Functionalization of a Cotton Fabric Surface with Titania Nanosols: Applications for Self-Cleaning and UV-Protection Properties

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ABSTRACT In this study, cotton fabric was successfully modified by titania nanosols prepared by means of the sol−gel process with tetrabutyl orthotitanate [$Ti(OC_4H_9)_4$] as the active ingredient. The cotton fabric was padded with the nanosol solution, dried at 60 °C, and cured at 150 °C. Scanning electron microscopy showed the presence of a titania film on the fiber surface. The photocatalytic properties of titania-nanosol-treated cotton fabric were investigated. The results showed that stains of coffee and red wine were successfully decomposed by exposure of the stained fabric to UV radiation. Furthermore, titania-nanosol treatment imparted to the cotton fabric a very good protection against UV radiation. The durability of the treatment was investigated by performing repeated home laundering, and the results showed no effect of laundering on the UV-protection efficiency.

KEYWORDS: titania nanosol • functionalization • cotton fibers • sol−gel • modification • coatings • UV radiation

INTRODUCTION

It has been reported that titania coatings exhibit a powerful photocatalytic activity (1−6). When illuminated, degradation of various organic compounds could be achieved (7−15). This activity is attributed to the fact that upon exposure to ultraviolet (UV) radiation (wavelength less than 385 nm) the photon energy generates an electron hole pair on the TiO_2 surface (16, 17). The hole in the valence band can react with H_2O or hydroxyl ions adsorbed on the surface to produce hydroxyl radicals, and the electron in the conduction band can reduce O_2 to produce superperoxide ions (O_2^-). Both hydroxyl radicals and superoxide ions are extremely reactive particles, and they can decompose organic compounds upon contact with them. Therefore, functionalization of the cotton fabric surface with titania nanosols may have efficient antibacterial properties and may exhibit self-cleaning and disinfecting properties.

Bozzi et al. reported that cotton fabric can be modified by TiO_2 at low temperature to impart self-cleaning properties (1). For this purpose, cotton fabric was first activated by radio-frequency plasma, microwave plasma, and UV irradiation in order to introduce functional groups to anchor TiO_2 particles on the fabric surface. TiO_2 colloidal particles were prepared from titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$) and titanium tetrachloride ($TiCl_4$). The efficiency of the treated fabric to decompose organic stains (red wine, coffee, make up, and grease) when exposed to UV daylight was investigated. It was reported that the amount of CO_2 generated from the organic stains increased with exposure time to UV daylight (50 mW/cm^2).

Daoud and Xin reported the successful nucleation and growth of anatase crystallites on cotton fabrics at low temperature (18−20). The precursor used for TiO_2 particle preparation was titanium tetraisopropoxide. The photocatalytic activity of the film formed on the fabric surface was investigated (2, 18). It was reported that coating with titania imparted UV protection, antibacterial performances, and self-cleaning properties. Room temperature synthesis of rutile nanorods and their applications on cotton fabrics achieved promising bactericidal photocatalytic activity and excellent protection against UV radiation (21).

Meilert et al. used chemical spacers (succinic acid, 1,2,3-propanetricarboxylic acid, and 1,2,3,4-butanetetracarboxylic acid) to attach TiO_2 particles to cotton fabric surfaces (22). In this process, the spacers were attached on the cotton by the formation of ester bonds, which are then used to anchor TiO_2 particles. The results showed that TiO_2-coated cotton fabric possessed stable self-cleaning properties and allowed the partial elimination of the chromophore of the red wine under daylight radiation.

