.69 \pm 0.3
	4	2.98	49.32	9.59	11.75	1.71 \pm 0.1
	5	3.15	51.32	8.13	12.35	1.83 \pm 0.2

continuous stirring (100 rpm). The degradation degree of the methylene blue was calculated according to following equation:

$$\text{Degradation (\%)} = (C_0 - C_e) / C_0 \quad \dots (1)$$

where C_0 and C_e correspond to the initial and final concentrations of dye before and after sunlight irradiation respectively.

The colorfastness of treated wool fabrics to light was also evaluated after 72 h UV lamp irradiation. The CIE Lab color coordinate values (L^* , a^* , and b^*) for each specimen were measured before and after UV irradiation. L^* represents the lightness/darkness, a^* value represents the red or green chroma, and b^* represents the chromaticity coordinate for yellow/blue. The total color difference (ΔE^*) was calculated according to following equation:

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

The burning method was used to determine the percentage of the zinc oxide on weight of fabric (owf). Weight-cured samples were placed in a porcelain crucible and kept in an oven with a range of room temperature (28 °C) to 900 °C for 140 min. The calculations were conducted in such a manner that the remainder weight was subtracted from the remainder weight of the blank sample, and then the percentage was obtained.

AATCC 100-2004 test method as a quantitative technique was chosen for measuring antibacterial properties of the treated samples against *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) as ordinary pathogenic bacteria. Antibacterial activity was expressed in terms of the bacteria reduction percentage (R), as shown below:

$$\text{Bacteria reduction (R), \%} = (A-B)/A \times 100 \quad \dots (3)$$

where A is the number of bacterial colonies recovered from the inoculated treated test specimen incubated over 24 h, while B is the number of bacterial colonies recovered from the inoculated treated test specimen immediately after inoculation (at '0' contact time).

UV-blocking activities of the wool samples were evaluated according to AATCC 183-2004 standard method (transmittance or blocking of erythemally weighted ultraviolet radiation through fabrics).

3 Results and Discussion

3.1 Characterization

XRD patterns were used to confirm the presence of zinc oxide on the fabric surface and to estimate the

crystalline size. Figure 1 illustrates the XRD patterns of nano-ZnO treated wool fabrics with and without natural dye. The diffraction peaks monitored around $2\theta=13.7^\circ$ and 16.5° related to diffraction peaks of wool. For nano-ZnO treated fabrics in presence of the natural dye, there are no obvious differences of diffraction peaks in comparison the treated wool with zinc oxide alone. Six reflection peaks that appeared at 2θ values of 31.9° , 36.5° , 47.7° , 56.8° , 63.1° , and 68.7° could be indexed as the hexagonal wurtzite structure of zinc oxide. In addition, based on following equation, the crystal size is calculated at $2\theta = 47.7^\circ$ and for the zinc oxide it is calculated at 387\AA .

$$\text{Crystal size (\AA)} = (K \times \lambda \times 180) / (\text{FWHM} \times \pi \times \cos \Theta) \quad \dots (4)$$

where $K = 0.9$ is the shape factor; $\lambda = 1.54$ is the wavelength of X-ray of Cu radiation; FWHM is full width at half maximum of the peak; and Θ is the diffraction angle.

Figure 2 shows the FE-SEM micrographs of pristine wool and nano-ZnO treated fabric in presence of natural dye henna. Overlapping of the scales is the characteristic element of raw wool fiber. The smooth surface of wool scales with sharp edges can clearly be observed [Figs 2(a) & (b)]. After synthesis of zinc oxide, nano-ZnO particles distribute on the surface of the wool fabric [Figs 2(c)-(e)]. The nanoparticles are well distributed on the fiber surface. The images at higher magnification indicated that the particles are roughly agglomerated, which could be attributed to the high surface energy of nanoparticles. The size of synthesized ZnO particles are around 26–40 nm [Fig. 2(f)].

