Superior Self-Cleaning Features on Wool Fabric Using TiO$_2$/Ag Nanocomposite Optimized by Response Surface Methodology

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ABSTRACT: Wool fabrics with superior self-cleaning properties produced using titanium dioxide/silver nanocomposite. The TiO$_2$/Ag nanocomposite first synthesized under ultraviolet (UV) irradiation and sonication and then applied on wool fabrics along with citric acid (CA) as a crosslinking agent to stabilize the nanoparticles on the wool surface. The optimum conditions of different properties of the treated wool fabrics obtained using response surface methodology as a statistical method. The role of three independent variables including titanium dioxide/silver nanocomposite (TiO$_2$/Ag), CA, and sodium hypophosphite evaluated to optimize the processing conditions. Fabrics color variation determined after irradiation with three diverse UV sources including sunlight, UV-A, and UV-C rays. Increasing the concentration of TiO$_2$/Ag nanocomposite increased the color removal and decreased the water absorption time. Further, increasing the concentration of CA led to increase adsorption of TiO$_2$/Ag nanocomposite on the fabric surface improved self-cleaning features of treated wool fabrics. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: self-cleaning; TiO$_2$/Ag nanocomposite; wool; UV irradiation; daylight
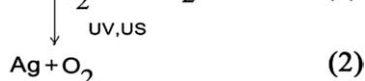
INTRODUCTION

Among various nanoparticles, nano TiO$_2$ is one of the most famous photocatalysts which have widely been used in diverse industries. TiO$_2$, used for self-cleaning surfaces, has now emerged in commercial products ranging from kitchen and bathroom ceramic tiles, and fabrics, to indoor air filters and window glass sections. TiO$_2$ under ultraviolet (UV) rays, with equal or greater energy from its band gap (i.e., 3.2 eV for anatase TiO$_2$), shows the photocatalytic properties.[1] In this situation, electrons are excited, promoting to the conduction band, producing pairs of negative electrons and positive holes.[2] Meanwhile, Tung and Daoud remarked that nano TiO$_2$ has a lower toxicity on the surface of coated material.[3] Although there is a lot of evidence to suggest that pure TiO$_2$ is an appropriate nano substance to prepare new products with novel properties, there are some demerits hindered its application. In the first place, the high recombination rate of generated negative electrons and positive holes is noteworthy; second, TiO$_2$ shows the photocatalytic properties just under UV rays.[4–10] One of the most useful remedies is adding noble metal ions to the TiO$_2$ structure. There are numerous pieces of research in which the variation of the photocatalytic features of metal loaded TiO$_2$ has been discussed. Some metals, such as Au,[11,12] Ag,[13] Pt,[14,15] and Cu[14,15] have been used.[13] This phenomenon occurs through mitigating the rate of electrons and holes recombination by trapping the electrons, expanding the light efficiency into visible territory, and modifying the surface properties of photocatalysts.[14–17] In fact, loading special metals such as Ag on TiO$_2$ leads to producing the TiO$_2$/Ag nanocomposite compounds. Exposing to the sunlight, TiO$_2$/Ag structure provides a space to capture electrons which are involved in electron-hole recombination.[18–24] This can decrease this extraneous phenomenon (hole-electron recombination).[18–24] Among various noble metals which are used in this field, Ag seems to be more economical in comparison with others.[25,26] Because Ag has some outstanding characteristics such as suitable reaction with chemicals (in terms of chemical durability, electrical conductivity, and photocatalytic activity), antimicrobial activity, environmental friendliness, and reasonable price, it is used as a suitable substance to improve the photocatalytic features of TiO$_2$.[27,28] Nowadays, nano silver is used in washing machines, refrigerators, air conditioners, purification and waste

water industry, water treatment, and so on. A lot of studies have been conducted to assess the synergistic effects of Ag on the photocatalytic features of TiO_2.[13] Notwithstanding the drawbacks of pure TiO_2, scientists have evaluated its applications on textiles.[13] For instance, Daoud and Qi obtained self-cleaning keratins and cottons through a sol–gel method.[29,30] Also, Montazer and Pakdel reduced the photo yellowing of wool by TiO_2.[31] The same group obtained self-cleaning wool fabrics through applying the nano TiO_2 particles stabilized by carboxylic acids as well as antimicrobial wool fabrics.[32,33] Likewise, superhydrophilic wool was produced using nano TiO_2.[34,35] Moreover, Bozzi et al. obtained the self-cleaning wool-polyamide on which plasma irradiations were used as a pretreatment.[36] From practical point of view, nano Ag particles are effective in enhancing the antimicrobial properties of TiO_2.[13] The process of preparing the TiO_2/Ag nanocomposite in an ultrasound bath and under UV rays is proposed as follows.[37–39]

$$AgNO_3 \xrightarrow{UV,US} Ag_2O + NO_2 + NO \qquad (1)$$
$$\downarrow UV,US$$
$$Ag + O_2 \qquad (2)$$
$$Ag + TiO_2 \xrightarrow{UV,US} Ag/TiO_2 \qquad (3)$$

The discoloring mechanism of methylene blue (MB), with the chemical formula $C_{16}N_3SCl$, in the presence of TiO_2/Ag nanocomposite and under UV rays has been reported by Mills and Wang.[40] The effects of TiO_2/Ag nanocomposite described on the wool fabrics. On the one hand, TiO_2/Ag nanocomposite is a suitable photocatalyst, and on the other hand, lack of complete research concerning the properties of treated wool fabrics with TiO_2/Ag nanocomposites led the researchers of this study to examine these features as well as determining the role of each contributing factor through a statistical method.