Titania coating on cotton fabric also imparts UV-protection properties (23, 24). This property is largely attributed to the scattering effect of UV radiation by the TiO_2 particles. In previous work, we reported on the cotton fabric surface modification to improve the UV-radiation protection using the sol−gel process (25). Cotton fabrics were treated with titania nanosols or titania−silica nanosols. These nanosols were prepared from tetraethyl orthotitanate [$Ti(OC_2H_5)_4$] and tetraethyl orthosilicate [$Si(OC_2H_5)_4$]. The resulting titania-nanosol-treated cotton fabric exhibited excellent and durable UV-radiation protection. In this paper, we report on the efficiency of titania-nanosol-treated cotton fabric to decompose organic stains. Titania nanosols were prepared from tetrabutyl orthotitanate [$Ti(OC_4H_9)_4$]. Treated cotton fabrics

were stained with coffee and red wine and exposed to a UV-radiation source for a specified period of time, and the stain removal efficiency was evaluated.

MATERIALS AND METHODS

Materials. The fabric used in this study was desized, scoured, and bleached 100 % cotton. The fabric characteristics were as follows: 79.4 ends, 65.4 picks, yarn count of 23.4 × 22 tex, and a weight of 161.98 g/m^2 (4.8 $oz/yard^2$). The chemicals used to prepare the sol were purchased from Fisher Scientific: tetrabutyl orthotitanate $[Ti(OC_4H_9)_4]$, ethanol (C_2H_5OH), and hydrochloric acid (HCl; 37.7 %). All chemical reagents were used as received.

Titania-Nanosol Preparation. A total of 45 mL of $Ti(OC_4H_9)_4$ was first mixed with 15 mL of absolute C_2H_5OH. C_2H_5OH was added dropwise with stirring. Upon completion of the C_2H_5OH addition, HCl was added until the desired pH (1.5, 2, 3.5, and 4.5) was reached, and the solution was stirred for 45 min. The sol obtained was clear and homogeneous.

Fabric Treatment. Cotton fabric samples were dipped in the titania nanosol, soaked for 5 min, and passed through a two-roller laboratory padder (BTM 6-20-190) at a speed of 3.66 m/min and an air pressure of 2.76×10^5 Pa. The padded fabric samples were then dried at 60 °C for 10 min by passing through a Ben Dry-Cure Thermosol Oven (IT500 with 0.45 m working width) at 0.27 m/min to evaporate the solvent (C_2H_5OH) and then cured in the same oven at 150 °C for 5 min at a speed of 0.64 m/min. The samples were subjected to hydrothermal treatment by boiling them in water for 1 h. Then, the samples were dried, ironed, and finally conditioned in a laboratory maintained at 65 ± 2 % relative humidity and 21 ± 1 °C for at least 24 h before analysis was performed. Three replications were performed. The percent add-on on the fabric was calculated as follows: % add-on = $(m - m_0)/m_0 \times 100$, where m is the weight of the treated fabric and m_0 is the weight of untreated control fabric.

Scanning Electron Microscope. A Hitachi scanning electron microscope (TM-1000, Hitachi, Japan) with an accelerating voltage of 15 kv was used to visualize the cotton fabrics. Cotton fabrics were placed on a carbon disk, and no coating was performed prior to visualization.

Fabric Staining, Irradiation Procedure, and Evaluation of the Stain Removal Efficiency. The control sample and the titania-treated samples were stained with coffee and red wine following the standard method AATCC TM 130 (26). The same procedure was used for the stains of Cibacron red F–B (Ciba-Geigy, Greensboro, NC) using a solution of 0.010 g of the dye in 20 mL of water. The area stained on the fabric was marked. After staining, the samples were conditioned at 65 ± 2 % relative humidity and 21 ± 1 °C for at least 24 h and exposed to simulated sunlight radiation (Q-Sun Xe-3-HS, Q-Lab OH). The light intensity was 0.72 W/m^2 at 420 nm. The relative humidity in the chamber was maintained at 50 % and the temperature at 47 °C. The samples were conditioned again at 65 ± 2 % relative humidity and 21 ± 1 °C for at least 24 h before analysis.

