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Self-cleaning of wool-polyamide and polyester textiles by TiO_2-rutile modification under daylight irradiation at ambient temperature

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Abstract

This study presents radio frequency plasma (RF-plasma), microwave plasma (MW-plasma), and vacuum-UV light irradiation as pretreatment of synthetic textile surfaces allowing the loading of TiO_2 by wet chemical techniques in the form of transparent coatings constituted of nanoparticles of diverse sizes. These loaded textiles show a significant photo-oxidative activity under visible light in air under mild conditions, which discolors and mineralizes persistent pigment stains contained in wine and coffee. The mineralization of stains on the textile loaded with TiO_2 was monitored quantitatively to assess the appropriate surface pretreatment in conjunction with the most suitable deposition method of TiO_2 colloids, powders, or combination of both. Their photocatalytic activity allowed, in kinetically acceptable times, the almost complete discoloration of coffee and wine stains. The observed discoloration of colored stains seems to involve visible light sensitization of the stain pigment on the TiO_2-loaded textile. The size of the particles obtained from colloidal precursors of TiO_2 varied between 5 and 25 nm.

Keywords: Photocatalysis; Synthetic fibers; TiO_2 clusters; TiO_2 colloids; Self-cleaning; Daylight irradiation; Rutile loaded synthetic fibers

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1. Introduction

This study aims to increase the bondability of TiO_2 on wool-polyamide and polyester textiles by surface textile modifications induced by RF-plasma, MW-plasma and UV irradiation. These pretreatments at low-pressure in air leave the bulk of the textile intact and only modify the upper surface layers from 1 to 20 nm [1]. Surface pretreatments of fabrics and polymers have been carried out by etching [2], plasma [3], and corona discharge [4]. Man made fabrics and textiles in Europe represent 72% of the total textile market and improvements increasing their properties are sought for products having high added value [5]. The application of TiO_2 loading technology on textiles or flexible supports is in its infancy compared with TiO_2 films intended to harvest solar energy and depollute water or air, where the TiO_2 is deposited on glass, silica or ceramic supports [6,7]. Recently, the growth of TiO_2 crystallites was reported to produce photoactive films at 100 °C on glass surfaces [8–11]. In Japanese studies related to TiO_2 coated textiles [6–8], emulsions were prepared using acrylate, additives, fluidizers and TiO_2. The emulsion was then sprayed on the textile fabric. Then the textile was heated to around 100 °C for a few minutes to produce the polymer on the textile containing the TiO_2. Chinese studies also used this approach with some variations [12].

Our work uses a different approach. It consists in modifying the structure of the textile surface by introducing a variable density of negative groups $-COO^-$, $-O-O^-$, through RF-plasma, MW-plasma or vacuum-UV irradiation. Then, the TiO_2 is attached to the modified textile surface by exchange with the positively loaded Ti^{4+} of TiO_2. The surplus charge is 3+, which is quite considerable in electrostatic terms. Deposition of TiO_2 clusters on natural cotton textiles has recently been reported, showing the formation of anatase crystals of small dimensions stably grafted onto cotton fabrics [12]. Also, in this study we intend to optimize the formula-

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tion of colloids to produce efficient discoloration of some persistent stains on synthetic textiles.

2. Experimental section

2.1. Materials

Polyester (100% Trevira) and wool (90%)-polyamide (10%) textiles were used throughout this work. Titanium tetrachloride ($TiCl_4$), titanium tetra-isopropoxide (TTIP), nitric acid (HNO_3), and hydrochloric acid (HCl) were Fluka p.a. reagents and used as received. Triply distilled water was used in all experiments.

2.2. Pretreatment of synthetic textiles fabrics

2.2.1. RF-plasma

The polyester and wool-polyamide fabrics were pretreated in a RF-plasma cavity (13.56 MHz, 100 W) instrument from Harrick and Co., UK, using a vacuum of 0.8 Torr. A variety of functional groups C–O, C=O, –O–C=O, –COH, –COOH, were introduced on the fabric surface through the reaction between the active O-species (singlet $^1O_2$, atomic O, anion-radical O^-, and cation-radical $O^{\bullet +}$) induced by the plasma activation of the gas phase on the carbon of the textiles surface [13]. Besides functional groups mentioned above, synthetic textile fibers have been shown to form a significant number of percarboxylate, epoxide, and peroxide groups upon irradiation with RF-plasma [14]. The overall hydrophilicity of the textile surface was drastically increased upon this pretreatment. These oxygen functions were located in the top layers of the materials 10–40 nm depth and attained a higher concentration with longer treatment times (up to ∼30 min). This time has been chosen for RF-plasma treatments performed in this study. Recently, the preparation of diverse catalysts using plasma technology has been described [15].

2.2.2. MW-plasma

The polyester and wool-polyamide fabrics were also pretreated in a MW-plasma cavity (Vacotec Corp., Neuchatel, Switzerland) operated at 2450 MHz and 100–600 W under a pressure of 0.8 Torr (oxygen atmosphere). The time of treatment was varied between 5 and 45 s depending on the fabric stability and on its resistance to the temperature reached in the plasma chamber. A 120 °C temperature was not exceeded, which would be higher than the flowing point of the synthetic fabrics used.