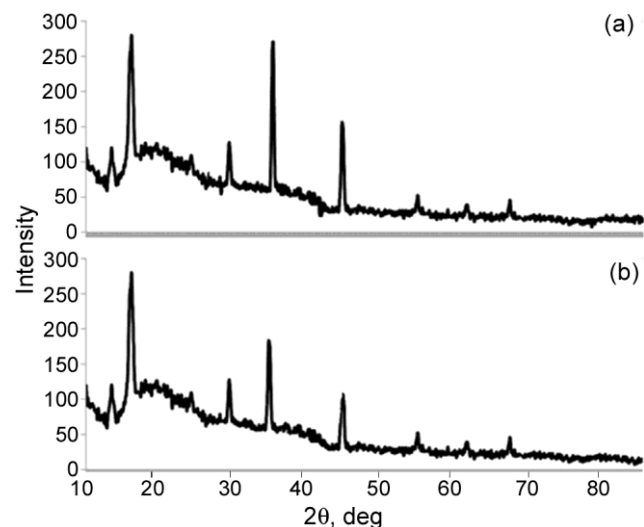


Fig. 1 — XRD patterns of treated wool fabric with (a) 5g zinc acetate and (b) 5 g zinc acetate along with natural dye henna

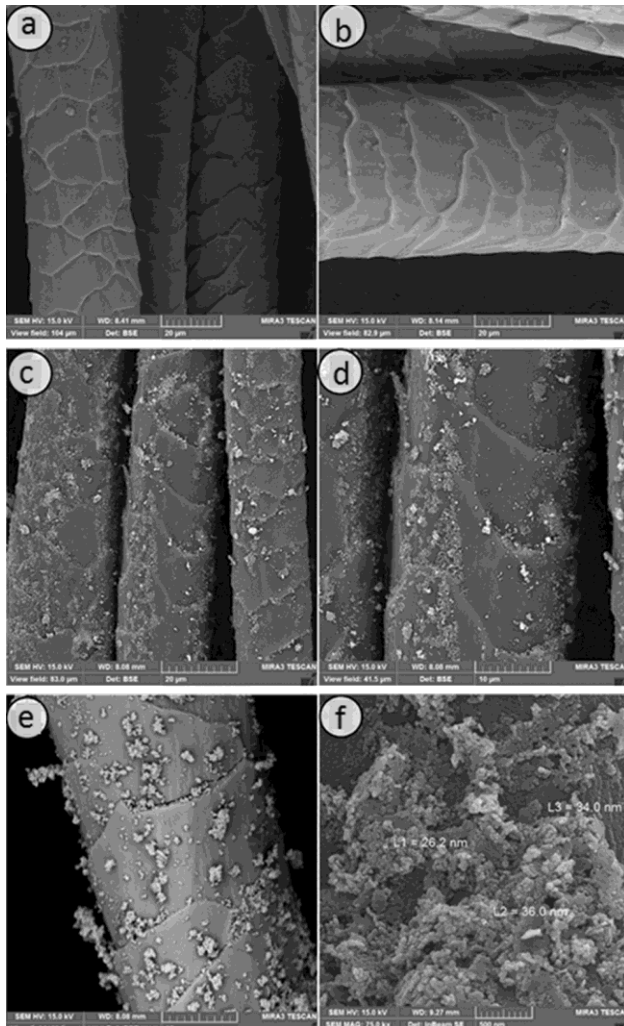


Fig. 2 — FE-SEM images of various wool fabric samples (a) blank sample, (b) blank sample with different magnification, (c) treated with zinc oxide, (d) treated with zinc oxide in different magnification, (e) treated with zinc oxide in different magnification, (f) treated with zinc oxide in different magnification, (c-f—5 g zinc acetate in presence of natural dye henna)

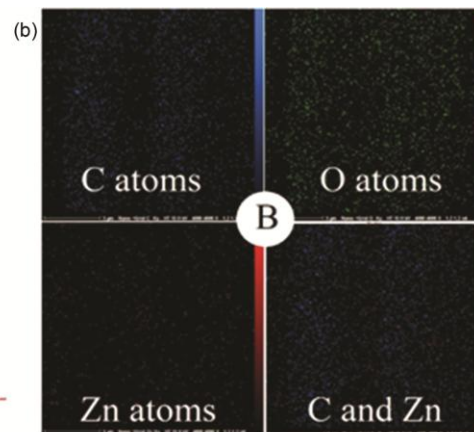
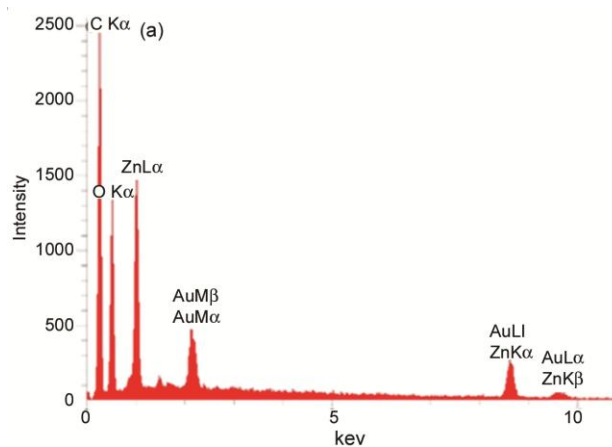