All color measurements were performed using a Macbeth spectrophotometer (EC3000). The untreated and unstained control fabric was used as the standard for color measurements. A white Macbeth reference ceramic tile in reflectance mode was used for the calibration. Measurements were taken from the marked stained area in a large area view (0.0254 m in diameter) with standard illuminant C and at a 2° observer angle. UV light was excluded, and the specular components were included. Color differences between the control sample and the stained samples are reported as ΔE_{cmc} and AATCC gray scale for staining (GS) (27–29). ΔE_{cmc} is a single number that represents the number of Color Measurement Committee (CMC) color difference units of a trial from a standard. The AATCC GS for color change is composed of 10 grades (1, 1–2, 2, 2–3, 3, 3–4, 4,

Scheme 1. Structure of Cibacron Red
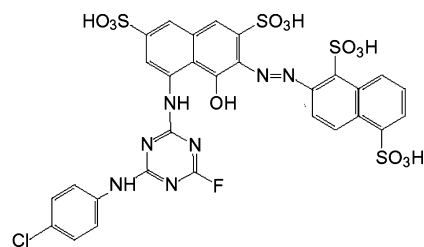
4–5, and 5). Grade 5 means that there is no color difference between the sample and the control; while grade 1 means that there is a drastic difference in color between the sample and the control.

Cibacron Dye Decomposition. Dye decomposition experiments were conducted as follows: A 0.1166 mM solution of Cibacron red (Ciba-Geigy, Greensboro, NC) in water was prepared. The structural formula of Cibacron red is shown in Scheme 1. In a plastic cuvette, 0.05 g of fabric was weighed and 3.5 mL of the dye solution was added. The cuvettes were sealed with a plastic film and were exposed to UV light in a C5 UV chamber (Ultraviolet Products, San Gabriel, CA). A 6 W long-wave Spectroline E series lamp (Westbury, NY) was used. The lamp spectra ranged from 320 to 400 nm. The intensity at 0.1524 m from the lamp was 9 W/m^2 at 365 nm. Samples were placed 0.1524 m below the lamp and exposed for a predetermined amount of time (from 0 to 46 h). The absorption of the samples was measured using a Lambda 650 UV–vis spectrophotometer (PerkinElmer, Shelton, CT) at 541 nm.

UV-Protection Measurement. The UV-protection factor (UPF) was measured using the SPF-290 analyzer equipped with an integrating sphere (Optometrics, Ayer, MA). This instrument is equipped with an automated X–Y stage, allowing automated measurements. The UV transmission measurements were performed according to AATCC TM 183 (30). Three specimens (0.1 m × 0.1 m each) from each sample were scanned, and 12 scans per specimen were acquired. The UPF (average of 12 scans) was computed using the following formula: $UPF = \sum_{290}^{400} E_\lambda S_\lambda \Delta\lambda / \sum_{290}^{400} E_\lambda S_\lambda T_\lambda \Delta\lambda$. In this equation, E_λ corresponds to the relative Erythemal effectiveness, S_λ is the solar spectral irradiance, T_λ is the average spectral transmittance, and $\Delta\lambda$ is the measured wavelength interval in nanometers (290 nm ≤ λ ≤ 400 nm).

Tests of the Durability of the Treatment to Repeated Laundering. The treated fabric samples were subjected to home laundering for up to 18 cycles according to AATCC TM 124 (31). AATCC standard detergent without optical brighteners was used throughout the laundering cycles.

RESULTS AND DISCUSSION

Figure 1 shows the morphological changes induced by treatment with titania nanosols prepared from $Ti(OC_4H_9)_4$. In contrast to the scanning electron microscopy (SEM) micrograph of untreated cotton fabric (Figure 1A), the micrograph of the cotton fabric treated with titania nanosols shows white particles deposited on the fiber surface (Figure 1B). At higher magnification, the formation of a thin layer of titania is observed on the fiber surface (Figure 1D). The percentage add-on of the titania on the fabric surface was 16 %.