2.2.3. Vacuum-UV

The textile polymer surface was also pre-treated using the 185 nm line of a 25 W low-pressure mercury lamp (Ebara Corp., Iwasaki Electric Co., Shiba, Japan). The lamp wall consisted of synthetic silica able to transmit the 184 nm light. This wavelength comprises 25% of the total lamp output. The other 75% of the lamp output consisted of a 254 nm radiation. Since the vacuum-UV activation proceeds with a lower energy than the plasma activation, no cationic or anionic oxygen species can be produced in the gas phase. Only atomic and excited oxygen species are formed. This leads to a more controlled and uniform modification of the textile surfaces with an increased polarity, which is related to the variety of oxygen functional groups formed by the reactions of free radicals with O_2 in the gas phase. The active upper textile layers are excited by the incoming UV radiation up to ∼10 nm depth (or the equivalent of 50 atomic layers with an average thickness of 2 Å/layer). Therefore, the bulk of the textile is not touched. At the pressures used for plasma or vacuum-UV pretreatment, the residual oxygen was sufficient to modify the textile surfaces owing to the absorption cross section of O_2 for plasma radiation or ultraviolet light [16].

2.3. Preparation of TiO_2 suspensions and colloids

Five different methods were used to prepare TiO_2 colloidal solutions intended to load the cotton fabrics.

(1) A suspension of 5 g/l of TiO_2 was prepared through the dilution of Degussa P-25 pigment in 500 ml of distilled water. The suspension was sonicated during 30 min at 60 °C before use.

(2) An aqueous solution of 1% in $TiCl_4$ (M_w 198.7) was made by slowly dropping reagent grade $TiCl_4$ into ice-cold distilled water (2 °C) previously acidified with HCl. Cellulose membranes were used to eliminate by osmosis Cl^- ions, which interfere with the self-cleaning photocatalytic process, if present on the textile surface.

(3) Titanium tetra-isopropoxide (20 ml) was added dropwise to 300 ml of 2-propanol acidified with 1 ml of concentrated HNO_3 and cooled to ∼0 °C. This solution was stirred for ∼1 h to achieve the total dissolution of resulting polymeric chains and produce a transparent solution.

(4) Colloidal TiO_2 (300 ml of an 8 wt% solution) was prepared using method 3. The hydrothermal treatment of this solution was then carried out by heating in an autoclave for 16 h at 100 °C to favor the growth of initial TiO_2 particles. After autoclaving, the TiO_2 particles were re-dispersed by stirring and sonication.

(5) Colloidal TiO_2 (300 ml of a 12 wt% solution) was prepared using method 4 and a hydrothermal treatment at 220 °C.

(6) A 4 cm × 12 cm textile sample (sample 14 in Table 1), RF-plasma pre-treated (30 min), was immersed in a TiO_2 colloidal solution prepared using method 4, then dried at 60 °C for 24 h and cured at 100 °C for 15 min after what a second layer of TiO_2 was deposited by immersing the textile in a suspension of TiO_2 Degussa P-25 (5 g/l). After final drying in air at room temperature and then at 100 °C, the sample was washed with distilled water under sonication to remove the unattached particles of TiO_2.

Table 1
Conditions used to load TiO_2 on wool-polyamide and polyester textiles

Sample number	Type of pretreatment	Time of pretreatment	TiO_2 source	Preparation number
1	RF-plasma	30 min	Degussa P-25 (water)	1
2	RF-plasma	30 min	$TiCl_4$ (water)	2
3	RF-plasma	30 min	TTIP (water)	3
4	RF-plasma	30 min	TTIP (water)[a]	4
5	RF-plasma	30 min	TTIP (water)[b]	5
6	Vacuum-UV	30 min	$TiCl_4$ (water)	2
7	Vacuum-UV	30 min	TTIP (water)	3
8	Vacuum-UV	30 min	TTIP (water)[a]	4
9	Vacuum-UV	30 min	TTIP (water)[b]	5
10	MW-plasma	3 × 10 s	$TiCl_4$ (water)	2
11	MW-plasma	3 × 10 s	TTIP (water)	3
12	MW-plasma	3 × 10 s	TTIP (water)[a]	4
13	MW-plasma	3 × 10 s	TTIP (water)[b]	5
14	RF-plasma	30 min	TTIP (water)[a] + Degussa P-25	4 + 1

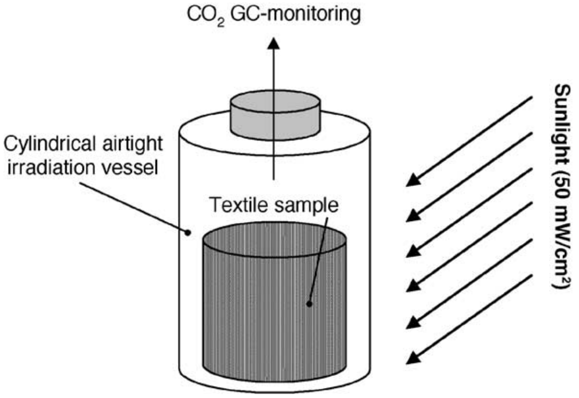
[a] Hydrothermal treatment (16 h at 100 °C).
[b] Hydrothermal treatment (16 h at 220 °C).