Fig. 3 — EDS spectrum (a), and X-ray mapping images (b), of treated wool fabric with zinc oxide (5 g zinc acetate) in presence of natural dye henna

Figure 3(a) displays the EDS pattern of treated wool fabric with zinc oxide in presence of natural dye henna, which indicates the presence of C, O, Zn and Au elements on the surface of the fabric. The presence of Au element in the EDS pattern is due to coating of gold layer on the fabric before FE-SEM observation. The distribution of C, O and Zn elements in treated wools is investigated by the elemental mapping [Fig. 3(b)]. It is clearly illustrated that the distribution of Zn on the fabric surface is uniform.

The data for burning test are presented in Table 1. The results indicate that the greater amount of zinc acetate in impregnation bath leads to more ZnO nanoparticles on the fabric surface. Hence, the zinc oxide percentage of coated wool samples is increased from 0.58% to 3.15 % by increasing the concentration of zinc acetate from 1g to 5 g.

The coloring effect of the applied treatment on the wool fabrics is obtained using a data color spectrophotometer according to the CIELAB system. As shown in Table 1, the raw wool fabric has a white color with a high L^* value and negligible a^* and b^* values. In comparison with the raw fabric, the L^* value of the treated fabrics with nano-ZnO is increased due to the whiteness of the zinc oxide nanoparticles immobilized on the fabric surface. Based on the obtained results, the L^* value of treated wool samples increases from 39.59 to 51.32 by increasing the amount of zinc acetate from 1 g to 5 g in the impregnating bath, which is due to the aggregation of white ZnO nanoparticles on wool surface. The a^* and b^* values for zinc oxide treated fabrics in presence of the natural dye are in the range of 7.86 - 9.59 and 11.32 - 12.35

respectively, which corresponds to the brown color of the samples.

3.2 Self-cleaning Performance

When a photocatalyst such as ZnO is illuminated by a light with energy higher than its bandgap energy, electron-hole pairs diffuse out to the surface of the photocatalyst. The created negative electrons and oxygen combine into O_2^- , and the positive electric holes and water generate hydroxyl radicals. This highly active oxygen species can oxidize organic pollutants¹⁴. Figure 4 shows the degradation degree (D%) of methylene blue dye solution after sunlight irradiation for the wool samples. The methylene blue concentration change is negligible during irradiations in contact with raw wool. Also, the dyed wool fabrics (without nano-ZnO) show no photocatalytic activity under sunlight irradiation. The results acquired indicate that increasing the concentration of ZnO in the impregnating bath increase the degradation rate of the dye solution.

Based on the obtained results, adding natural dye to zinc oxide has tangible effect on its photocatalytic activity. D% values of the nano-ZnO treated wool fabrics in the presence of natural dye henna are found more than that of the ZnO-treated wool fabrics alone. This improvement is due to the adsorption of dye molecules on zinc oxide surface which leads to increase in photo current. The natural dye is excited rather than ZnO by visible light and the excited dye molecule transfers an electron into the conduction band of the semiconductor, and the injected electron in the conduction band reacts with the oxygen

molecule adsorbed on ZnO surface to generate active oxygen species. The charge injected into the conduction band of the ZnO is affected by the type of attraction between the sensitizer and its anchoring group with ZnO³³. The dye structure of henna possesses C=O and -OH groups, which are capable of anchoring to the Zn sites on the zinc oxide surface.

The photocatalytic activity of nano-ZnO leads to color fading of dyed textiles due to the degradation of the chemical structures of the dyes³⁴. The colorfastness of nano-ZnO treated fabrics in presence of natural dye henna is assessed by examining their color changes after high intensity UV irradiation. As shown in Table 1, the ΔE^* values of the treated wool fabrics after 72 h UV irradiation are not significantly different from the dyed fabric (without nano-ZnO). Therefore, photocatalytic activity of zinc oxide does not cause remarkable changes in the color of the treated samples. Consequently, the colorfastness properties of the treated wool samples are satisfactory.