The effect of the pH of the nanosol solution was first investigated. Cotton fabrics were treated with different nanosol solutions with pH 1.5, 2, 3.5, and 4.5. Stains of Cibacron red dye were made on the treated cotton fabric and exposed to UV radiation (0.72 W/m^2) for different
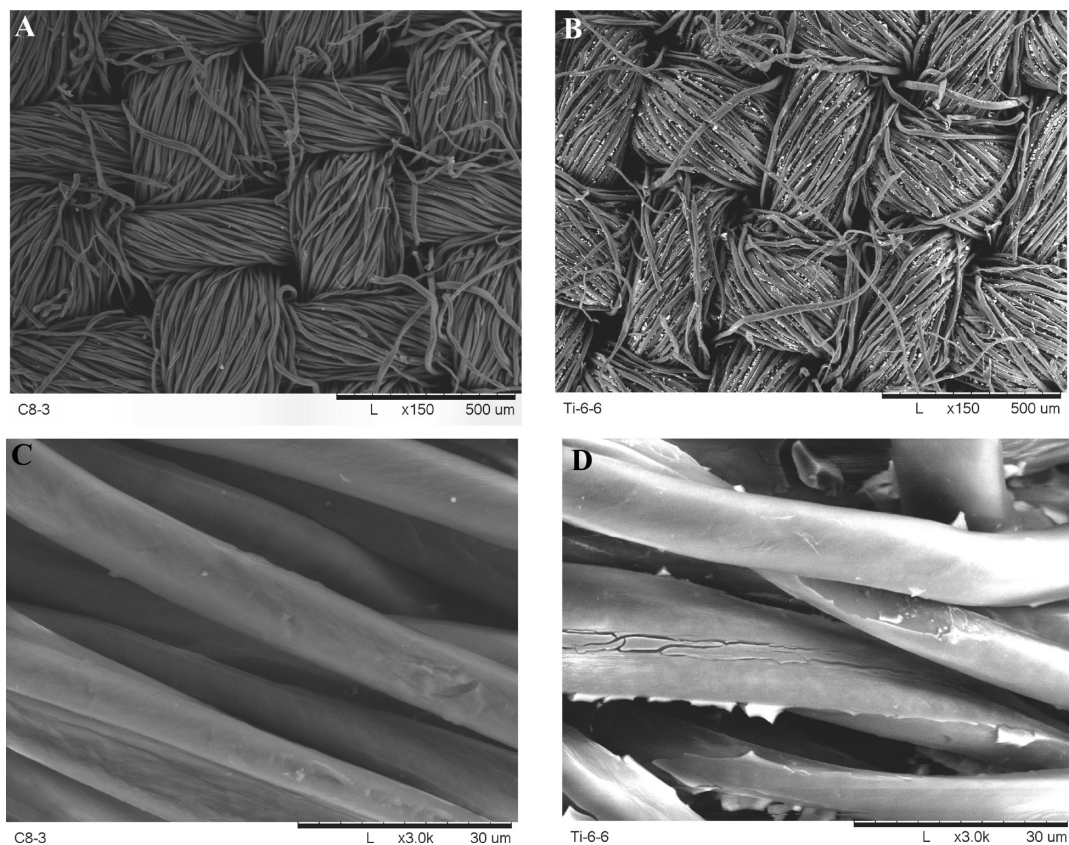
FIGURE 1. SEM images of (A) untreated fabric at 150×, (B) titania-nanosol-treated fabric at 150×, (C) untreated fabric at 3000×, and (D) titania-nanosol-treated fabric at 3000×.
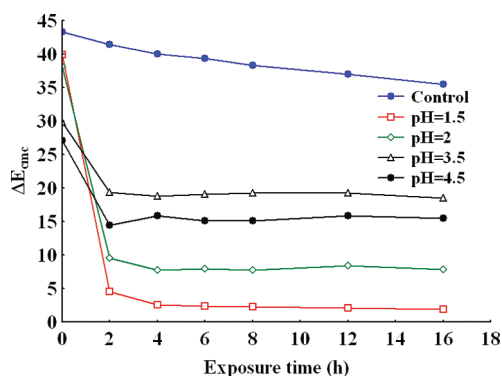

FIGURE 2. Decomposition of the Cibacron red dye stain: Effect of the pH of the nanosol solution on ΔE_{cmc}.