2.4. Preparation of TiO_2 coated textiles

Plasma or UV pre-treated textiles samples (4 cm × 12 cm) (see Table 1) were immersed in the selected TiO_2 suspension/colloidal solutions for 30 min. Then, the samples were dried in air at 22 °C (laboratory temperature) for 24 h and then heated at 100 °C for 15 min. The exchange operation was carried out immediately after the pretreatment using any of the three techniques mentioned above. The reason for this is that the radicals formed at the fabric surface react with humidity and oxygen of the air, slowly deactivating the radicals induced on the pre-treated fabrics. The textile samples were then washed with distilled water under sonication to remove TiO_2 particles that did not attach to the fabric surface. During this study, we found that only pre-treated surfaces were able to fix TiO_2 from colloidal solutions or suspensions or the combination of both. The attachment of TiO_2 to the surface of the textile fabric is electrostatic in nature since the semiconductor TiO_2 is positively charged and the textile surface was charged negatively during the pretreatment. The negative charge due to the $-COO^-$ and $O-O^-$ groups induced on the textile surface by the atomic and ionized O_2 generated in the cavity of the plasma or vacuum-UV during pretreatment.

2.5. Irradiation procedure and evaluation of the textile cleaning action

The photochemical reactor consisted of 80 ml cylindrical Pyrex flasks containing a strip of textile of 48 cm^2 positioned immediately against the wall of the reactor (see Scheme 1). Except when mentioned in the text, irradiation of the samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air-cooled at 45 °C. The Suntest lamp emitted 7% of the photons in the 290 and 400 nm spectral range. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum with a light intensity of 50 mW/cm^2 corresponding to 50% of AM1 (AM1 corresponding to the light intensity of the midday equatorial solar radiation). The radiant flux was monitored by a LSI Corporation power meter of Yellow Springs, CO, USA. The CO_2 produced during irradiation was measured in a gas chromatograph (Carlo Erba, Milano) provided with a Poropak S column.



Scheme 1.

2.6. Elemental analysis and dust test

Elemental analysis of the TiO_2-loaded on the textile fabrics was carried out by atomic absorption spectrometry using a Perkin-Elmer 300 S unit. A flow of dust was applied on the textiles and the dust adherence was estimated from color changes of the textile surface in a relative scale of 1–5.

2.7. High resolution transmission electron microscopy (HRTEM)

A field emission TEM microscope (Philips CM 120) was used to measure the particle size of titania clusters on the textile surfaces. The electron microscopy (120 kV, 0.35 nm point resolution) was equipped with energy dispersive X-ray analysis (EDS) allowing the identification of TiO_2-clusters deposited on the textile fabrics. The textiles were coated with an epoxy resin and the fabric was cut with a microtome to a thin layer of 50 nm thickness for experimental observations at a 90° angle. Probes having a 10 micron diameter were examined to monitor the supported TiO_2 cluster size and distribution. After a dry cleaning cycle, transmission electron microscopy was carried out to investigate whether or not the TiO_2 was present and resisted dry cleaning.

2.8. Diffuse reflectance spectroscopy (DRS) and X-ray diffraction measurements (XRD) of TiO_2-loaded textiles

The diffuse reflectance of TiO_2-loaded textiles was measured using a Cary 5 UV–vis–NIR spectrophotometer equipped with a specular reflectance attachment. Calibration was performed using a MgO powder and measurements were achieved on 2.5 cm size samples. The crystallinity and phase of the titanium oxide loaded on the textile surface was studied with a Siemens X-ray diffractometer using Cu Kα radiation.

3. Results and discussion

3.1. Production of CO_2 with the degradation of wine and coffee stains on polyester and wool-polyamide textiles

The mineralization of organic stains on textiles, activated by TiO_2, leads to the production of CO_2 and a small amount of anions and cations. The amount of CO_2 produced in the reactor was used to monitor the mineralization of coffee and wine stains during light irradiation. Fig. 1(a) and (b) show the amount of CO_2 produced after 24 h irradiation for the loaded polyester and wool-polyamide, respectively. To verify that CO_2 was not generated by the textile but actually due to the organics composing the stain, the amount of CO_2 generated by photocatalytic decomposition of a non-loaded textile sample was measured in a blank experiment. No CO_2 was observed in the absence of TiO_2 on polyester and wool-polyamide textiles. Fig. 1(a) and (b) show that self-cleaning was optimal for sample 14 (Table 1), which consisted of a mixture of colloidal TiO_2 and Degussa P-25 deposited on a textile that had been previously pre-treated by RF-plasma. We explored six different TiO_2 loading procedures on both synthetic fibers throughout this study. The best one (no. 14) has been studied in detail but the other procedures are also described. The first five procedures mentioned in Section 2.3 used either TiO_2 powder (1st), colloidal TiO_2 (2rd, 3th and 4th), or hydrothermally grown colloidal TiO_2 (4th and 5th). But only the 6th procedure combining the hydrotermal treated

