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Self-cleaning of modified cotton textiles by TiO_2 at low temperatures under daylight irradiation

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Abstract

This study shows that samples of bleached cotton (C_2) and of mercerized cotton (E) textiles can be activated by RF-plasma, MW-plasma and UV-irradiation introducing functional groups negatively charged to anchor TiO_2 on the textile surface. The preparation of the TiO_2 colloids and the cotton surface functionalization are described in a detailed way. The photo-discoloration and mineralization of stains of red wine, coffee, make up and grease were monitored following the CO_2 evolved upon daylight irradiation with 50% full solar light intensity (AM 1). For base treated cotton (C_2), UV activated textile followed by TiO_2 deposition from Degussa TiO_2 P25 was the most active sample during the discoloration of wine and coffee stains under daylight irradiation. In the case of the mercerized cotton samples (E), MW-plasma activation of the textile surface followed by TiO_2 deposition from a titanium tetra-isopropoxide (TTIP) colloid showed the most favorable discoloration kinetics. The images obtained by electron microscopy (TEM) and by (HRTEM) show 5–7 nm TiO_2 crystallites for the MW-plasma (E) cotton samples at time zero and for the same after 20 machine household washings. The coating of TiO_2 on the textiles presented variable thickness of 120–300 nm. The TiO_2 cluster size and distribution from sol–gel precursors after daylight induced stain discoloration did not vary with respect to the TiO_2 cluster size before irradiation. This is the evidence the stable nature of the TiO_2 cluster deposition on the cotton surface. X-ray evidence for rutile formation on the C_2 cotton fibers was obtained. Elemental analysis revealed Ti-loadings of 1–1.5% (w/w) for the TiO_2 attached by different techniques. The self-cleaning leading to the stain discoloration was quantified to assess the photo-activity of the TiO_2 clusters prepared under different experimental conditions. This process shows promise for the total removal of stains containing persistent colored pigments on the cotton fibers.

Keywords: Low temperature plasma; V–UV; Self-cleaning; Daylight irradiation; TiO_2 rutile clusters; TiO_2 colloids; Cotton textiles

1. Introduction

In recent years, crystalline TiO_2 has received much attention due to their interesting properties as photocatalyst [1–3]. Nano-sized particles show high photoactivity due to their large surface area per unit mass and diffusion of the electron/holes before recombination. The commercial use of TiO_2 as photocatalyst is becoming widespread in the areas of: (a) for water purification [4]; (b) air purification [5]; (c) sterilization/disinfection [6]; and (d) systems involving applications of the recently reported superhydrophilic effect [7]. Further applications of transparent and antistatic films of TiO_2 on diverse substrates is beginning to be explored. This study intends to show work in this new direction.

Much work has been carried out depositing TiO_2 on heat resistant surfaces like glass and silica by sol–gel methods. Temperatures up to 500 °C produce anatase or anatase/rutile clusters or films on silica surfaces [1–7]. The present study addresses the coating of TiO_2 on textiles with poor heat resistance. Temperatures up to 100 °C are employed for the deposition of TiO_2 on the cotton textiles. Recently several studies report the nucleation of anatase at relatively low temperatures: (a) from sol–gel coated substrates exposed to boiling

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water [8]; (b) at 100 °C from sol–gel exposed to water vapor [9]; (c) at temperatures 60–180 °C from TiO_2–SiO_2 films exposed to water vapor [10]. In the last case, the treatment with water vapor reduced the temperature necessary to produce anatase crystallites in the sol–gel films to temperatures below 100 °C by phase separation of the TiO_2 from the SiO_2; (d) anatase nano-crystals were produced more recently on cotton fabrics from the TTIP alkoxide solution at low temperature by sol–gel process with grain sizes of ∼20 nm. The anatase phase was attained on the cotton textile surface by boiling the textiles in water for 3 h [11].

Acrylic emulsions of TiO_2 have been coated on textiles with the purpose of inducing self-cleaning effects under daylight irradiation [12], but the coating showed some degradation after being exposed to the action of daylight. Another low temperature fixation of TiO_2 anatase nanocrystals on plastic substrates has been carried out recently from silica–titania gels showing anatase cluster formation after hot water treatment [13]. The direct preparation of anatase/polymer nano-composite films from sol–gel titania on polymer films is generally not possible due to the low resistance of the organic polymers to heat treatment [14,15]. Recently polymers films with negative surface groups have been exchanged with TiO_2 to attach the titania on their surface by electrostatic attraction [14]. One of the reasons to undertake the present research is to explore the commercial potential of the TiO_2 semiconductor on cotton textiles prepared at relatively low temperatures for self-cleaning purposes. This study aims at the discoloration of organic materials including dyes, pigments and grease on the modified cotton textile loaded with TiO_2. The use of TiO_2 loaded flexible substrates will possibly allow their application during the photodegradation of micelles, oils, solvents, sooth, aromatic and aliphatic hydrocarbons under daylight.

2. Experimental

2.1. Materials

Base treated cotton (C_2) and mercerized cotton samples (E) were used throughout this work. The mercerized cotton network contained a variety of stabilizers, oxidants and tensides to eliminate the natural grease, pectine, lignine and stains associated with untreated cotton fibers. 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. Triple distilled water was used in all experiments.