MATERIALS AND METHODS

Materials

A 100% wool fabric purchased form Iran Merinos Company (Iran), with 159 g/m^2 fabric mass was used. Nano titanium dioxide powder (Degussa P-25) with average particle size about 21 nm was bought from the Evonik Company (Germany). Silver nitrate solution, citric acid (CA), and sodium hypophosphite (SHP) all with purity of more than 99% were purchased from the Merck Company (Germany). MB (C. I. Basic Blue 9) from Uhao Company (China) was used as a barometer of discoloring under UV rays.

Equipment

A UV-A bulb, HPA model, with the electrical power of 400 W from Philips Company (Belgium), and a UV-C bulb, with the electrical power of 8 W made in Philips Company (Poland), were used as two artificial UV sources. X-ray diffraction (XRD) patterns were obtained using Philips X′ Pert MPD with a Cu generator bulb and 40 kV voltage and 40 mA (Holland). An absorbent spectrophotometer (Varian-Cary 300) with a territory between 200 and 800 nm (Australia) was used to calculate the color variation of samples before and after the illumination in CIELab color system. Scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy (EDS) spectra were obtained using SEM (EDAX), model XL30, voltage ACC.V:30 kV from Philips Company (Holland). An ultrasonic bath from DSA Company (Taiwan), model 100-XN1-2.5L, with the electrical power of 100 W and frequency of 40 kHz was used to sonicate the ingredients of the impregnating bath.

Preparation of TiO_2/Ag nanocomposite

To produce TiO_2/Ag nanocomposite, first, TiO_2 was added into a volumetric flask, containing 100-mL distilled water. Next, the solution was put in an ultrasonic bath for 10 min to suspend the nano TiO_2 particles in water. Subsequently, the silver nitrate solution was added into the finishing bath, and the obtained solution was irradiation with UV-A rays for 15 min. Producing a cream-brown color solution, the nanocomposite has been obtained. To produce the TiO_2/Ag nanocomposite, various ratios of TiO_2 over Ag were used through which the influence of the precursors' concentration on achieved results was determined.

Scouring

The wool samples were cut in 9×9 cm^2 and were washed in a bath containing 2 g/L colorless nonionic detergent with $L : G \to 50 : 1$ (liquor to goods ratio) at 50°C for 15 min. Then, they were rinsed with distilled water and dried in an oven at 110°C for 5 min.

TiO_2/Ag nanocomposite treatment

A 100-mL finishing bath containing TiO_2/Ag nanocomposite, CA, and SHP was prepared in a beaker in an ultrasonic bath. After 10 min sonication, TiO_2/Ag nanocomposite particles were suspended in water, and subsequently, the fabric was immersed into the bath and maintained for 30 min. The samples were taken out and dried in an oven at 110°C for 5 min. The samples were then cured at 160°C for 4 min. The exact formation and corresponding

TABLE I
Summery of the Exact Formation and Corresponding Number of Some Samples

Sample no.	Used material (mg/L)				Self-cleaning under different lights ($\Delta E \pm$ SD)			Water absorption (s)
	TiO$_2$	AgNO$_3$	CA	SHP	Sunlight	UV-A	UV-C	
Blank	–	–	–	–	19 ± 2	9 ± 4	9 ± 7	Above 60
1	2×10^4	2×10^2	1.9×10^3	1.15×10^3	33 ± 1	31 ± 2	24 ± 5	1 ± 1
2	2×10^4	2×10^2	9.6×10^2	5.76×10^2	29 ± 2	27 ± 2	19 ± 5	1 ± 1
3	2×10^4	2×10^2	–	–	28 ± 1	25 ± 3	17 ± 5	Above 60
4	5×10^3	50	1.9×10^3	1.15×10^3	27 ± 1	24 ± 2	17 ± 5	12 ± 2
5	5×10^3	50	9.6×10^2	5.76×10^2	26 ± 2	24 ± 3	17 ± 5	23 ± 3
6	2×10^4	–	1.9×10^3	1.15×10^3	29 ± 1	27 ± 3	21 ± 5	2 ± 1
7	2×10^4	–	9.6×10^2	5.76×10^2	27 ± 1	25 ± 3	20 ± 5	5 ± 1
8	2×10^4	–	–	–	25 ± 1	23 ± 2	16 ± 5	Above 60
9	5×10^3	–	1.9×10^3	1.15×10^3	23 ± 1	23 ± 4	16 ± 5	14 ± 2
10	5×10^3	–	9.6×10^2	5.76×10^2	23 ± 1	20 ± 2	15 ± 5	26 ± 3
11	–	2×10^2	1.9×10^3	1.15×10^3	20 ± 2	13 ± 5	11 ± 7	Above 60
12	–	2×10^2	4×10^2	2.4×10^2	20 ± 2	13 ± 7	11 ± 7	Above 60
13	–	2×10^2	–	–	19 ± 2	12 ± 7	10 ± 9	Above 60

number of some of the samples is summarized in Table I.