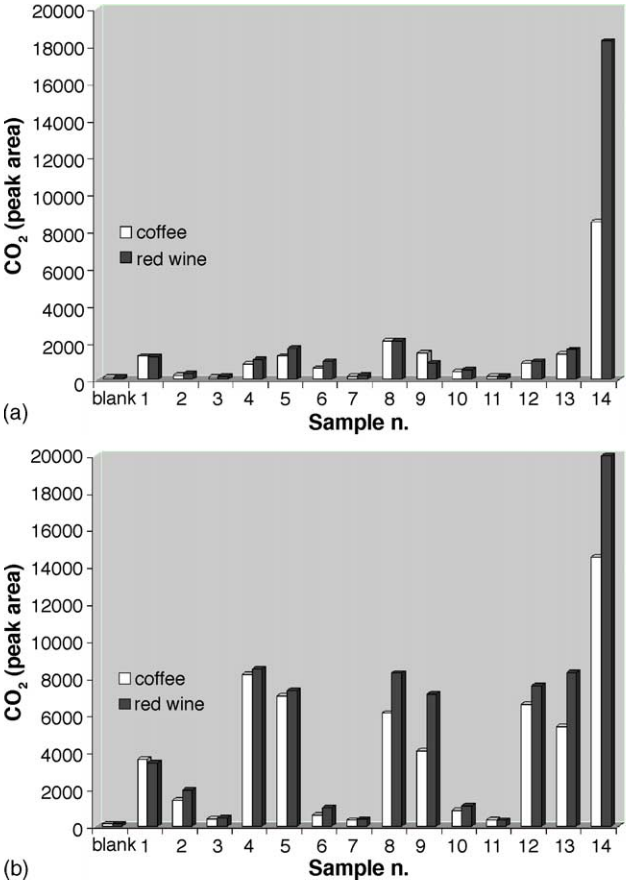


Fig. 1. CO_2 produced during the photocatalytic degradation of stains of coffee and red wine on TiO_2-loaded polyester (a) and wool-polyamide (b). Irradiation time: 24 h. During this study a Suntest sunlight simulator was used with a power of 50 mW/cm^2.

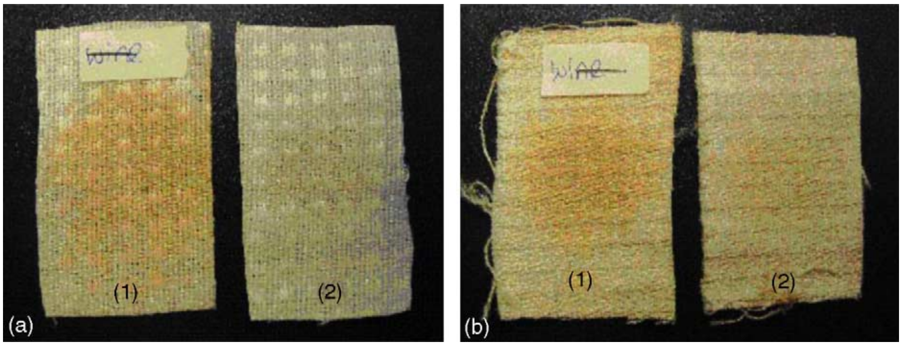


Fig. 2. Discoloration of red wine stains on the sample 14. (a) Polyester fabrics, (b) wool-polyamide. Textile before irradiation (1) and after 24 h Suntest irradiation (2).

colloidal TiO_2 as a basic layer with a second coating of TiO_2 Degussa P-25 having bigger crystallite size led to best discoloring performance. This is presumably due to the small TiO_2 colloidal particles deposited on the textile providing effective anchoring sites for the bigger Degussa P-25 TiO_2 crystallites.

Fig. 1(a) and (b) show that the self-cleaning action was enhanced for wool-polyamide compared to the polyester textile. This is reflected by the higher CO_2 peak areas seen in Fig. 1(b) compared to Fig. 1(a). The wine stains also seem to mineralize more easily than coffee stains.

3.2. Photo-induced discoloration on polyester and wool-polyamide textiles

Fig. 2(a) and (b) show the aspect of a wine stain on polyester and wool-polyamide, respectively, before and after 24 h Suntest visible light irradiation. In both cases, a partial discoloration induced by light can be observed. It means that wine stains are partially degraded on the TiO_2-loaded surfaces and will be more prone to the action of detergents during household washing. Longer time intervals between conventional washings and the corresponding cost saving should thus ensue.

3.3. Diffuse reflection of TiO_2-loaded textiles

Fig. 3(a) and (b) show the specular reflectance of textiles pre-treated by RF-plasma and loaded with TiO_2 (sample 14, Table 1). Specular reflectance spectra shown in Fig. 3 refer to (a) a coffee stain on polyester fabric and (b) a red wine stain on wool-polyamide fabric. When hot coffee is poured on the polyester fabric, the textile color turns from white to brown. When wine is poured, a dark red stain is observed on the wool-polyamide fabric. These colorations result in greater absorptions of the stained textiles in the visible spectral range, yielding the weaker reflectance illustrated in Fig. 3(a) and (b) before irradiation. After irradiation, the enhanced reflectance depicts a decrease in the absorption related to wine and coffee.