2.2. Pretreatment of synthetic textiles fabrics

2.2.1. RF-plasma

Cellulose is the main component of wood and plant fibers. Cotton is almost pure cellulose formed by D-glucose units and its macro-structure is heterogeneous consisting of crystalline and amorphous regions. The C_2 and E cotton samples were pretreated in a conventional RF-plasma cavity (Harrick and Co., UK). A variety of functional groups like: C=O, –O–C=O, –COH, –COOH, CH_2–OH 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^+) induced by the plasma activation of the gas phase on the carbon textile surface [16]. These oxygen functionalities obtained in the 0.1 mbar cavity of the RF-plasma attained a higher concentration with longer treatment times up to ∼30 min. This time has been chosen for RF-plasma pretreatment during this study. Recently, the preparation of diverse catalysts using plasma technology has been described [17,18]. The experimental conditions used during the RF-plasma pretreatment were: plasma generator at 13.56 MHz; plasma power 100 W and a residual gas pressure of 0.1 mbar.

2.2.2. MW-plasma

The C_2 and E cotton samples were also pretreated in a MW-plasma cavity (Vacotec Corp., Neuchatel, Switzerland). A schematic representation of the MW-plasma unit is shown in Fig. 1. Experiments were performed at 2.45 GHz. The power was varied from 100 to 600 W, the reaction times were changed from 10 to 180 s, the gas flow was between 20 and 100 ml/min, and the gas pressure varied from 0.02 to 2 mbar. Before the sample treatments the plasma MW-chamber was evacuated for 2 h up to 0.01 mbar. MW-plasma in air (air-MW-Plasma) was used to oxidize the cotton surface. The pretreatment time was varied between 5 and 45 s and usually 120 °C were not exceeded in this way. This is below the temperature of 180 °C the upper limit for cotton textiles. The ionized gas is composed atomic oxygen, ionic forms of oxygen (negative and positive), radicals formed due to the interaction of O-excited species and residual water vapor.

2.2.3. Vacuum–UV (V–UV)

The cotton fabrics were also pretreated using the 185 nm line of a low pressure mercury source from Ebara Corp., Iwasaki Electric Co., Shiba, Japan having a power of 25 W. The scheme of the installation used is shown in Fig. 2. The lamp wall consists of synthetic silica able to transmit the

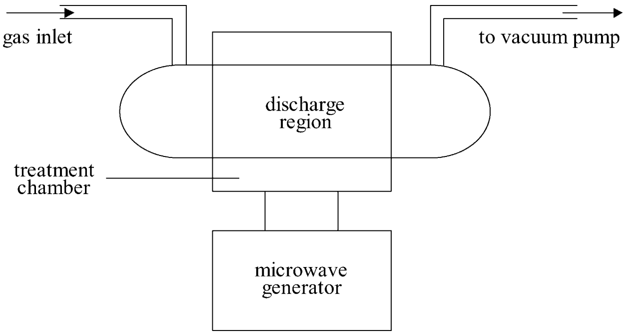

Fig. 1. Schematic of a microwave-plasma (MW-plasma) unit used to pretreat the surface of cotton textiles.

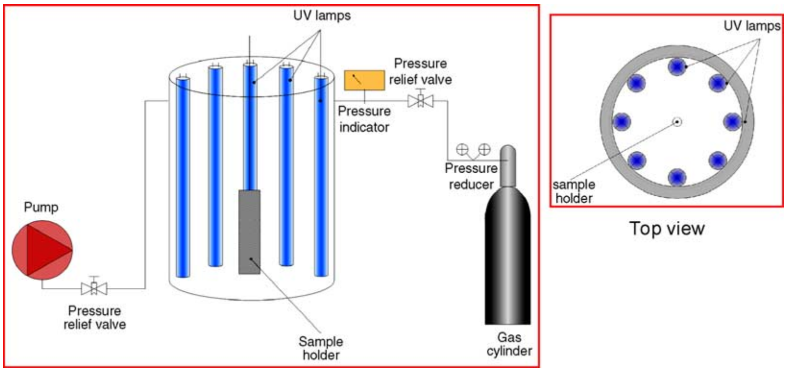

Fig. 2. Schematic of the V–UV unit used to pretreat the surface of cotton textiles.

184 nm lights. This wavelength comprises 25% of the total lamp output. 75% of the lamp output consisted of 254 nm bactericide radiation. Since the vacuum–UV activation proceeds with a lower energy than the plasma activation, no cationic or anionic oxygen species are formed in the gas phase. Only atomic and excited oxygen species are formed and this is the difference with the plasma methods described in section (a) and (b) above. This leads to a more defined and uniform modification of the textile surfaces with an increased polarity because it contains a variety of oxygen functional groups formed by the reactions of free radicals with the O_2 in the gas phase. The upper textile layers are excited by the incoming UV light up to ∼100 Å or the equivalent of about 50 atomic layers [17,18]. Either by plasma or by vacuum–UV pretreatment the residual oxygen at the pressures worked was sufficient to modify the textile surfaces due to the absorption cross-section of the O_2 for plasma radiation or ultraviolet light. Fig. 3 shows in a simplified way the functional groups introduced in the cotton fibers by plasma or V–UV treatment. A significant number of carboxylic, percarboxylic, epoxide and peroxide groups form upon either pretreatment [17]. The overall hydrophilicity of the textile surface was observed to drastically increase due to this pretreatment.