FIGURE 3. Evolution of ΔE_{cmc} as a function of the exposure time to UV radiation: (A) control fabric with no stain; (B) control fabric stained with coffee; (C) titania-nanosol-treated fabric stained with coffee. The pH of the titania-nanosol solution was 2.

periods of time (from 0 to 16 h). A Macbeth spectrophotometer was used to measure ΔE_{cmc} as a function of the exposure time to UV radiation (Figure 2). The analysis of variance shows significant effects of the pH [$F(1,4) = 948.32$, $p = 0.000\,001$] and the exposure time [$F(1,6) = 239.97$, $p = 0.000\,001$] on ΔE_{cmc}. There is also significant interaction of pH × exposure time. The nanosols prepared with a pH of 1.5 provide the best results (after 16 h of exposure to UV radiation, ΔE_{cmc} is 1.89). However, some of treated samples showed signs of degradation. Therefore, we decided to work with a pH of 2.

The photocatalytic activity of titania nanosols deposited on the fabric surface was investigated. For this purpose, stains of coffee and red wine were made on untreated and titania-nanosol-treated fabrics. Cotton fabric, which did not
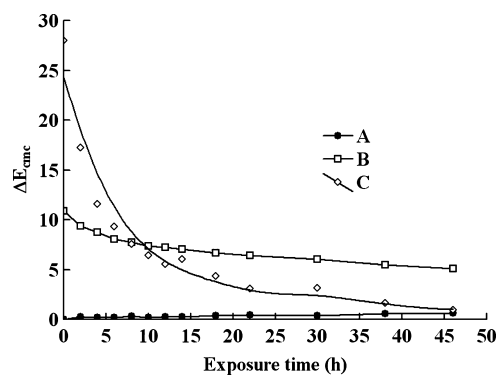
receive any treatment, was used as a control. The stained fabrics and the control fabric were exposed to UV radiation (0.72 W/m^2) for different periods of time (from 0 to 46 h). A Macbeth spectrophotometer was used to measure the AATCC GS and ΔE_{cmc} as a function of the exposure time to UV radiation. The evolution of ΔE_{cmc} of the coffee stain is shown in Figure 3 for a fabric treated with Ti(OC$_4$H$_9$)$_4$ nanosols and the control fabrics. The results presented in this graph are the average of three replications. Overall, there is a decrease of ΔE_{cmc} with increasing exposure time to UV radiation. The analysis of variance shows a significant effect of the treatment and exposure time (Table 1). There is also a statistically significant interaction of treatment × exposure time. ΔE_{cmc} decreased from 28.0 at 0 h to 0.9 after 46 h of exposure to

Table 1. Analysis of Variance: Effect of the Exposure Time to UV Radiation and Treatment on ΔE_{cmc}: (A) Control Fabric with No Stain; (B) Control Fabric Stained with Coffee; (C) Titania-Nanosol-Treated Fabric Stained with Coffee[a]

| parameter	df	F	probability	ΔE_{cmc}[b]		
				A	B	C
intercept	1	12 972.47	0.000 001			
treatment	2	2 891.68	0.000 001			
treatment × time	24	191.62	0.000 001			
time (h)	12	314.82	0.000 001			
0				0.0 b	10.9 a	28.0 a
2				0.2 ab	9.4 b	17.3 b
4				0.2 ab	8.7 bc	11.5 c
6				0.2 ab	8.1 cd	9.3 d
8				0.3 ab	7.7 d	7.5 e
10				0.2 ab	7.4 de	6.4 ef
12				0.3 ab	7.2 de	5.5 fg
14				0.2 ab	7.1 de	6.0 f
18				0.4 ab	6.7 ef	4.3 ig
22				0.5 a	6.4 ef	3.1 i
30				0.4 ab	6.0 fg	3.1 i
38				0.6 a	5.5 gh	1.7 hi
46				0.6 a	5.1 h	0.9 j
error	78					

[a] df = degrees of freedom; F = variance ratio. [b] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

UV radiation. This corresponds to a 97% reduction, while for the stained control fabric, ΔE_{cmc} decreased only slightly (from 10.9 to 5.1).