Discoloration of MB

Treated wool samples were stained by 0.1 mL of MB with concentration of 100 mg/L. Then, the samples were dried at room temperature. After that, the samples were exposed to three different radiations to completely examine different radiation effects on their self-cleaning properties. Thus, to examine the self-cleaning property in sunlight, the samples were exposed to sunlight for 3 days after being stained. Some samples were also exposed to UV-A and UV-C rays, for 20 min and 180 min, respectively.

Water drop absorption time measurement

This experiment was conducted according to the AATCC-79-2000 test method. At first, the sample fabric was spread completely flat on the surface without folding. Then, from a distance of 10 mm, a water drop was thrown on the fabric surface. The time that a water drop completely spread on the surface was recorded. To reduce the experiment error, six drops were dropped on different parts of the fabric and their average absorption time was recorded as a drop absorption time.[41]

RESULTS

Self-cleaning properties

The treated samples with TiO$_2$/Ag nanocomposite were stained by 0.1 mL of MB solution. After being stained, the samples were exposed to different radia-tions (sunlight, UV-A, and UV-C). The sample colors were measured by the means of a spectrophotometer before and after illumination, and based on their color variation (ΔE), their self-cleaning properties were compared. It was observed that the treated sample with the highest concentration of TiO$_2$/Ag nanocomposite had the highest discoloring level. In a higher concentration of TiO$_2$/Ag, the amount of generated active species is more in comparison with lower concentrations; as a result, the pace of MB discoloring is higher. Also, increasing the amount of crosslinkers in the impregnating bath increased the amount of TiO$_2$/Ag nanocomposite on the surface of wool, resulting in a better discoloring. The self-cleaning properties of the samples exposed to UV-C rays were similar to the samples irradiated with both sunlight and UV-A rays. The only difference was that the highest self-cleaning activity in different types of radiations were due to sunlight, UV-A, and UV-C, and its reason was due to the presence of all range of wavelength in the sunlight.

The results of Table I showed increasing the absorption of TiO$_2$/Ag nanocomposite on the samples surface increased the photocatalytic activity. Likewise, it can be clearly seen that increasing the concentration of CA as a crosslinking agent in an impregnating bath raised the nanocomposite absorption amount on the fabric surface and as a result of which increased the photocatalytic activity. Nano TiO$_2$ has a higher photocatalytic activity level in comparison with TiO$_2$/Ag nanocomposites (ratio of 100 : 1). This result corresponded well with the photocatalytic activity of nano TiO$_2$ and TiO$_2$/Ag nanocomposite in the solution. It was observed that the sample treated with SHP, CA, and TiO$_2$/Ag nanocomposite had a better self-cleaning activity while
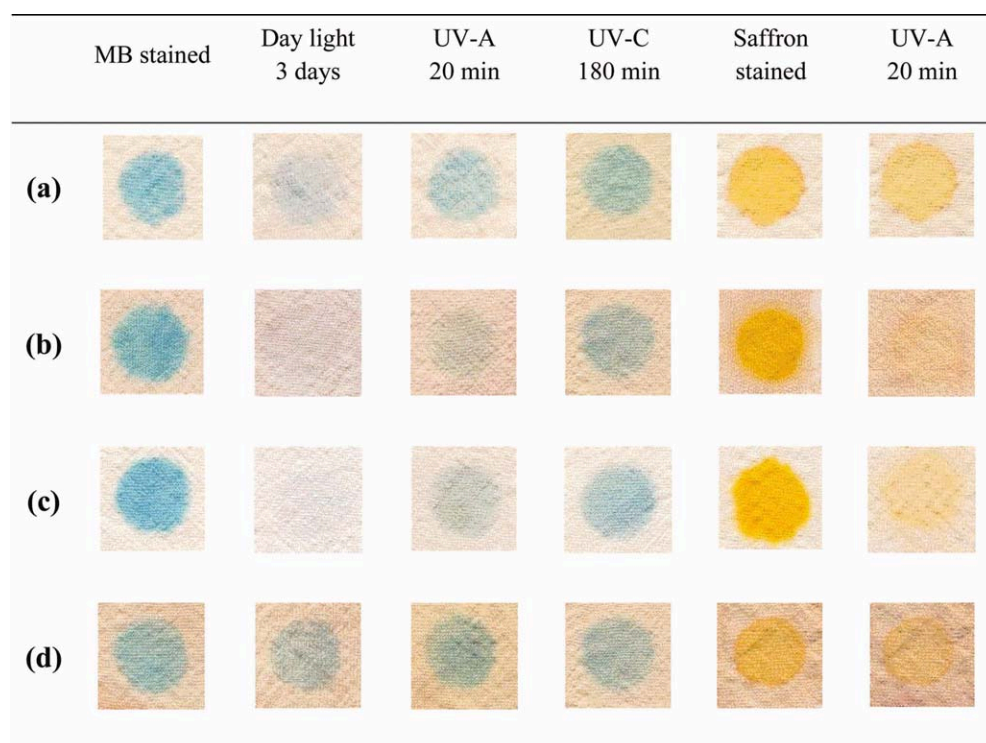
Figure 1 Self-cleaning of various samples (a) blank (b) 1, (c) 6, and (d) 11, stained either methylene blue or saffron under different lights. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

being exposed to different radiations. Thus, the sample treated with TiO_2/Ag nanocomposite, crosslinking agent, and catalyst is capable of discoloring the stain on the sample made by MB solution. The sample treated with SHP, CA, and TiO_2 nanoparticles had a photocatalytic activity while exposed to different radiations; however, its activity level was lower in comparison with that of TiO_2/Ag nanocomposites' [Fig. 1(b)]. The important point is that, on the treated samples with silver nitrate, CA, and SHP, some brown stains were observed after illumination with sunlight, UV-A, and UV-C due to the formation of silver dioxides on the surface of fabric.