2.3. Preparation of TiO_2 colloids

2.3.1. TTIP as colloidal TiO_2 precursor

Titanium tetra-isopropoxide (TTIP, 20 ml) was added drop-wise to 300 ml of 2-propanol acidified by 1 ml of concentrated HNO_3 and cooled at ∼0 °C in an ice bath. The solution was stirred for ∼1 h to attain total dissolution of the polymeric chains and produce a transparent colloidal solution.

2.3.2. $TiCl_4$ as colloidal TiO_2 precursor

An aliquot of 10 ml $TiCl_4$ were slowly added to 1 L (0.5 M HCl) aqueous solution. The reaction vessel was immersed in an ice-bath to prevent precipitation of TiO_2 polymeric-sol during to the kinetically fast and highly exothermic hydrolysis process. The Cl^--ions in the solution were eliminated by dialysis adding continuously distilled water within 2 days

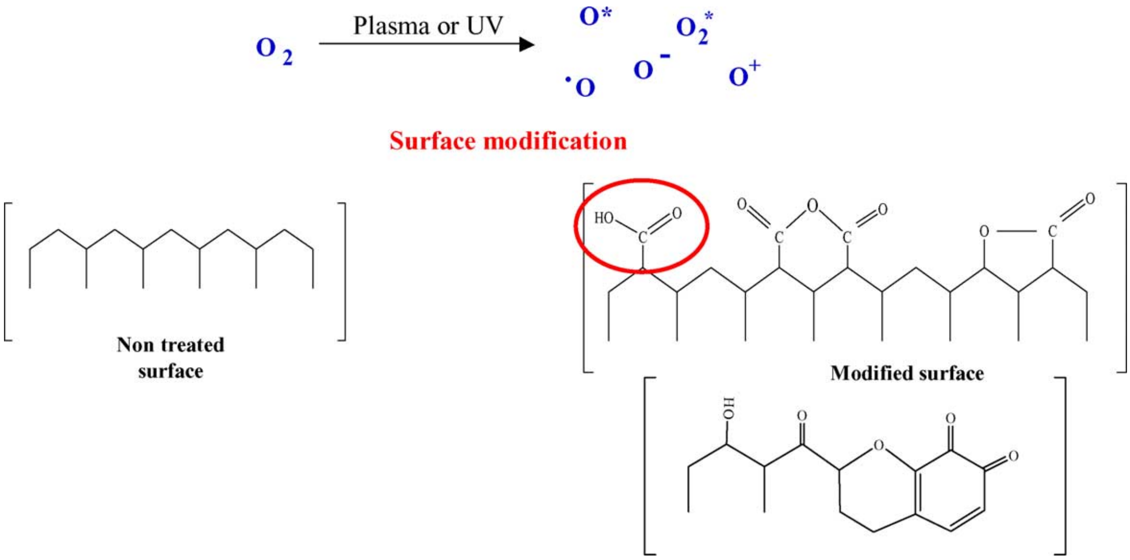

Fig. 3. Diagram indicating the modification of cotton textiles induced by plasma or V–UV pretreatment.

using a cellulose membrane. The Cl^--ions have to be eliminated since they interfere during the photo-catalytic destruction of the stains by the TiO_2 clusters on the textile surface [16].

2.4. Deposition of colloidal and TiO_2 Degussa P25 powder coated textiles

2.4.1. Colloidal TiO_2

Pretreated 4 × 12 cm textiles samples were immersed in the chosen TiO_2 colloidal suspension and exchanged for 30 min as described in Section 2.2. Afterwards, the samples were dried in two steps: (a) first in air for 24 h at 22 °C (laboratory temperature) and (b) followed by heating at 100 °C for 15 min. The exchange operation to load the TiO_2 on the textiles was carried out immediately after the fabric pretreatment by any of the three techniques mentioned above. The reason for this is that the radicals formed at the fabric surface react with the humidity and oxygen of the air. This deactivates the radicals induced by the pretreatment. The textile samples were then washed with distilled water under sonication to remove the TiO_2 particles that did not attach to the fabric surface. During this study we found that only pretreated surfaces were able to fix TiO_2 from colloidal solutions (or powder suspensions or the combination of both. The dyes with carboxylate groups have been recently reported to be able to anchor TiO_2 via coordination [14].

2.4.2. TiO_2 Degussa P25 powder

The pretreated cotton textiles were immersed in a previously sonicated (30 min) aqueous solution of TiO_2 Degussa P25 (5 g/l) and heated for 1 h at 75 °C. The textile was dried for 1 h at 100 °C and then the unattached TiO_2 particles on the textile surface were washed out in distilled water by 5 min sonication. A loading of 1.0–1.5% (w/w) for the sample 7 of Table 3 was determined by elemental analysis (see Section 2.6).

