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Synthesis, activity and characterization of textiles showing self-cleaning activity under daylight irradiation

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Abstract

The preparation, activity and characterization of TiO_2 clusters on several of textiles are presented having a self-cleaning effect under daylight irradiation. The textile pretreatment was carried out by RF-plasma, MW-plasma or vacuum-UV irradiation. The textile upper layers are modified in such a way that negatively charged TiO_2 chelating groups such as carboxylic groups are introduced by the pretreatment methods used. The pretreatments used in this study were 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. The quantitative results obtained during the discoloring of spots of wine, coffee, make up and grease indicate that the photoactivity observed on the TiO_2 modified textiles upper layers strongly depends on the nature of the TiO_2 used and on the procedure used to apply the TiO_2 on the textile. When light is harvested directly by the TiO_2, like in the case of grease stains 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. Also, chemical spacers able to graft TiO_2 on suitable functional groups of the textile and through a second link bond to the TiO_2 clusters have been studied with promising results in photoactivated light induced discoloration processes. The TiO_2 loaded textiles were characterized by transmission electron microscopy (TEM), by elemental analysis (EA), by X-ray photoelectron spectroscopy (XPS), by infrared spectroscopy (IR), X-ray diffraction (XRD) and by gas adsorption studies (BET).

Keywords: X-ray photoelectron spectroscopy; Infrared spectroscopy; X-ray diffraction

1. Introduction

This study intends to show the bondability of TiO_2 on artificial fibers like wool–polyamide and polyester textiles and also in natural fibers like cotton 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 Å [1]. Surface pretreatments of fabrics and polymers have been carried out by etching [2], plasma [3], and corona discharge [4]. Japanese workers have coated TiO_2 on textiles by using emulsions containing acrylate, additives, fluidizers and TiO_2 [5–7]. The emulsion is then sprayed on the textile fabric. Then the textile is heated to around 100 °C for a few minutes to produce the polymer on the textile containing the TiO_2. Recent Chinese work uses a similar approach with some variations as cited in reference [8].

Our work uses a different approach. It consists in modifying the structure of the textile surface introducing a variable density of negative groups $-COO^-$, $-O-O^-$, by RF-plasma, MW-plasma and 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 [8] and using other oxide/composites on different supports [9–11]. Also in our work we intend to optimize the formulation of colloids to produce efficient discoloration of some persistent stains on synthetic textiles. These TiO_2 modified textiles will be stained with organic dyes, pigments and grease and the discoloration or degradation of these stains will be tested under daylight (and other weak light sources) at room temperature for self-cleaning

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purposes. The attachment of a TiO_2 through a chemically stable spacer is also possible and is the object of our recent studies.

2. Experimental methods

2.1. Materials

Polyester (100% Trevira) and wool (90%)–polyamide (10%) textiles were used throughout this work. Cotton textiles were used as received either bleached or bleached and mercerized. Chemicals were p.a. and used without further purification

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 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 [12,13]. The overall hydrophilicity of the textile surface was drastically increased upon this pretreatment. These oxygen functional groups were located in the top layers of the materials, (1–40 Å) 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 [14,15].

2.2.2. Vacuum-UV

The textile polymer surface was also pretreated 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. 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 [13].

2.3. Preparation of TiO_2 suspensions and colloids and mixtures of both

Many TiO_2 formulations are tried to impregnate the textiles based on powders, colloids or combination of both. The photodiscoloration results give the data of the best starting formulation to use for each particular textile

Table 1
Details of the binding of TiO_2 to cotton C2

Entry	Spacer	Conc. c [mol/L^{-1}]	Drying T [°C]	Curing T [°C]	Elemental analysis [%TiO_2]
1	**1**	0.50	85	115	0.96
2	**1**	0.50	90	200	1.06
3	**1**	1.01	90	200	1.34
4	**2**	0.34	90	175	0.47
5	**2**	0.34	90	200	1.36
6	**2**	0.68	90	200	0.76
7	**3**	0.25	85	175	0.93
8	**3**	0.25	90	200	0.82
9	**3**	0.51	90	200	1.09

2.4. Preparation of TiO_2 coated textiles

Plasma or UV pretreated 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 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 pretreated 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 pretreated surfaces were able to fix TiO_2 from colloidal solutions or suspensions or the combination of both. Samples exhibited comparable amount of TiO_2 around 1.5–2.5% (w/w).