Saffron, as a natural dye, was used to evaluate the color removing features of treated samples. It was observed that the saffron stain on the surface of raw wool sample was relatively unchanged after being exposed to UV-A radiation. Results showed that the treated sample with TiO_2/Ag nanocomposite and irradiated by UV-A rays made the saffron stain pale in a way that the color differences before and after UV-A exposure was about $\Delta E = 45$. However, the treated samples with pure TiO_2 nanoparticles show a color difference about $\Delta E = 43$ after UV-A exposure (Fig. 1). It was observed that the silver nitrate-treated wool samples, without nano TiO_2, became darker in both stained part and nonstained part; in large measure, it was related to the photo yellowing of wool under UV rays.[31,32]

The UV–vis spectra showed the best self-cleaning activity on TiO_2/Ag treated samples as compared with TiO_2 and Ag treated samples. Higher discoloration of MB observed between 600 and 700 nm due to high photocatalytic activity of TiO_2/Ag. This confirmed the result of the self-cleaning analyses. This also showed a small release of the nanocomposite as seen in UV–vis spectra in the range of 200–300 nm (Fig. 2).

Water drop absorption time

The positive holes that were increased by adding silver on titanium dioxide particles led to higher hydroxyl radical production.[18] These radicals increased the fabric hydrophilicity and decreased the contact angle between water drop and the surface of wool fabric.[42] To conduct this experiment, the fabric was spread on a flat surface without folding. Then, a water drop was dropped on the fabric surface and its absorption time was recorded (Table I). It was observed that, on samples which were treated with TiO_2/Ag nanocomposite, the water droplets were more rapidly absorbed than samples which were treated with pure nano TiO_2. In samples processed with nanocomposites and crosslinkers, the absorption time was highly decreased.

The results showed that increasing the nano TiO_2 concentration led to the increased photocatalytic
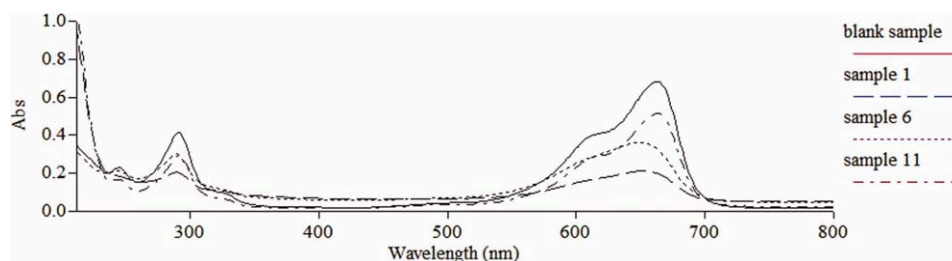
Figure 2 UV–vis absorption spectrum of different solutions (a) blank, (b) 1, (c) 6, and, (d) 11, after immersion in 8 mg/L methylene blue under UV-A irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activities of sample under radiation. Additionally, the photocatalytic activity of nano TiO_2 strongly decreased in the presence of CA and SHP. The sample processed with silver nitrate along with CA and SHP showed photocatalytic activity in UV radiation; however, silver nitrate particles created brown stains on the sample surface after being exposed to UV radiations. The produced nanocomposite from titanium dioxide and silver nitrate in an ultrasonic bath and under UV rays showed a more suitable self-cleaning activity than the activity shown by titanium nanodioxide and silver nitrate separately.

XRD patterns

Analysis of the X-ray diffraction patterns is a suitable method to identify the crystallinity of the samples. Also, it is used to calculate the phase content and investigate the changes of phase structure of the samples before and after the treatment.[41] The XRD patterns of raw and treated wool are shown in Figure 3. Concerning raw wool, two major peaks can be seen around $2\theta = 13.7°$ and $2\theta = 16.45°$, which are related to the hydrated crystalline structure of wool and α-keratin, respectively.[41] In the treated sample, the major peak is around $2\theta = 25.3°$ related to anatase structure of nano TiO_2 applied on the surface of wool, and in $2\theta = 37.9°$, the minor peaks of rutile structure of TiO_2 exist. One of the ingredients of the impregnating bath was Ag/TiO_2, as a result of which peaks of Ag appeared around $2\theta = 38°$. These results are consistent with the previous findings.[31,39] Also, through the full width at half maximum of peaks (FWHM), the crystal sizes can be compared.[39] Higher FWHM shows the small crystals, whereas lower FWHM indicates bigger crystals.[31] Based on eq. (4), the crystal sizes were calculated and for raw wool at $2\theta = 16.45°$ and treated one at $2\theta = 25.3°$ were 129.26 Å and 169.17 Å, respectively.

$$\text{Crystals size (A)} = \frac{K \times \lambda \times 180}{\text{FWHM} \times \pi \times \cos\theta} \quad (4)$$