2.5. Irradiation procedure and evaluation of the textiles cleaning action

The photochemical reactor consisted of 80 ml cylindrical Pyrex flasks containing a strip of textile of 48 cm^2 positioned immediately behind the wall of the reactor. The wine stains are introduced on the cotton fabric using a micro-syringe with 50 μl of red wine. The irradiation of samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air-cooled at 45 °C. The Suntest lamp had a wavelength distribution with 7% of the photons between 290 and 400 nm. 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 is 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 volume produced during the irradiation was measured in a GC (Carlo Erba, Milano) provided with a Poropak S column.

2.6. Elemental analysis

Elemental analysis of the TiO_2 loading on the textile fabrics was carried out by atomic absorption spectrometry using a Perkin-Elmer 300 S unit.

2.7. Transmission electron microscopy (TEM)

A Philips CM 300 (field emission gun, 300 kV, 0.17 nm resolution) HRTEM microscope and a Philips EM 430 (300 kV, LaB_6, 0.23 nm resolution), provided with energy dispersive spectrometers (EDS) were used to measure the particles sizes of the titania clusters coating the textile fabrics. The textiles were embedded in epoxy resin (Embed 812) and the fabrics were cross-sectioned with an ultra-microtome (Ultracut E, Reichert-Jung) to a thin section of 50–70 nm. Magnification from about 1000× to 450,000× were used to characterize the samples and this allowed the determination of the TiO_2 cluster size up to the nanometer range.

2.8. X-ray diffraction

The crystallographic phase of the TiO_2 on the textile samples was determined by a Siemens X-ray diffractometer using Cu Kα radiation.

3. Results and discussion

3.1. Development of CO_2 due to the degradation of wine, coffee, make-up and grease stains on C_2 and E cotton textiles prepared by different methods

Table 1 shows the values of the CO_2 volumes formed during mineralization of organic various stains by TiO_2 under light. In practice besides the CO_2 a small amount of inorganic anions and cations are also produced during the mineralization process since the chromophore functional groups of red wine contain lycopenes, carotenoids and other natural pigments besides a small amount of cations and anions. The reaction vessel described in Section 2.5 of the experimental part was used for the CO_2 determination. The evolution of CO_2 of a red wine stain on C_2 cotton pretreated by RF-plasma after 24 h irradiation is shown in the first line of Table 1 to produce the highest amount of CO_2 (2000 μl) under solar simulated light (50 mW/cm^2).

Fig. 4 shows the evolution of CO_2 as a function of irradiation time for wine stains. It is seen that the CO_2 evolution increases at a slower pace at the beginning and more steeply above 8 h irradiation (trace c). Very small amounts of CO_2 were observed when cotton was irradiated with daylight in the absence of TiO_2 and wine (trace a). Also, small amounts of CO_2 were observed when the cotton was stained with wine in the absence of TiO_2 (trace b).

Table 1
Textile type C_2

Sample name	Pre-treatment	Pre-treatment time	TiO_2 precursor	Red wine spot CO_2 (µl)	Coffee spot CO_2 (µl)	Make-up-spot CO_2 (µl)	Grease spot CO_2 (µl)
C2–2	RF-plasma	60 min	$TiCl_4$	2000	1800	1350	1900
C2–3	V–UV	15 min	TTIP	1700	1430	1050	1270
C2–4	V–UV	30 min	TTIP	1000	960	680	860
C2–5	V–UV	15 min	$TiCL_4$	1800	1280	880	1010
C2–6	V–UV	60 min	TTIP	700	700	530	710
C2–13	MW-plasma	15 s	TTIP	1200	1150	550	540
C2–14	MW-plasma	30 s	TTIP	1200	1830	890	1330
C2–15	MW-plasma	15 s	$TiCl_4$	600	690	720	620
C2–16	MW-plasma	30 s	$TiCl_4$	600	790	400	290

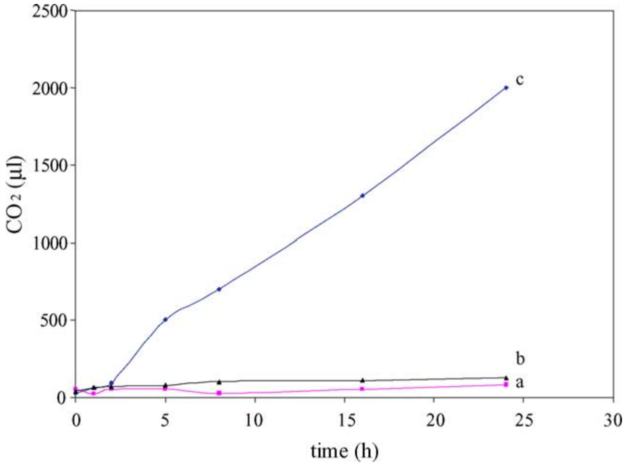

Fig. 4. CO_2 evolution under Suntest light irradiation (50 mW/cm^2 equivalent to the daylight intensity in Switzerland in an average day) for C_2 cotton samples pretreated for 30 min by V–UV as a function of time: (a) cotton C_2 alone; (b) cotton C_2 with wine stain; and (c) cotton sample C2-2 stained with wine.