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 Fig. 1). Except when mentioned in the text, irradiation of the samples was

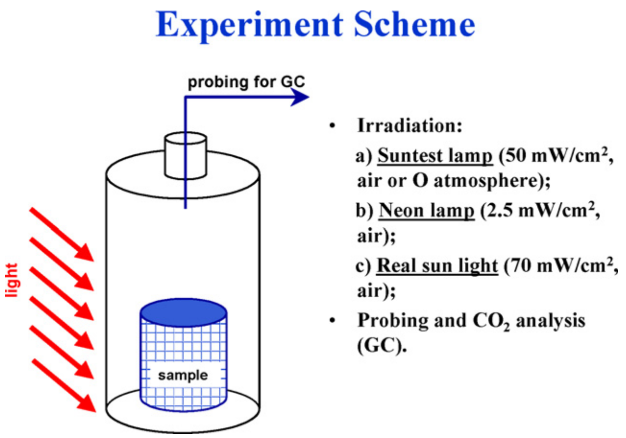


Fig. 1. Self-cleaning vessel used for the evaluation of the CO_2 evolved on a Lantal loaded tissue under light irradiation.

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 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 CO_2 produced during irradiation was measured in a gas chromatograph (Carlo Erba, Milano) provided with a Poropak S column. The quantitative test for the self-cleaning action of the TiO_2 loaded textiles is shown in Fig. 1. The textile strip without TiO_2 loading did not evolve any significant amounts of CO_2. By visual inspection the discoloration of the sample was observed to be in relation with the amount of CO_2 evolved under light irradiation. An increase in specular reflectance taken in a spectrophotometer for tissues before and after irradiation was also observed.

2.6. *Transmission electron microscopy (TEM)*

A field emission TEM microscope (CM 300FE-UT, 300 kV, Cs 0.7 mm point-to-point resolution at scherzer defocus 0.17 nm) and a Philips EM 430 (300 kV, source LaB6 resolution point 2 Å) were used to measure the particle size of titania clusters on the textile surface. The Philips CM 300 was equipped with energy dispersive X-ray analysis (EDS) spectrometer allowing the identification of the Ti-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 for experimental observations at a 90° angle. Probes having a 10 μm 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.

2.7. *X-ray diffraction measurements of TiO_2 loaded textiles*

The amount of 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 during the photodegradation of wine and coffee stains on TiO_2 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 [16]. The amount of CO_2 produced in the reactor was used to monitor during light irradiation due to the mineralization of coffee and wine stains as shown in Fig. 1. 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 a non-loaded photocatalytic decomposition of the textile sample was measured in a blank experiment. For wool–polyamide textiles loaded combining the hydrothermal treated colloidal TiO_2 as a basic layer with a second coating of TiO_2 Degussa P-25 having bigger crystallite size lead the best discoloring performance. The reason for the better performance of the coating is 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 [16]. The self-cleaning action was enhanced for wool–polyamide compared to the polyester loaded TiO_2 textile. The wine stains mineralized more easily than coffee stains. When hot coffee is poured on either the polyester fabric or the wool–polyamide fabric the textile color turns from white to brown. When wine is poured, a dark red stain is observed on both fabrics.

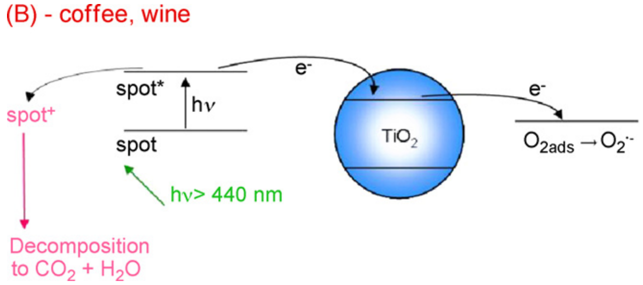


Fig. 2. Mechanism for the production of oxidative radicals on TiO_2 with a stain absorbing simulated sunlight.

Three types of light sources were tested to irradiate the wool–polyamide 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 photo-catalytic 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. 2. In Fig. 2, the oxidation and decomposition of the organic reactant would occur due to the light photosensitization of the coffee or wine unstable cation, and allows the injection of an electron into the conduction band of TiO_2 in reaction (1) leading to the formation $O_2^{\bullet -}$.