3.4. Reproducibility and light influence

To verify the reproducibility of our results, three different samples of wool-polyamide textiles were loaded with TiO_2 using the procedure of sample 14. The TiO_2-loaded samples were subsequently stained with red wine and irradiated during 24 h with a Suntest light. Results of CO_2 evolution showed that the difference between the three samples lay within an experimental error of 10%. This shows the reproducibility of the self-cleaning action towards red wine stains.

Three types of light sources were tested to irradiate the fabrics stained with wine or coffee: (a) a Suntest solar simulator with a light intensity of 50 mW/cm^2; (b) a neon room emitting light in the range 350–560 nm with 2.2 mW/cm^2, and (c) a mercury blue light emitting at $\lambda = 366$ nm with 3.5 mW/cm^2. Both the neon and mercury blue lights yielded a very poor photocatalytic discoloration of stains compared to the Suntest simulator. Using the neon light, about 120 h irradiation were necessary to achieve a discoloration equivalent to that obtained after 24 h with the Suntest simulator. No significant discoloration was observed when the mercury lamp was employed to remove wine or coffee stains. This suggests that absorption by wine or coffee stains of the visible light emitted by the Suntest simulator is essential for the discoloration of these stains. The colored pigments of wine and coffee seem to sensitize this discoloration by the mechanism suggested in Fig. 4(a) and (b). In this mechanism, the oxidation and decomposition of the organic reactant would occurring either via the coffee or wine pigment cation, injecting an electron

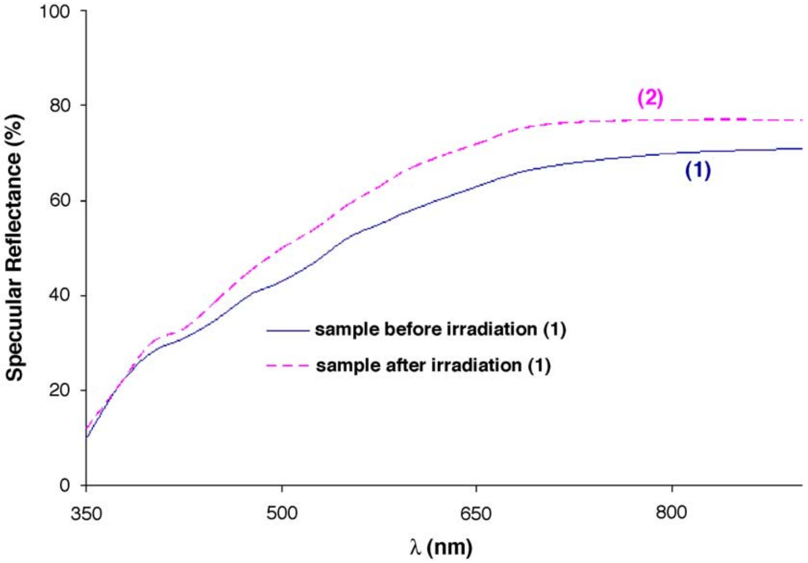


Fig. 3. Specular diffuse reflectance spectra on textile samples 14. (a) Coffee stain on polyester fabrics, (b) red wine stain on wool-polyamide. Textiles before irradiation (1) and after 24 h Suntest irradiation (2).

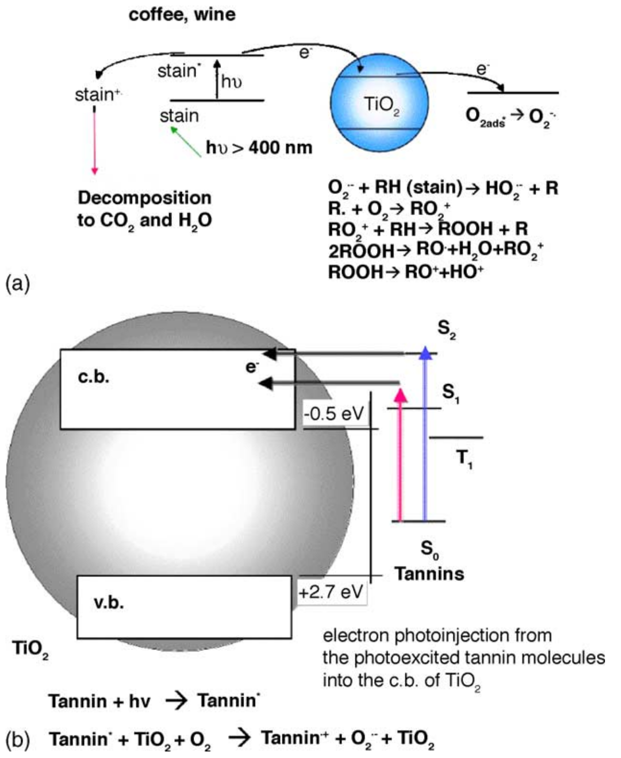


Fig. 4. (a) General mechanism for the production of oxidative radicals on TiO_2 with a stain absorbing light in the visible region, (b) suggested mechanism for the discoloration of wine stains by Suntest solar simulated light in air on the TiO_2-loaded textiles.