Table 2 presents the results for the evolution of CO_2 from the discoloring and/or decomposition of the wine stain on mercerized cotton samples (E). The sample E-19 with a red wine stain shows the most favorable CO_2 evolution after 24 h Suntest light irradiation. It was prepared using TTIP as the TiO_2 precursor and pretreating with MW-plasma for 15 s. The MW-plasma treatment that is accompanied by heat seems to increase the contact between the cotton tissue and the surface TTIP sol–gel having a favorable action on the TiO_2 structure and dispersion on the textile surface. Generally the amount of CO_2 evolved under Suntest light irradiation on cotton (C_2) is significantly higher than for the mercerized cotton (E) samples. This is due to the adverse effect of the networking, surface and oxidative additives used to mercerize the cotton (E) samples. The TiO_2 loaded textile allows for bigger time intervals for the cleaning by conventional methods since the red wine stains are already partially degraded on the TiO_2 loaded textiles due to the action of daylight and will be more receptive towards the application of detergents during household washing with the accompanying cost saving.

Table 3 shows the discoloration of red wine stains prepared from different procedures on the cotton sample (C_2) but pretreating with the UV-irradiation unit shown in Fig. 3. By inspection of Table 3 it is seen that the surface textiles pretreated with two UV low-pressure mercury lamps evolved the highest quantity of CO_2 from red wine stains. These quantities are 5–7 times higher in µl CO_2 compared to the to CO_2 evolved by red wine stains on textiles not coated with TiO_2 (see Table 1) for textiles pretreated with only one UV lamp. The results shown in Table 3 use the reactor shown in Fig. 3 to perform the experiments allowing for a better geometry and a closer distance between the cotton sample and the light source. The TiO_2 Degussa P25 powder loading of the cotton sample consisting of 80% anatase and 20% rutile having crystalline sizes of 30–40 nm seems to be the most suitable titania active in the removal of the pigments associated with red wine stains.

Table 2
Textile type E

Samples name	Pre-treatment	Pre-treatment time	TiO_2 precursor	Red wine spot CO_2 (nl)	Coffee spot CO_2 (nl)	Make-up spot CO_2 (Hi)	Grease spot CO_2 (nl)
E-7	RF-plasma	60 min	TTIP	200	300	250	360
E-8	RF-plasma	60 min	$TiCl_4$	125	160	150	150
E-9	V–UV	15 min	TTIP	150	150	140	190
E-10	V–UV	30 min	TTIP	140	170	130	120
E-11	V–UV	15 min	$TiCl_4$	100	130	160	190
E-12	V–UV	60 min	$TiCl_4$	160	220	150	160
E-17	MW-plasma	15 s	$TiCl_4$	550	450	370	460
E-18	MW-plasma	30 s	$TiCl_4$	170	250	330	280
E-19	MW-plasma	15 s	TTIP	700	800	690	620
E-20	MW-plasma	30 s	TTIP	600	650	610	640

Table 3
UV pretreated cotton type C_2 red wine stains

Sample name	Gas	Lighted lamps	TiO_2 source	Stain	CO_2 after 24 h irradiation (area)
Sample 7	Air	2 lamps	Degussa P25	Wine	11807
Sample 14	Argon	8 lamps	TiO_2 (TTIP 10–15 nm)	Wine	11501
Sample 13	Argon	8 lamps	Degussa P25	Wine	11112
Sample 10	Air	8 lamps	TiO_2 (TTIP 10–15 nm)	Wine	11064
Sample 3	Vacuum	2 lamps	Degussa P25	Wine	9783
Sample 6	Vacuum	8 lamps	TiO_2 (TTIP 10–15 nm)	Wine	9724
Sample 11	Argon	2 lamps	Degussa P25	Wine	9391
Sample 5	Vacuum	8 lamps	Degussa P25	Wine	8986
Sample 9	Air	8 lamps	Degussa P25	Wine	8792
Sample 12	Argon	4 lamps	Degussa P25	Wine	7659
Sample 4	Vacuum	4 lamps	Degussa P25	Wine	7407
Sample 8	Air	4 lamps	Degussa P25	Wine	7003

Table 4
UV pretreated cotton type C_2 coffee stains

Sample name	Gas	Lighted lamps	TiO_2 source	Stain	CO_2 after 24 h irradiation (area)
Sample 7	Air	2 lamps	Degussa P25	Coffee	12308
Sample 14	Argon	8 lamps	TiO_2 (TTIP 10–15 nm)	Coffee	11769
Sample 13	Argon	8 lamps	Degussa P25	Coffee	10192
Sample 3	Vacuum	2 lamps	Degussa P25	Coffee	9748
Sample 10	Air	8 lamps	TiO_2 (TTIP 10–15 nm)	Coffee	9407
Sample 6	Vacuum	8 lamps	TiO_2 (TTIP 10–15 nm)	Coffee	7682
Sample 8	Air	4 lamps	Degussa P25	Coffee	7578
Sample 12	Argon	4 lamps	Degussa P25	Coffee	7294
Sample 5	Vacuum	8 lamps	Degussa P25	Coffee	7224
Sample 4	Vacuum	4 lamps	Degussa P25	Coffee	6530
Sample 9	Air	8 lamps	Degussa P25	Coffee	6183
Sample 11	Argon	2 lamps	Degussa P25	Coffee	6132

Table 4 shows the discoloration of a coffee stain from different TiO_2 precursors on the cotton sample (C_2) and pretreating with the UV unit shown in Fig. 3. By inspection of Table 4, it is seen that the pretreated cotton with two UV low pressure mercury lamps evolved the highest quantity of CO_2 from the coffee stains.