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.[31]

SEM images and EDS spectra

To study the wool fabrics morphology of samples, an electron microscope with different magnifications was used. To use this microscope, at first, the samples were cut in very small dimensions (about 1 cm^2) and then they were covered with a gold layer to make the final image much clearer.[43] The obtained results from Figure 4(a) indicated that the raw wool fabric surface had been covered with scales, overlapping each other. However, considering the samples treated with CA in an ultrasound bath, it can be observed that the wool fiber surfaces changed a little, which can be due to
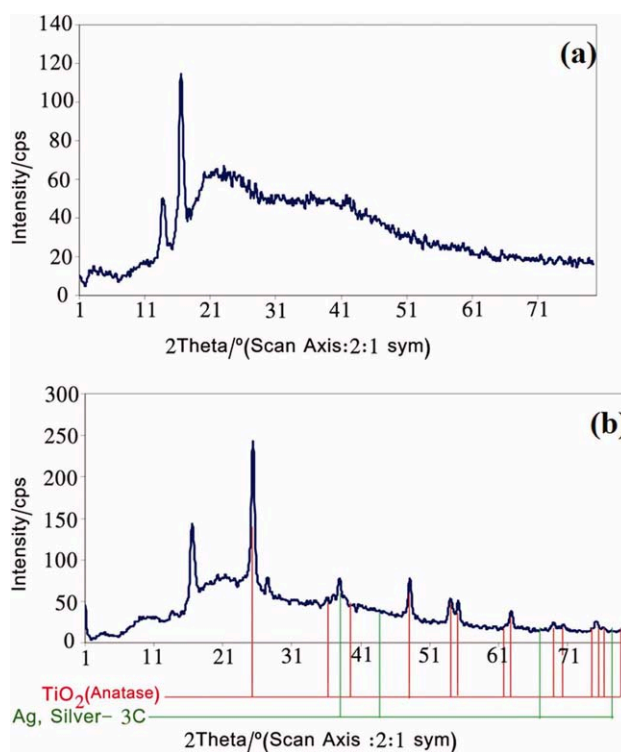
Figure 3 XRD pattern of various wool samples (a) raw and (b) treated with $Ag/TiO_2/CA/SHP$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
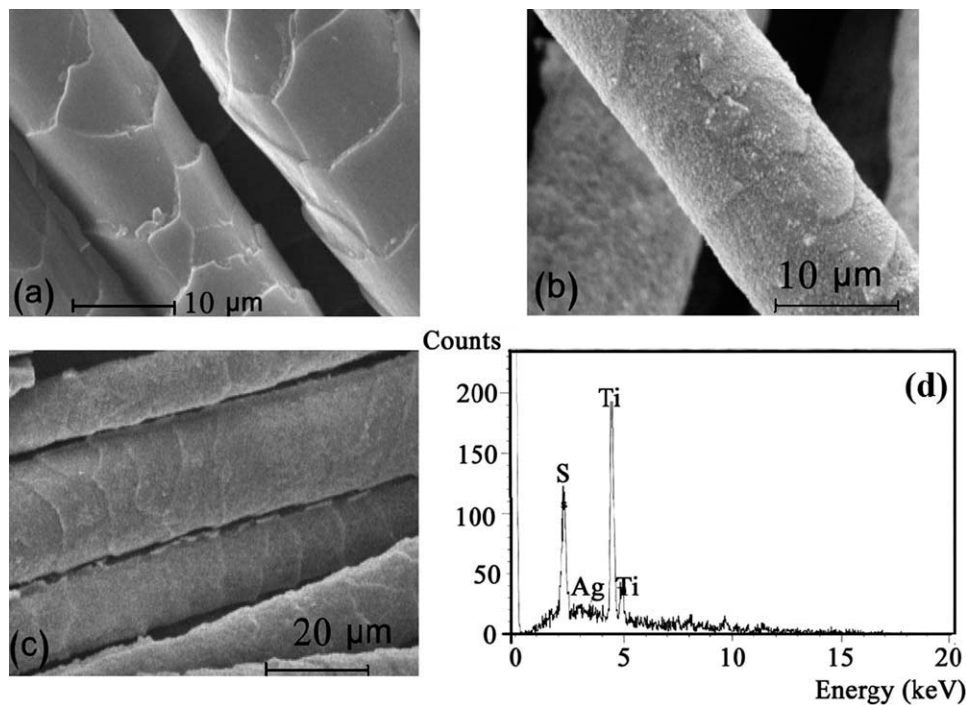
Figure 4 SEM images of various wool samples (a) raw (×2000), (b) treated with $Ag/TiO_2/CA/SHP$ (×2000), (c) sample (b) (×10,000), and (d) EDS spectrum of sample (b).

the removal of some fat and waxes from fiber surfaces. Considering the results recorded in SEM images of samples processed with SHP, CA, and TiO_2/Ag nanocomposite [Fig. 4(b,c)], it is evident that a homogeneous layer of TiO_2/Ag nanocomposite was situated on the fiber and EDS patterns also proved the existence of silver and titanium nanodioxide on the fiber. Moreover, through the EDS spectra, the presence of titanium and silver particles on the treated sample surface was proved [Fig. 4(d)].