into the conduction band of TiO_2 that would allow theformation of highly oxidizing $O_2{}^-$ radicals

$$e_{cb}{}^- + O_2(ads) \rightarrow O_2{}^- \tag{1}$$

or by direct reaction of the excited pigment of the organic compound (R*) with photo-induced holes (h^+)

$$R* + h_{vb}{}^+ \rightarrow R^{\bullet +} \rightarrow \text{degradation products} \tag{2}$$

As an example of this second process, it is known that holes can react directly with carboxylic acids generating CO_2 through a photo-Kolbe type reaction [17]

$$RCOO^- + h_{vb}{}^+ \rightarrow R^\bullet + CO_2 \tag{3}$$

Fig. 4(a) shows how visible light induces an excited state in the wine or coffee pigment. Then, this excited state (a) produces an unstable cation that further decomposes to CO_2, and (b) concomitantly injects an electron into the conduction band of TiO_2. This leads to the formation of $O_2{}^{\bullet -}$. Due to the conduction band electron, the reaction with O_2 leads to the highly oxidative radicals $HO_2{}^{\bullet -}$, $OH^\bullet$, $RO^\bullet$ and $RO_2{}^\bullet$, which are able to decompose the textile stains.

Fig. 4(b) shows the mechanism of discoloration of the tannin pigments of red wine on TiO_2 coated textiles under visible light. The electron photo-injection from the photoexcited tannin molecule into the conduction band of TiO_2 and the ensuing reactions according to studies on the dye sensitization under visible light have been reported recently for lycopene [18,19]. This pigment is found in carotene and is responsible for the pigment coloring of tomatoes and different berries.

3.5. Elemental analysis and dust test

For the five most active TiO_2-loaded fabrics presented in Fig. 1, elemental analysis was carried out to determine the weight of TiO_2 per cm^2 of textile fabric. All samples exhibited comparable amount of TiO_2 around 1.5–2.5% (w/w). Thus, the amount of TiO_2 cannot explain differences in the photocatalytic efficiency illustrated in Fig. 1.

The results of the dust test are shown for both types of textiles in Fig. 5. It is readily seen in Fig. 5(a) and (b) that textiles pre-treated by RF-plasma for 30 min and coated with the procedure applied for sample 14 show a weaker dusting than of the untreated textiles.

3.6. Transmission electron microscopy

We focused this study mainly on the wool-polyamide loaded textiles since the self-cleaning activity was greater and showed a more stable long term performance than in the case of a polyester textile. The crystallite size was observed to vary depending on the preparation of the colloidal TiO_2. The crystallite size was about 5–7 nm for TiO_2 particles prepared by methods 2 and 3. Autoclaving at 100 °C (method 4) and 220 °C (method 5) promoted the growth of particles with a size of 10–12 and 20–25 nm, respectively. The TiO_2 (sample 14) was deposited via a combination of method 4 and Degussa P-25 particles was the most active as reflected by the CO_2 evolution results reported in Fig. 1. Sizes of 30–40 nm have been reported elsewhere for Degussa P-25 particles [6,7,9]. In this case, the coating consists of a 100–300-nm thick layer, where the small colloidal TiO_2 clusters support the bigger TiO_2 P-25 particles.

3.7. Resistance to dry-cleaning

The wool-polyamide and polyester loaded with TiO_2 exhibiting the best self-cleaning activity (samples 14) were submitted to dry-cleaning. Fig. 6 shows that the TiO_2 coating remains on the surface of (a) wool-polyamide and (b) polyester fabrics after a dry-cleaning cycle. The discoloration of wine and coffee stains was observed to decrease after dry-cleaning due to organic and chloride-ions residues introduced by the perchloroethylene used to dry-clean. However, a significant amount of CO_2 was still produced during visible light irradiation performed after dry-cleanings, showing that the TiO_2 remains photoactive on the fabric surface.

3.8. X-ray diffraction of coated textiles

Fig. 7 shows the XRD pattern of a wool-polyamide sample before and after loading with TiO_2 using method 4.