It should be pointed out that ΔE_{cmc} is higher for the stained and titania-nanosol-treated fabric compared to the stained and control fabric. This is attributed to some type of chemical reaction between the stain and the titania nanosols. The AATCC GS of the fabric stained with coffee before exposure to UV radiation was 2. After 46 h of exposure to UV radiation, the GS increased to 5. This indicates that there is no noticeable difference for the human eye between the control (unstained white control fabric) and the titania-nanosol-treated cotton fabric that has been stained with coffee and exposed to UV radiation for 46 h.

Figure 4 shows the changes in color of the titania-nanosol-treated cotton fabric stained with coffee. The picture in Figure 4A shows the coffee stain on the titania-nanosol-treated cotton fabric before exposure to UV radiation. ΔE_{cmc} was 33.4, and the GS was 2. This level of coloration is very dark and easily noticeable on the white cotton fabric. The picture in Figure 4B shows the fabric after 28 h of exposure to UV radiation (0.72 W/m^2). The values of $\Delta E_{cmc} = 0.6$ and GS = 5 mean that the human eye cannot distinguish between this fabric and the control white fabric (the picture in Figure 4C).

The evolution of ΔE_{cmc} of the red wine stain is shown in Figure 5 as a function of the exposure time to UV radiation. The results presented in this graph are the average of three replications. The analysis of variance shows a significant
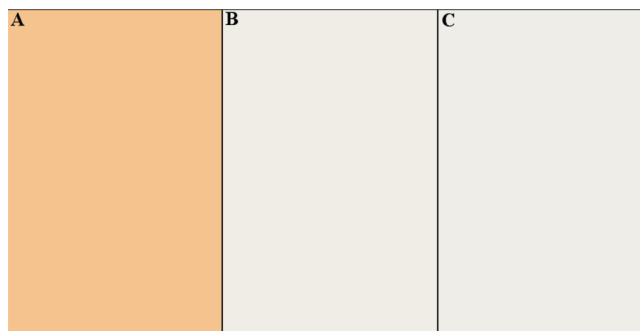
FIGURE 4. Decomposition of the coffee stain: (A) nanosol-treated cotton fabric and stained with coffee before exposure to simulated sunlight; (B) sample A after exposure to simulated sunlight for 28 h; (C) control white fabric with no treatment and no stain. The pH of the titania-nanosol solution was 2.
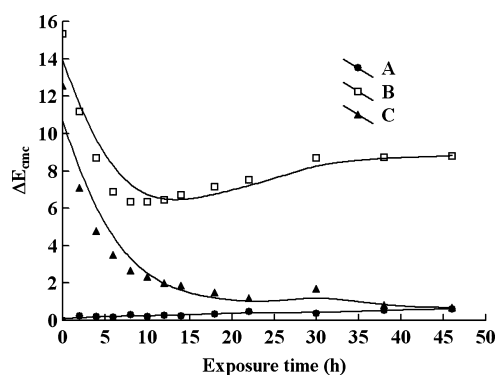
FIGURE 5. Evolution of ΔE_{cmc} as a function of the exposure time to UV radiation: (A) control fabric with no stain; (B) control fabric stained with red wine; (C) titania-nanosol-treated fabric stained with red wine. The pH of the titania-nanosol solution was 2.

effect of the treatment with the titania nanosols on ΔE_{cmc} (Table 2). ΔE_{cmc} decreased from 12.6 at 0 h to 0.7 after 46 h of exposure to UV radiation. This corresponds to a 94% reduction, while for the untreated fabric, ΔE_{cmc} decreased only slightly (from 15.2 to 8.8). The AATCC GS increased from 2 before exposure to UV radiation to 5 after 46 h exposure to UV radiation. These results suggest that the titania nanosol coating prepared from the tetrabutyl orthotitanate precursor imparts very good photocatalytic activities.