3.2. *Transmission electron microscopy of the most efficient samples used in red wine discoloration on cotton textiles*

Fig. 5 presents the cross section of one cotton fibre on the sample C2-2 loaded with TiO_2 after 20 household washings. The TiO_2 layer was observed to be present in the same form as before the washing cycles. This lends support to the stable fixation achieved for TiO_2 on the cotton C2-2 fibres. This sample has been described in Table 1. The TiO_2 layer had a thickness of 180–300 nm. The sample C2-2 shows the highest CO_2 evolution from the decomposition of wine stains under daylight irradiation. This is the reason why this sample was selected to perform the TEM observation. These TEM results strongly suggested that TiO_2 crystalline clusters on the cotton surface accounts for only a small amount of the total area of the textile covered by TiO_2. The titania on the textiles was identified by energy dispersive spectrometry (EDS) showing that only a fraction of the TiO_2 on the cotton was in a crystalline phase. The multilayer TiO_2 coating was prepared from the $TiCl_4$ precursor. Since one monolayer of TiO_2 accounts only for the absorption of 4% of the incident light [1–4] a multilayer TiO_2 coating would be favourable for the photocatalytic activity specially leading to increased or total TiO_2 light absorption.

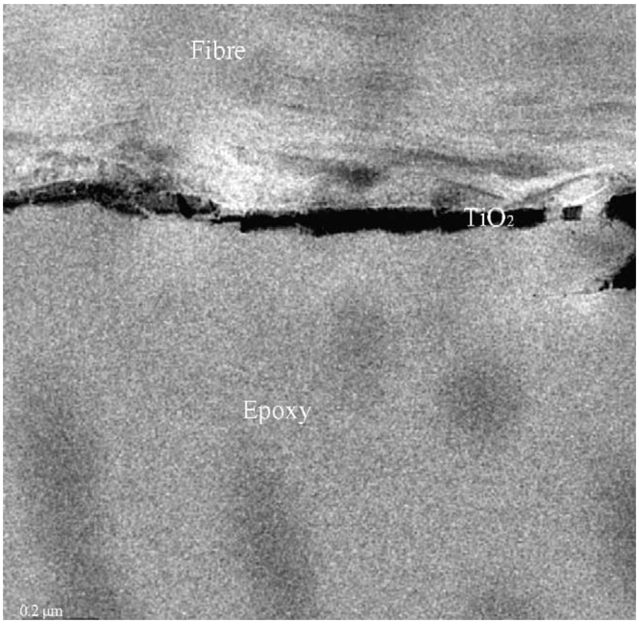

Fig. 5. Transmission electron microscopy of a cotton textile sample C2-2 showing the stable TiO_2 coating after 20 washings. For other experimental details see text.

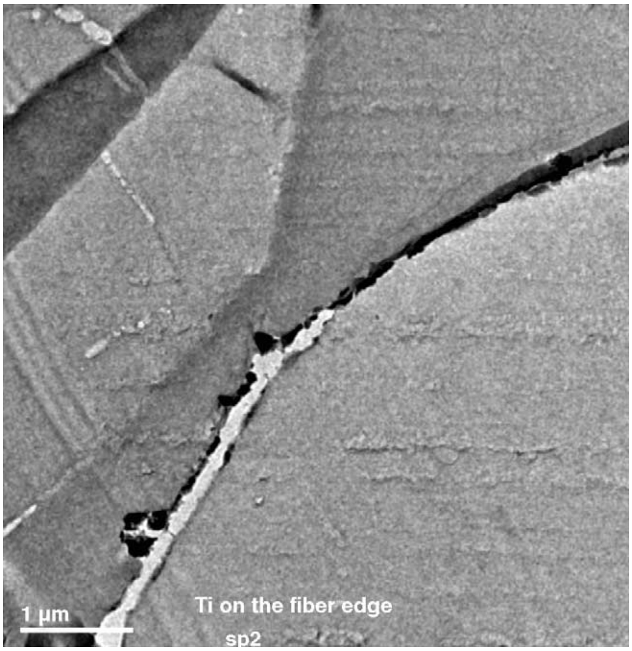

Fig. 6. Transmission electron microscopy of a cotton textile sample E19 showing the TiO_2 coating around a single cotton fiber. For other experimental details see text.

Fig. 6 shows the TiO_2 coating around E-19 single cotton fiber loaded with TiO_2 in the way described in Table 2. A TiO_2 coating of 150–220 nm thick was observed by TEM. Clusters of TiO_2 between 5.77 and 6.80 nm were found by HRTEM on the E-19 surface and are shown in Fig. 7. This is a confirmation that a high dispersion of TiO_2 clusters was attained on the E-cotton samples.