Statistical analysis

This study was conducted according to response surface methodology and central composite design (CCD).[44,45] In total, 20 experimental CCD designed runs were conducted according to Table II. In this model, the impacts of independent variables including Ag/TiO_2 nanocomposite, CA, and SHP concentrations in the impregnating bath on four response surfaces were assessed. For each of them, optimum condition was obtained (Table II), through which the variation of four response surfaces including Y_1, Y_2, Y_3, and Y_4 was discussed. These explain self-cleaning activity of treated samples against UV-A, UV-C, sunlight irradiation, and water absorption, respectively. Based on the results of relations between surface responses and independent factors, several mathematical models were obtained [eqs. (5)–(8)], whose related responses were a function of its independent variables. The response surfaces are proposed in Figure 5.

Mathematical models related to self-cleaning activity of treated samples against UV-A, UV-C, sunlight irradiation, and water absorption is shown in eqs. (5)–(8), respectively:

$$
\begin{aligned}
Y_1 = {} & 15.59 + 12.53(Ag/TiO_2) + 0.51(CA) \\
& + 0.24(SHP) + 0.11(Ag/TiO_2)(CA) - 0.06(Ag/TiO_2) \\
& (SHP) + 0.02(CA)(SHP) - 5.19(Ag/TiO_2)^2 \\
& \qquad\qquad - 0.03(CA)^2 - 0.04(SHP)^2 \quad (5)
\end{aligned}
$$

$$
\begin{aligned}
Y_2 = {} & 11.3 + 19.11(Ag/TiO_2) + 0.49(CA) - 0.42(SHP) \\
& + 0.07(Ag/TiO_2)(CA) - 0.12(Ag/TiO_2) \\
& (SHP) + 0.04(CA)(SHP) - 6.73(Ag/TiO_2)^2) \\
& \qquad\qquad - 0.02(CA)^2 - 0.03(SHP)^2 \quad (6)
\end{aligned}
$$

$$
\begin{aligned}
Y_3 = {} & 10.22 + 11.26(Ag/TiO_2) + 0.38(CA) - 0.14(SHP) \\
& + 0.11(Ag/TiO_2)(CA) - 0.29(Ag/TiO_2) \\
& (SHP) - 0.01(CA)(SHP) - 5.33(Ag/TiO_2)^2 \\
& \qquad\qquad - 0.01(CA)^2 - 0.01(SHP)^2 \quad (7)
\end{aligned}
$$

$$
\begin{aligned}
Y_4 = {} & 81.8 - 67.50(Ag/TiO_2) - 2.89(CA) - 1.08(SHP) \\
& + 1.08(Ag/TiO_2)(CA) + 0.97(Ag/TiO_2) \\
& (SHP) + 0.09(CA)(SHP) + 16.2(Ag/TiO_2)^2 \\
& + 0.01(CA)^2 - 0.07(SHP)^2 \qquad\qquad (8)
\end{aligned}
$$

As shown in Figure 5, increasing the self-cleaning agent resulted in more increase in self-cleaning properties. In addition, increasing the concentration

TABLE II
Results and Experimental Situation Based on CCD

Run	TiO$_2$ (mg/L)	AgNO$_3$ (mg/L)	CA (mg/L)	SHP (mg/L)	Self-cleaning activity against UV-A (Y_1)	Self-cleaning activity against UV-C (Y_2)	Self-cleaning activity against Sunlight (Y_3)	Water absorption (Y_4)
1	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	28	15
2	4.10×10^3	41	1.54×10^2	9.24×10^2	26	17	26	19
3	1.60×10^4	1.60×10^2	4.00×10^2	2.40×10^2	24	16	24	17
4	1.60×10^4	1.60×10^2	4.00×10^2	9.24×10^2	24	19	25	19
5	2.01×10^4	2.01×10^2	9.60×10^2	5.76×10^2	25	20	26	1
6	1.01×10^4	1.01×10^2	9.60×10^2	1.15×10^2	26	19	25	13
7	4.10×10^3	41	4.00×10^2	2.40×10^2	21	17	23	45
8	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	28	17
9	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	28	14
10	0	0	9.60×10^2	5.76×10^2	12	9	19	60<
11	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	27	17
12	1.01×10^4	1.01×10^2	0	5.76×10^2	20	16	22	25
13	4.10×10^3	41	1.54×10^2	2.40×10^2	22	17	23	17
14	1.60×10^4	1.60×10^2	1.54×10^2	2.40×10^2	26	20	28	12
15	4.10×10^3	41	4.00×10^2	9.24×10^2	20	15	22	32
16	1.60×10^4	1.60×10^2	1.54×10^2	9.24×10^2	27	20	28	15
17	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	28	15
18	1.00×10^4	1.00×10^2	9.60×10^2	0	26	20	28	11
19	1.01×10^4	1.01×10^2	1.90×10^3	5.76×10^2	27	21	29	6
20	1.01×10^4	1.01×10^2	9.60×10^2	5.76×10^2	26	20	28	17

of CA led to a higher adsorption of nanocomposites on the wool surface. This shows the self-cleaning depends on the both adsorbed Ag/TiO$_2$ on the wool and the concentration of crosslinking agent. This also leads to more and uniform coating of nanocomposite on the wool surfaces.