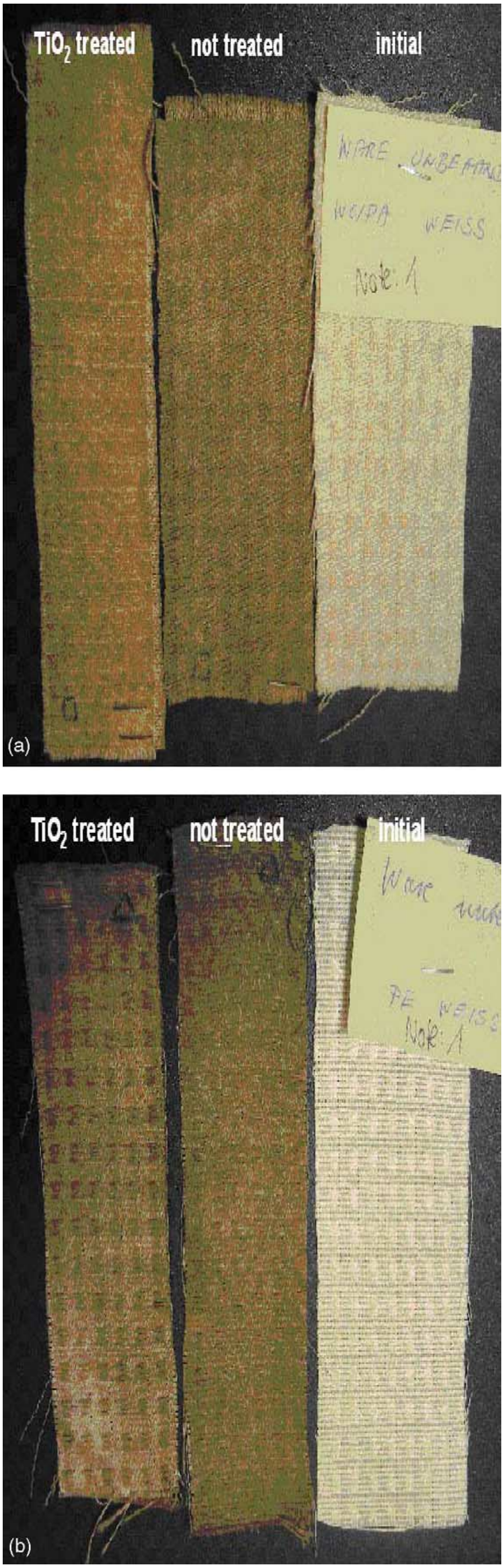


Fig. 5. Dusting tests on (a) wool-polyamide and (b) polyester fabrics.

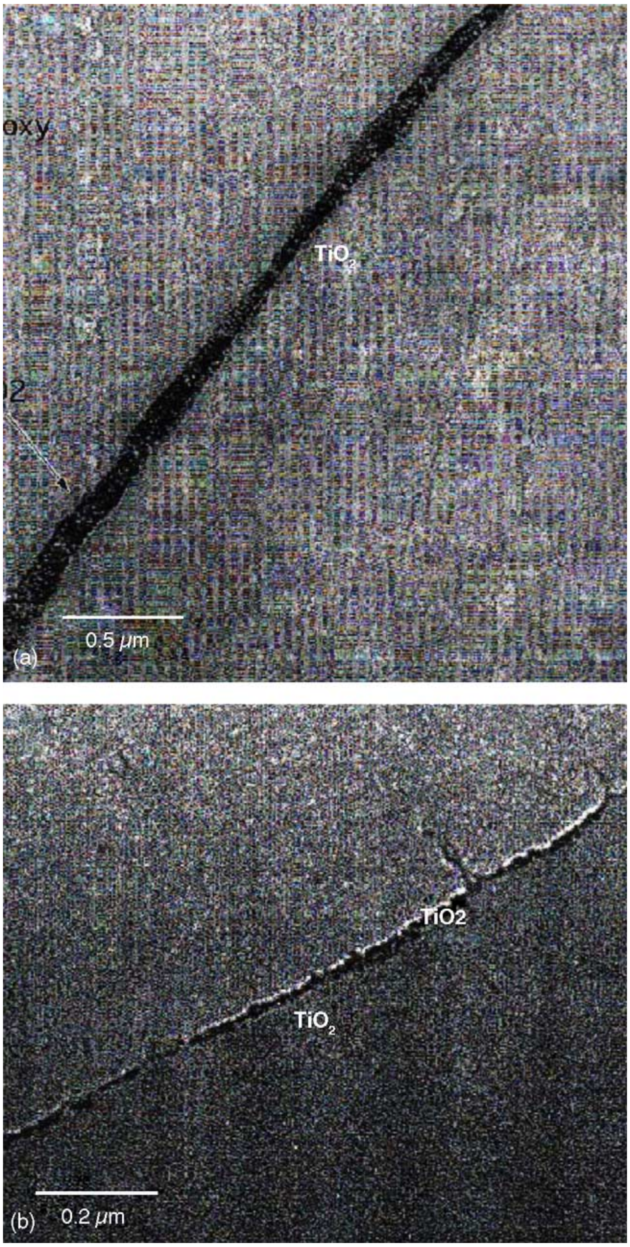


Fig. 6. HRTEM of the TiO_2 coating after dry-cleaning for (a) a wool-polaymide textile and (b) a polyester textile.

After loading, the peaks of rutile can be seen (Fig. 7). At the low temperatures worked to deposit TiO_2 on the wool-polyamide sample (100 °C) we expected the formation of amorphous or anatase from TTIP. Because rutile formation was observed, this implies that the wool-polyamide textile has a structure forming function on the TiO_2 colloid. It is widely known that rutile is less photochemically active than anatase [6,11]. This form of titania on the wool-polyamide sample should, therefore, be less aggressive towards the textile substrate upon light irradiation than the anatase form.