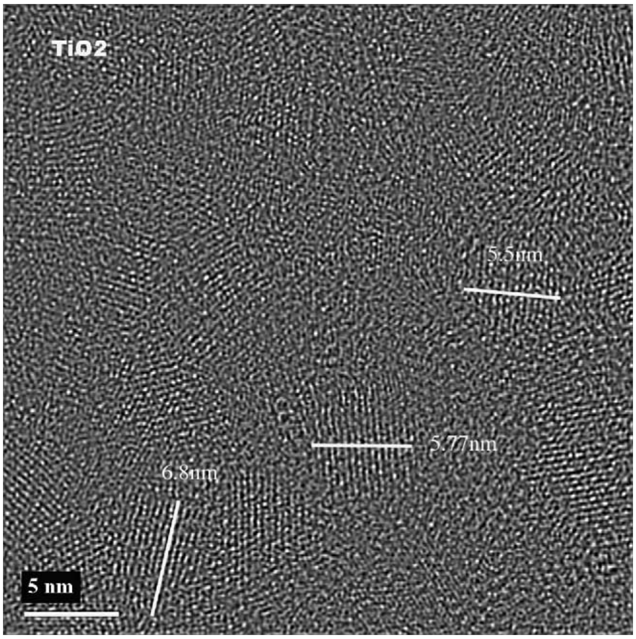

Fig. 7. High resolution transmission electron microscopy (HRTEM) of a cotton textile sample E19 showing the TiO_2 clusters before washing. This figure was Fourier filtered to enhance the atomic lattice constant. For other experimental details see text.

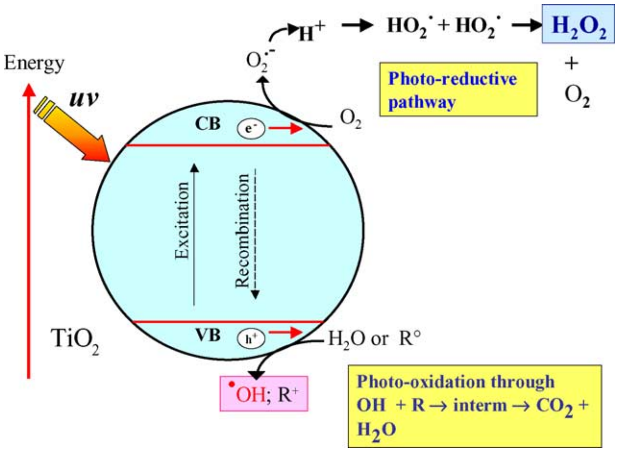

Fig. 8. Classical scheme for the production of highly oxidative species by TiO_2 under light irradiation with wavelengths <400 nm.

3.3. Mechanism suggested for the discoloration of stains on cotton textiles

Fig. 8 shows the accepted mechanism during the last 25 years for the generation of highly oxidative radicals on the TiO_2 surface when light below 400 nm is applied on the photocatalyst surface [19,20]. Fig. 9a shows the intervention of TiO_2 under daylight irradiation when photo-decomposing a grease stain. The Suntest light which follows the solar

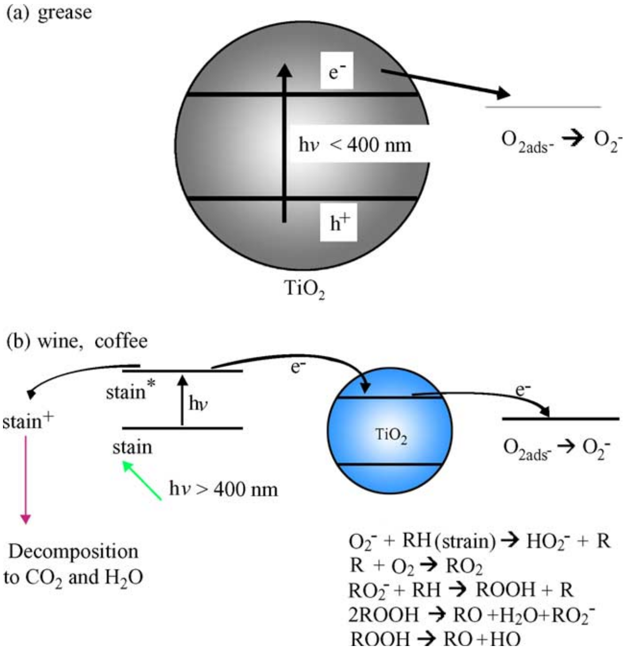

Fig. 9. (a) Suggested scheme for the discoloration of grease stains under Suntest light irradiation mediated by TiO_2 photocatalyis. (b) Suggested scheme for the discoloration of wine and coffee stains under Suntest light irradiation by TiO_2 photocatalyis.

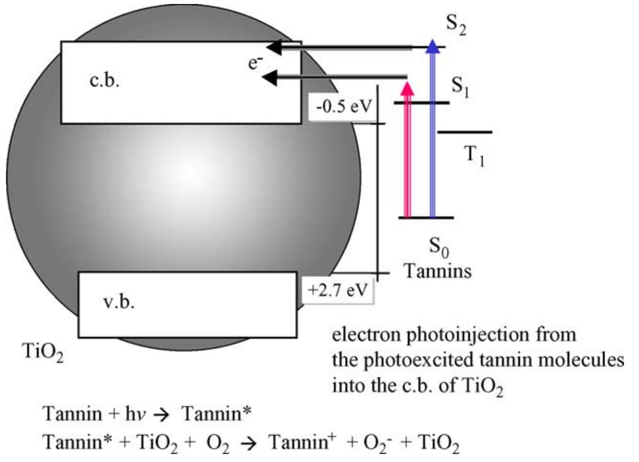

Fig. 10. Mechanism of photo-discoloration of the tannin pigment of wine under daylight irradiation.

spectrum is absorbed directly by the TiO_2 since the grease absorbs light only <290 nm.