Analysis of variance (ANOVA) was used to analyze the data to obtain the interaction between the
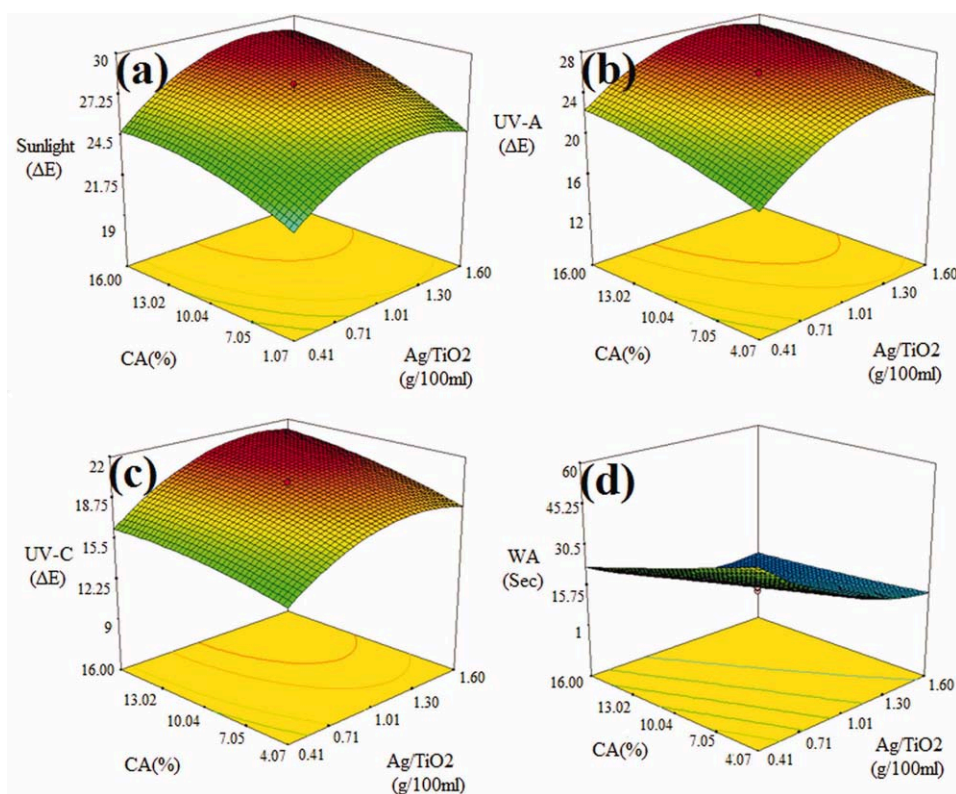

Figure 5 Response surface for antibacterial activity as a function of Ag/TiO$_2$/CA/SHP for treated samples against (a) sunlight, (b) UV-A, (c) UV-C, and (d) water absorption time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

process independent variables and the responses. The results were then analyzed by ANOVA to assess the "goodness of fit." The lack of fit describes the variation of data around the fitted model. If the model does not fit the data well, this will be significant. It was observed that designed model for self-cleaning activity of treated samples under UV-A is statistically significant at F value of 6.31 and values of prob $> F$ (<0.0040). Similarly, self-cleaning activity under UV-C and sunlight were significant at F values of 7.05 and 8.81, and values of prob $> F$ (<0.0026) and prob $> F$ (<0.0011), respectively. Result showed that designed model for water absorption of treated samples is statistically significant at F value of 11.55 and values of prob $> F$ (<0.0003). Additionally, through adjusted R^2, it was confirmed that the model of self-cleaning activity under sunlight irradiation is more significance in comparison with UV-A and UV-C. In other words, their amounts are close to each other and their difference is not so obvious.[43,44] Finally, low values of used models CV% indicated a good precision and reliability of the experiments.[44,45]

CONCLUSIONS

Application of pure silver nitrate on wool fabric and exposure to the sunlight, UV-A, and UV-C rays caused a creation of brown stain on the fabric; conversely, this negative result was not observed when silver loaded on nano titanium dioxide-treated fabrics after being exposed to different irradiations. Increasing the concentration of TiO_2/Ag nanocomposite, CA, and SHP in an impregnating bath increased the self-cleaning properties of the wool fabric. SEM images and the EDS spectra showed the presence of a layer of TiO_2/Ag nanocomposite on the surface of finished wool samples. Also, a relatively uniform layer of TiO_2/Ag nanoparticles was observed by SEM images. However, a small amount of silver was located beside TiO_2/Ag nanoparticles, which improved the self-cleaning property of treated samples.