Fig. 3 shows the mechanism of discoloration of a grease spot having commonly an absorption edge <290 nm. In this case the TiO_2 absorb the incoming UV-light. The peroxides and highly oxidative radicals $HO_2^{\bullet -}$, $OH^{\bullet}$, $RO^{\bullet}$ and $RO_2^{\bullet}$ are able to decompose the stains adsorbed on TiO_2 as outlined in Fig. 3 plays and play an important role in the abatement of these stains. This is presented schematically in Fig. 4.

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

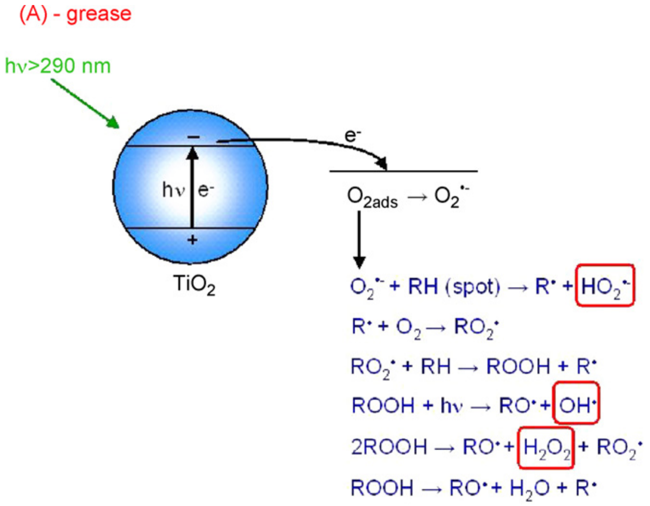


Fig. 3. Suggested mechanism for the discoloration of wine stains by Suntest solar simulated light in air on the TiO_2 loaded textiles.

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]

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

The release of CO_2 is proportional to the oxidative decomposition of the wine stain and occurs with the concomitant formation of a small amount of cations and anions

$$C_xH_yN_vS_w\,(\text{wine stain}) + H_2O_w + O_2 + h\nu \rightarrow CO_2 + H_2O + SO_p + NO_q \tag{4}$$

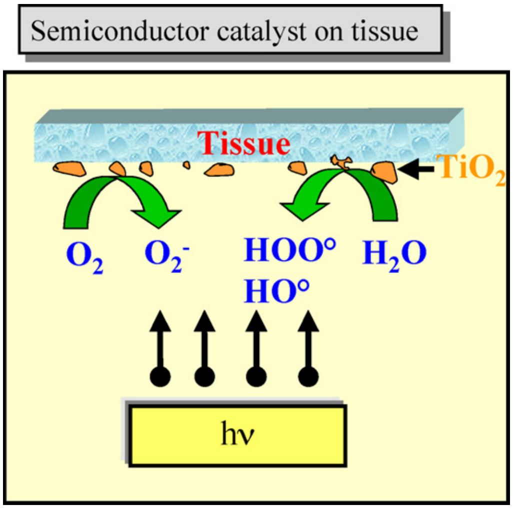


Fig. 4. Schematic of the generation of highly oxidative radicals under light irradiation at the surface of the TiO_2 deposited on textiles.

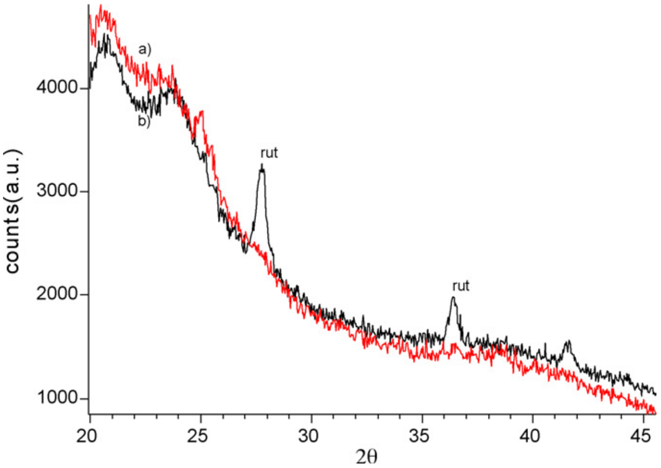


Fig. 5. X-ray diffractogram of wool–polyamide textiles: (a) base textile and (b) base textile with surface deposited TiO_2. For other details see text.