The change in the color of the white control sample exposed to UV radiation was also measured. The result showed a very minimal increase in ΔE_{cmc} from 0 to 0.6 after 46 h of exposure. This change in color could be due to the oxidation of cellulosic chains by UV radiation (32, 33).

Figure 6 shows the changes in color of the titania-nanosol-treated cotton fabric stained with red wine. The picture in Figure 6A shows the red wine stain on the titania-nanosol-treated cotton fabric before exposure to UV radiation. ΔE_{cmc} was 13, and the GS was 2. This level of coloration is very dark and easily noticeable on the white cotton fabric. The picture in Figure 6B shows the fabric after 28 h of exposure to UV radiation (0.72 W/m^2). The values of $\Delta E_{cmc} = 1.6$ and GS = 5 mean that the human eye cannot distinguish between this fabric and the control white fabric (the picture in Figure 6C).

To further test the efficiency of the photocatalytic properties of treated fabric with titania nanosols, a Cibacron red

Table 2. Analysis of Variance: Effect of the Exposure Time to UV Radiation and Treatment on ΔE_{cmc}: (A) Control Fabric with No Stain; (B) Control Fabric Stained with Red Wine; (C) Titania-Nanosol-Treated Fabric Stained with Red Wine[a]

parameter	df	F	probability	ΔE_{cmc}[b] A	B	C
intercept	1	25 113.80	0.000 001			
treatment	2	8 785.41	0.000 001			
treatment × time	24	145.38	0.000 001			
time (h)	12	410.99	0.000 001			
0				0.0 b	15.2 a	12.6 a
2				0.2 ab	11.2 b	7.1 b
4				0.2 ab	8.7 c	4.8 c
6				0.2 ab	6.9 de	3.5 d
8				0.3 ab	6.4 e	2.7 e
10				0.2 ab	6.3 e	2.3 ef
12				0.3 ab	6.4 e	2.0 fg
14				0.2 ab	6.7 de	1.8 gh
18				0.4 ab	7.1 de	1.5 hi
22				0.5 a	7.5 d	1.2 ij
30				0.4 ab	8.7 c	1.7 gh
38				0.6 a	8.7 c	0.8 jk
46				0.6 a	8.8 c	0.7 k
error	78					

[a] df = degrees of freedom; F = variance ratio. [b] Values not followed by the same letter are significantly different with α = 5% (according to Newman−Keuls tests).


FIGURE 6. Decomposition of the red wine stain: (A) nanosol-treated cotton fabric stained with red wine before exposure to simulated sunlight; (B) sample A after exposure to simulated sunlight for 28 h; (C) control white fabric with no treatment and no stain. The pH of the titania-nanosol solution was 2.