3.3 Antibacterial Activities

Zinc oxide nanoparticles possess unique characteristics, such as photocatalytic, electrical, optical, dermatological and antibacterial, which can make it possible to produce a textile with self-cleaning and antibacterial properties. Moreover, zinc oxide is bio-safe and biocompatible for applications in medicine textile³⁵. The ZnO treated textile can inhibit the growth of bacteria possibly by two mechanisms. The first important reason is the production and penetration of reactive oxygen species. The hydroxyl

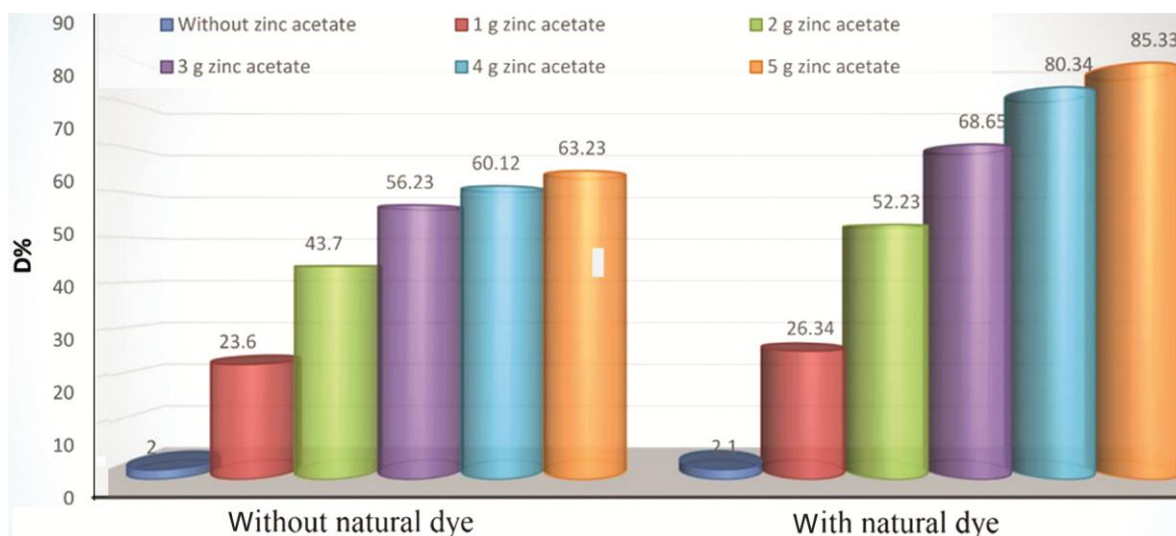


Fig. 4 — Photocatalytic activity of zinc oxide treated wool samples with and without natural dye henna

radical and hydrogen peroxide can penetrate into the cell membranes which lead to the death of bacteria. The second reason is of Zn^{2+} ions in the bacterial culture. These positive ions react with negatively charged cell surface of microorganism causing a variation of cell permeability, transforming normal metabolism of microorganisms leading to microorganism death⁹.

The antibacterial activities of the samples are evaluated quantitatively by suspension method against both *E. coli* and *S. aureus* bacteria (Fig. 5). There are a number of colonies of viable bacteria seen on agar plates of the blank fabrics. The nano-ZnO-treated wool sample exhibits 88% of reduction for *S. aureus* and 94% of reduction for *E. coli*. The nano-ZnO treated sample in presence of the natural dye henna indicates higher antibacterial activity than nano-ZnO treated wool. The nano-ZnO treated sample in presence of the natural dye henna exhibits 100% of reduction for both *S. aureus* and *E. coli*. Observed enhancement on the antibacterial activity of the treated samples is thought to be explained on the basis of the distinct antibacterial activity of the henna. The presence of phenolic compounds in henna leads to a considerable improvement in the antibacterial activity³⁶. Moreover, henna also contains mannite, tannic acid, mucilage and gallic acid³⁷.

3.4 UV Blocking

Long-term exposure to ultraviolet radiation causes serious health problems. Therefore, ultraviolet protection textiles and clothes should be used and developed. Figure 6 provides the transmission spectra of raw and treated wool samples. As expected, raw wool fabric is not perfect UV filter and high percentage of the UV light can penetrate into the

fabric. After finishing of wool by zinc acetate, the transmittance values of the sample decrease significantly because of the UV absorption ability of zinc oxide nanoparticles. Also, the dyed wool fabrics with natural dye henna have excellent UV blocking property. Moreover, the UV-blocking activity of the