References

1. Wang, C. C.; Chen, C. C. J Appl Polym Sci 2008, 97, 2450.
2. Souni, M. E.; Brandies, H. F.; Souni, M. E. Adv Funct Mater 2008, 18, 3179.
3. Tung, W. S.; Daoud, W. J Mater Chem 2011, 21, 7858.
4. Caballero, L.; Whitehead, K. A.; Allen, N. S.; Verran, J. J Photochem Photobiol A 2009, 202, 92.
5. Uddin, M. J.; Cesano, F.; Bertarione, S.; Bonino, F.; Bordiga, S.; Scarano, D. J Photochem Photobiol A 2008, 196, 165.
6. Yuranova, T.; Rincon, A. G.; Pulgarin, C.; Laub, D.; Xantopoulos, N.; Mathieu, H. J. J Photochem Photobiol A 2006, 181, 363.
7. Ibáñez, J. A.; Litter, M. I.; Pizarro, R. A. J Photochem Photobiol A 2003, 157, 81.
8. Robertson, J. M. C.; Robertson, P. K. J.; Lawton L. A. J Photochem Photobiol A 2005, 175, 51.
9. Radeti, M.; Vodnik, V.; Dimitrijevi, S.; Jovan, P. Polym Adv Technol 2008, 19, 1816.
10. Ansari Amin, S.; Pazouki, M.; Hosseinnia, A. Powder Technol 2009, 196, 241.
11. Subramanian, V.; Wolf, E.; Kamat, P. J Phys Chem B 2001, 105, 11439.
12. Wang, C. Y.; Liu, C. Y.; Zheng, X.; Chen, J.; Shen, T. Colloids Surf A 1998, 131, 271.
13. Sung-Suh, H. M.; Choi, J. R.; Hah, H. J.; Koo, S. M.; Bae, Y. C. J Photochem Photobiol A 2004, 163, 37.
14. Sclafani, A.; Herrmann, J. M. J Photochem Photobiol A 1998, 113, 181.
15. Wold, A. Chem Mater 1993, 5, 280.
16. Ye, S. Y.; Tian, Q. M.; Song, X. L.; Luo, S. C. J Photochem Photobiol A 2009, 208, 27.
17. Cernigoj, U.; Štangar, U. L.; Trebše, P.; Sarakha, M. J Photochem Photobiol A 2009, 201, 142.
18. Mellot, N. P.; Durucan, C.; Pantano, C. G.; Guglielmi, M. Thin Solid Films 2006, 502, 112.
19. Montazer, M.; Behzadnia, A.; Pakdel, E.; Rahimi, M. K.; Bameni Moghadam, M. J Photochem Photobiol B 2011, 103, 207.
20. Kafizas, A.; Kellici, S.; Darr, J. A.; Parkin, I. P. J Photochem Photobiol A 2009, 204, 183.
21. Senthilkumaar, S.; Porkodi, K.; Vidyalakshmi, R. J Photochem Photobiol A 2005, 170, 225.
22. Wu, G.; Chen, A. J Photochem Photobiol A 2008, 195, 47.
23. Rengaraj, S.; Li, X. Z. J Mol Catal 2006, 243, 60.
24. Rupa, A. V.; Manikandan, D.; Divakar, D.; Sivakumar, T. J Hazard Mater 2007, 147, 906.
25. Xin, B.; Jing, L.; Ren, Z.; Wang, B.; Fu, H. Phys Chem J 2005, 109, 2805.
26. Suh, H. M. S.; Choi, J. R.; Hah, H. J.; Koo, S. M.; Bae, Y. C. J Photochem Photobiol A 2004, 163, 37.
27. Vamathevan, V.; Amal, R.; Beydoun, D.; Low, G.; Evoy, S. J Photochem Photobiol A 2002, 148, 233.
28. Sahoo, C.; Gupta, A. K.; Pal, A. Desalin Water Treat 2005, 181, 91.
29. Qi, K.; Daoud, W. A.; Xin, J. H.; Mak, C. I.; Tang, W.; Cheung, W. P. J Mater Chem 2006, 16, 4567.
30. Daoud, W. A.; Leung, S. K.; Tung, S. K.; Xin, J. H.; Cheuk, K.; Qi, K. J Mater Chem 2008, 20, 1242.
31. Montazer, M.; Pakdel, E. J Photochem Photobiol A 2010, 86, 255.
32. Montazer, M.; Pakdel, E. J Text Inst 2011, 102, 343.
33. Montazer, M.; Pakdel, E. J Photochem Photobiol C 2011, 12, 293.
34. Montazer, M.; Pakdel, E.; Bameni Moghadam, M. Colloids Surf A 2011, 375, 1.
35. Montazer, M.; Pakdel, E.; Bameni Moghadam, M. Fibers Polym 2010, 11, 967.
36. Bozzi, A.; Yuranova, T.; Kiwi, J. J Photochem Photobiol A 2005, 172, 27.
37. Yu, J.; Xiong, J.; Cheng, B.; Liu, S. Appl Catal B 2005, 60, 211.
38. Sun, L.; Li, J.; Wang, C.; Li, S.; Lai, Y.; Chen, H.; Lin, C. J Hazard Mater 2009, 171, 1045.
39. Rammutla, K. E.; Savin, S. L. P.; Matshaba, M. G.; Chadwick, A. V. Phys Status Solidi C 2007, 4, 765.
40. Mills, A.; Wang, J. J Photochem Photobiol A 1999, 127, 123.
41. Tian, G.; Fu, H.; Jing, L.; Tian, C. J Hazard Mater 2009, 161, 1122.
42. Tada, H.; Teranishi, K.; Inubushi, Y.; Ito, S. Langmuir 2000, 16, 3304.
43. Zhu, P.; Sun, G. J Appl Polym Sci 2004, 93, 1037.
44. Amini, M.; Younesi, H.; Bahramifar, N.; Lorestani, A. A. Z.; Ghorbani, F.; Daneshi, A.; Sharifzadeh, M. J Hazard Mater 2008, 154, 694.
45. Box, G. E. P.; Draper, N. R. Empirical Model Building and Response Surfaces; Wiley: New York, NY, 1975.