The mechanism of stains absorbing the incoming daylight radiation is shown in Fig. 9b. This is known from several studies during the last 20 years suggesting a dye sensitized process when synthetic dyes like Orange are used [21,22]. Fig. 9b presents the scheme for the discoloration of the natural colored pigment RH due to the generation of OH°, $HO_2{}^\circ$ and H_2O_2 on the TiO_2 surface [23]. Fig. 9b suggests that in the case of synthetic dyes colored pigments sensitize a process leading to dye discoloration under daylight irradiation. The decomposition of the organic compound goes through a cation intermediate ($stain^+$) leading ultimately to the production of CO_2. The electron injected into the TiO_2 conduction band starts the oxidative radical-chain leading to stain discoloration.

Fig. 10 shows the mechanism for tannin photo-degradation in analogy with the photo-induced degradation reported recently for the lycopene, a natural pigment [24,25]. The tannins and lycopenes are pigments found in plants and fruits. Lycopene is a pigment of the carotenoid family. It is not only found in the red wine used a probe molecule during this study but it also gives its particular color to tomatoes and other vegetables.

3.4. *X-ray diffraction studies of loaded TiO_2 surfaces*

Fig. 11a shows the X-ray diffraction pattern for a blank C_2 sample (trace c) and for the samples C2-13 (see Table 1 for the preparation details). Traces (a) and (b) before and after discoloration of a wine stain after 24 h with Suntest light are also shown in Fig. 11a. No crystalline phases of TiO_2 were found in traces (b) and (c). It is interesting to note that the cotton sample C2-13 loaded with amorphous TiO_2 as shown by trace (b) was able to discolor the wine stain (Table 1). No difference is observed between traces (b) and (c) in Fig. 11 showing the stability of the amorphous TiO_2 coating on the cotton during the photo-degradation of the wine stain. Fig. 11b shows the C2-2 sample before irradiation. The position of the rutile peaks is indicated by arrows in Fig. 11b. The sample C2-2, shows a high stain mineralization efficiency for red wine, coffee, make-up and grease (Table 1) due to the presence of amorphous and rutile phase TiO_2.

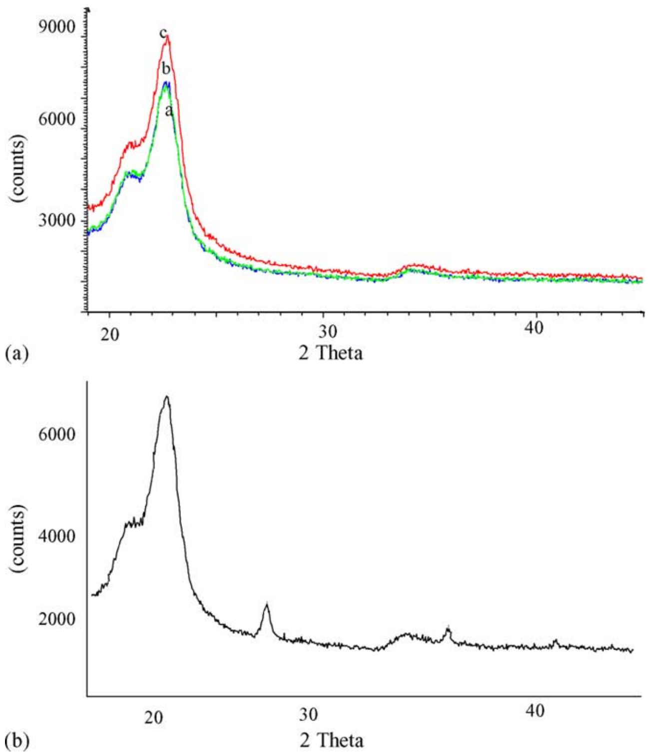

Fig. 11. (a) X-ray diffraction of (a) cotton C2-13 samples loaded with TTIP at time zero; (b) cotton C2-13 sample loaded with TTIP after 24 h irradiation with Suntest solar simulated light (50 mW/cm^2); and (c) cotton C_2 blank. (b) X-ray diffraction of cotton C2-2 samples loaded with $TiCl_4$ after RF-plasma pretreatment after a 60 min photo-discoloration of a wine stain using Suntest irradiation. The peaks marked with a small arrow correspond to the position of rutile peaks.

4. Conclusions

Cotton textiles of the type C_2 were treated with ammonia only mineralize more effectively stains of pigmented compounds and grease upon TiO_2 loading under daylight than E-cotton textiles containing several additives and surface forming agents. When light is harvested directly by the TiO_2, an increased CO_2 evolution was observed with respect to wine and coffee stains under similar experimental conditions on the same TiO_2 loaded textile. The surface pretreatment of the cotton textile used in this study allows to attach TiO_2 directly on the textile by functionalization of the cotton textile with a variable density of functional groups negatively charged. This pretreatment seems not to degrade the cotton surface. The pretreatment is applied in dry conditions in the absence of solvents. Also, the times employed for the cotton surface modification were short and involved reduced energy requirements.

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