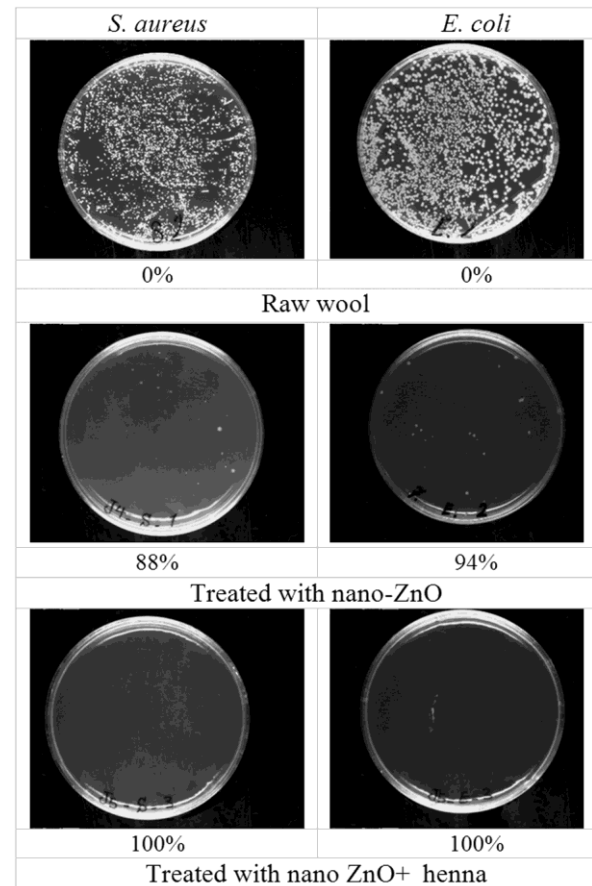


Fig. 5 — Antibacterial activity measurement of raw and treated wool fabrics

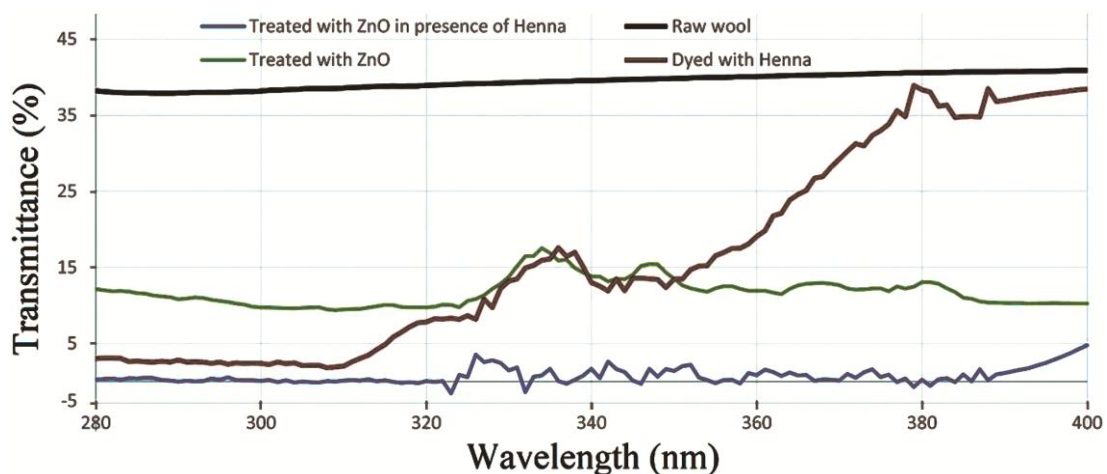


Fig. 6 — Transmittance spectra of raw and treated wool samples

nano ZnO-treated fabrics is improved by the presence of natural dye henna on the surface of wool fabrics, which is due to the synergetic UV absorption of zinc oxide and natural dye.

The UV protection factor (UPF) values are calculated using mean percentage transmission in the UV-A (320-400 nm) and UV-B (280-320 nm) regions. The UPF value of the raw wool fabric is found to be 12.56. An UPF value of <15 indicates no protection against transmittance of UV radiation through fabric onto skin. The UPF values of the treated wool fabrics are measured to be 174.41, 217.23 and 243.89 for natural dye, nano-ZnO and zinc oxide in presence of natural dye henna respectively. Therefore, results confirm the excellent UV-blocking activity of treated wool in presence of natural dye henna.

4 Conclusion

This research explores a new method for producing colored wool fabrics with special functions including self-cleaning, antibacterial, and ultraviolet (UV) blocking. Simultaneous coloration and finishing of wool fabric are performed using zinc oxide nanoparticles in presence of natural dye henna. The combination of nano-ZnO with natural dye in finishing process leads to exploit the properties of either zinc oxide nanoparticles or henna on wool fabrics. These colored antibacterial fabrics can be used in medical textiles, protective clothing, high quality fabrics, and textiles for high end fashions.

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