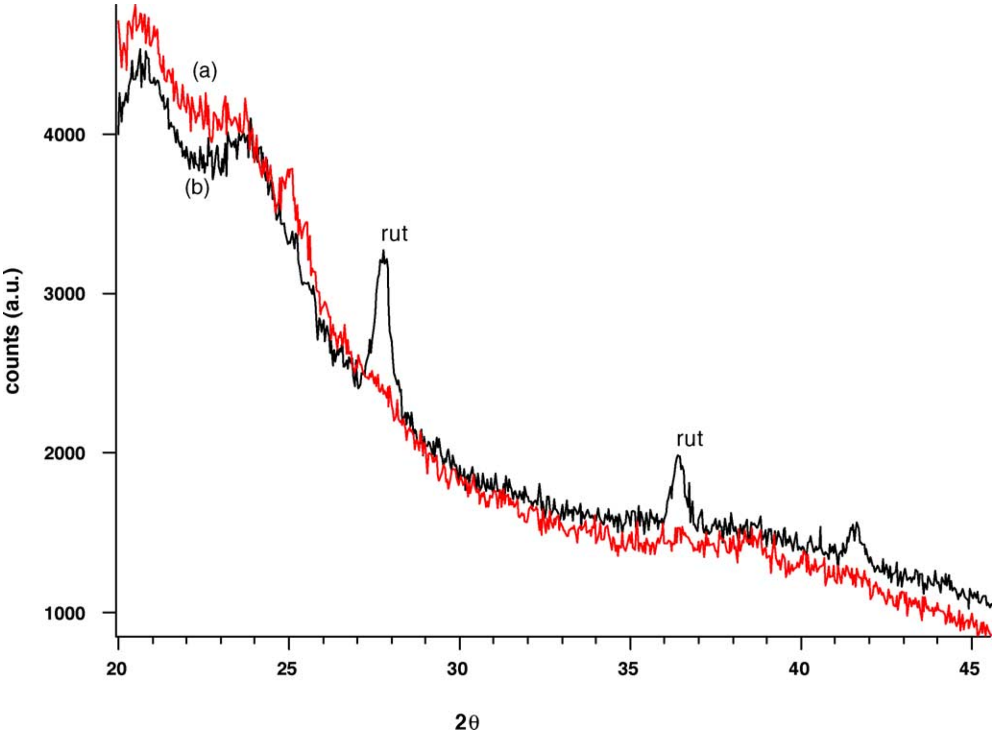


Fig. 7. X-ray diffractogram of wool-polyamide textile samples (a) base textile and (b) base textile with TiO_2. For other details see text.

4. Conclusions

Different pretreatment methods of synthetic textiles have been studied that allow the TiO_2 coatings to discolor wine and coffee stains under visible light in reasonable time. Post-treatment temperatures of 100 °C or less were shown to be sufficient to attach TiO_2 to the synthetic textiles. The nano-particles of TiO_2 remain fairly stable on the textile surface after the photochemical discoloring of stains. A combination of TiO_2 powder and TTIP colloids deposited on wool-polyamide or polyester textiles showed to be kinetically suitable for the self-cleaning of wine and coffee stains using a solar simulated light with 50% AM1. Under neon light the self-cleaning effect needed much longer times.

Acknowledgments

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References

[1] A. Kinloch, Adhesion and Adhesives, Chapman and Hall, New York, 1987.
[2] S. Wu, Polymer Interface and Adhesioin, Marcel Dekker, New York, 1992.
[3] E. Tomasetti, R. Daousti, P. Legrasi, Rouxhet, J. Colloid. Interf. Sci. 238 (2001) 43–53.
[4] A. Mirabedini, H. Rahimi, Sh. Hamdifar, M. Mosheni, Int. J. Adhes. Adhes. 24 (2004) 163–170.
[5] A. Mills, S. Lee, J. Photochem. Photobiol. A 152 (2002) 2339.
[6] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis, Fundamental and Applications, Bkc Inc., Tokyo, 1999.
[7] M. Kaneko, I. Okura (Eds.), Photocatalysis Science and Technology, Kodasha/Springer, Tokyo, 2002.
[8] H. Imai, H. Hirashima, J. Am. Ceram. Soc. 82 (1999) 2301–2306.
[9] J. Ovenstone, J. Mater. Sci. 36 (2001) 1325–1329.
[10] M. Langlet, A. Kim, M. Audier, J.M. Herrmann, J. Sol–Gel Sci. Technol. 25 (2002) 223–234.
[11] A. Mills, S. LeHunte, J. Photochem. Photobiol. A 108 (1997) 1–35.
[12] W. Daoud, J. Xin, J. Am. Ceram. Soc. 87 (2004) 953–955.
[13] J.M. Grace, L. Gerenser, J. Dispersion Sci. Technol. 24 (2003) 305–341.
[14] C.M. Chan, T.M. Ko, H. Hiroaka, Surf. Sci. Rep. 24 (1996) 1–54.
[15] Ch. Liu, G. Vissokov, B. Jang, Catal. Today 72 (2002) 173–184.
[16] J. Orphal, J. Photochem. Photobiol. A 157 (2003) 185–209.
[17] B. Kraeutler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 2239.
[18] T. Konovalola, J. Lawrence, L. Kispert, J. Photochem. Photobiol. A 162 (2004) 1–8.
[19] J. Pan, G. Genko, Y. Xu, T. Pascher, L. Sun, W. Sunstrom, T. Polivka, J. Am. Chem. Soc. 124 (2002) 13949–13957.