dye solution was prepared and the titania-nanosol-treated fabric was cut into small pieces and introduced into the dye solution. The solution was then exposed to a source of UV radiation for different periods of time as detailed in the Materials and Methods section. A Cibacron dye solution and a Cibacron dye solution containing a control fabric (untreated) were also exposed to UV radiation at the same time. The concentration of the dye in the solution was measured with a UV−vis spectrophotometer. The evolution of the concentration of the dye in the solution as a function of the exposure time is exhibited in Figure 7. The concentration of the dye in the solution containing the control fabric (Figure 7A) did not show any change with the exposure time to UV radiation. This is also true for the dye solution (Figure 7B).
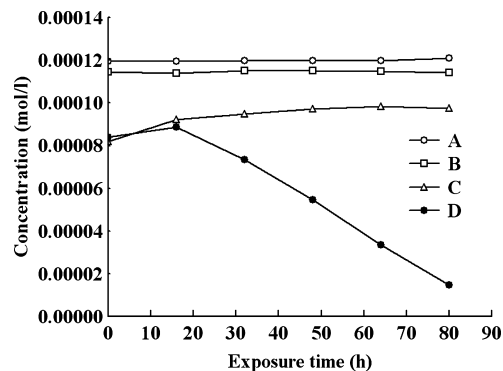
FIGURE 7. Decomposition of Cibacron red dye: (A) Cibacron red dye solution with no fabric; (B) Cibacron red dye solution containing control white fabric; (C) Cibacron red dye solution containing cotton fabric treated with titania nanosols and kept in the dark; (D) Cibacron red dye solution containing cotton fabric treated with titania nanosols and exposed to UV radiation for different periods of time.
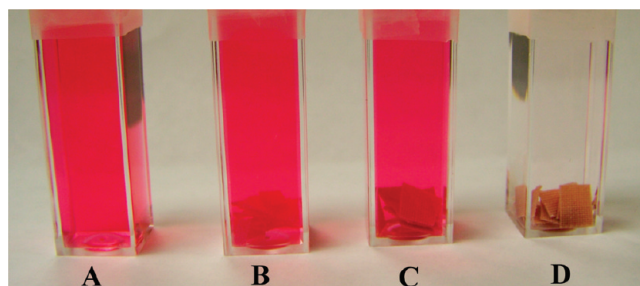
FIGURE 8. Decomposition of Cibacron red dye: (A) Cibacron red dye solution; (B) Cibacron red dye solution containing control white fabric with no treatment and no stain; (C) Cibacron red dye solution containing cotton fabric treated with titania nanosols and kept in the dark: (D) Cibacron red solution containing cotton fabric treated with titania nanosols and exposed to UV radiation for different periods of time.
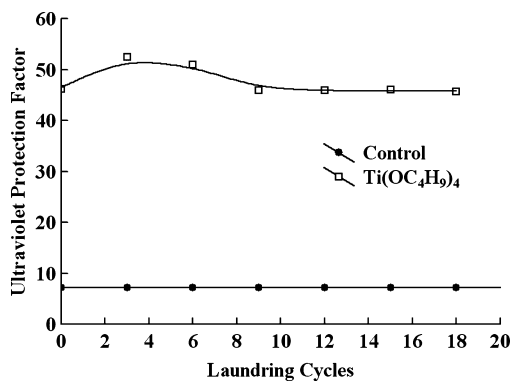
FIGURE 9. Evolution of the UPF as a function of the laundering cycles.

When the nanosol-treated fabric is immersed in the dye solution and kept in the dark, the concentration of the dye did not change with time (Figure 7C). However, the concentration of the dye decreased when the solution containing nanosol-treated cotton fabric was exposed to UV radiation. After 80 h of exposure, the concentration of the dye decreased by 83%. Figure 8 shows pictures of dye solutions after 80 h of exposure to UV radiation. The dye molecules in the solution containing titania-nanosol-treated fabric were decomposed, resulting in a clear solution.

Finally, the efficiency of the titania-nanosol-treated fabric to provide protection from UV radiation was investigated. The UPF was measured. The analysis of variance showed a significant effect of the treatment on the UPF [$F(1,1) = 925.02$, $p = 0.000 001$]. The UPF increased by 571 % (from 7 to 47). The durability of the treatment was investigated by performing repeated home laundering (Figure 9). The analysis of variance did not show any significant effects of laundering on the UPF [$F(1,6) = 0.65$, $p = 0.692226$].

CONCLUSION

A cotton fabric surface was successfully modified with titania nanosols prepared from $Ti(OC_4H_9)_4$. SEM images showed the formation of a film on the fiber surface at relatively low treatment temperature (150 °C). The photo-catalytic properties of the film deposited on the fabric surface imparted self-cleaning properties to the cotton fabric. Indeed, stains of coffee and red wine on the treated cotton fabric were decomposed by exposure to UV radiation. Furthermore, the treatment imparted excellent UV-radiation protection to the cotton fabric especially in the region of the UVB (290−315 nm).

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