3.2. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) on wool–polyamide

The TEM work on wool–polyamide textiles was carried out for TiO_2 samples deposited via colloidal TiO_2 from TTIP, and Degussa P-25 TiO_2 powder on the textile surface. The sizes of 30–40 nm have been reported for Degussa P-25 primary particles. On the wool–polymide textile, the coating consists of a layer 100–300 nm thick, where the small colloidal TiO_2 clusters were shown to support the bigger TiO_2 P-25 particles.

Fig. 5 shows the XRD pattern of a wool–polyamide before and after loading with TiO_2. After loadings, the peaks of rutile can be seen. 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. But 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. This form of titania on the wool–polyamide sample should therefore be less aggressive towards the textile substrate than the anatase form upon light irradiation.

3.3. Self-cleaning of natural fibers like cotton modified with TiO_2 Degussa P-25 under daylight irradiation

In a recent study [18], we reported that the same approach to load synthetic fibers as described above with TiO_2 particles can be used for base treated cotton a natural fiber widely used in the textile industry. This study shows that samples of bleached cotton (C_2) when UV-irradiation introduced functional groups negatively charged to anchor TiO_2 on the textile surface by the installation shown in Fig. 6. 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. The coating of TiO_2 on the textiles presented variable thickness of 120–300 nm. The TiO_2 cluster size and distribution after the stain discoloration process did not vary with respect to the TiO_2 cluster size before irradiation. Elemental analysis revealed

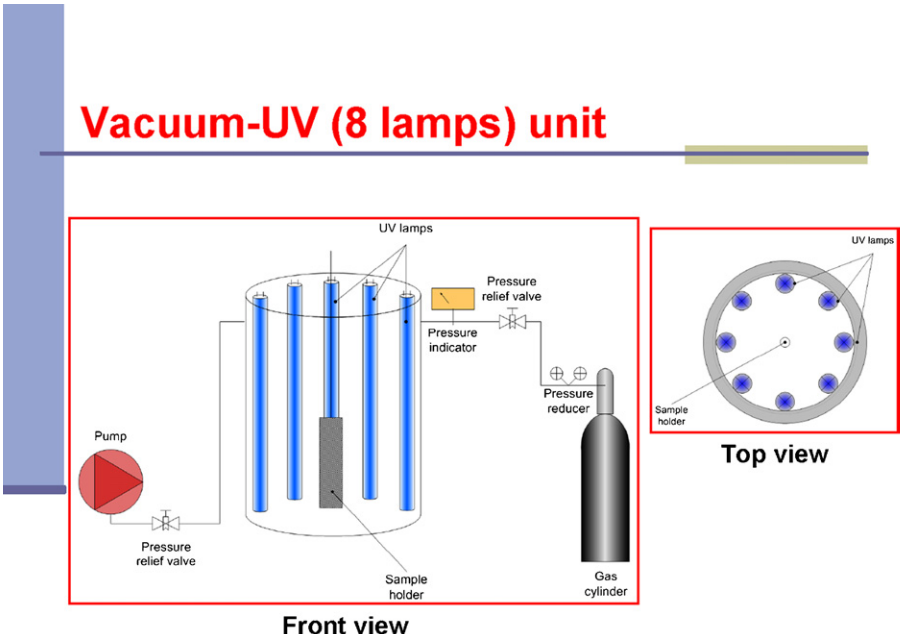


Fig. 6. Schematic of the vacuum-UV installation used to introduce the anchoring groups on textiles.

Ti-loadings of 1–1.5% (w/w) for the TiO_2 attached by different techniques.

The deposition of TiO_2 on the UV-activated textile was carried out activating the textile surface as shown in Fig. 6 and introducing the TiO_2 Degussa P25 powder in the following way: 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 with distilled water by 5 min sonication. A loading of 1.0–1.5% (w/w) was determined by elemental analysis.

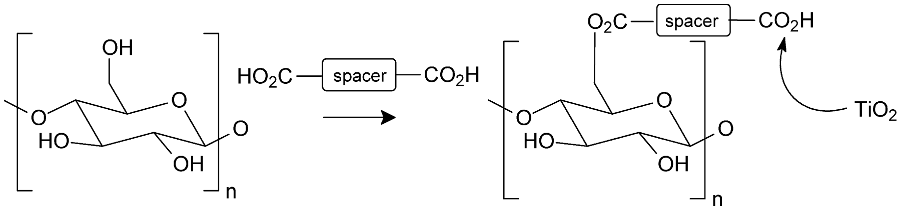
3.4. TiO_2 nano-clusters attachment on textiles of cilander AG inducing self-cleaning effects

In recent work out of our laboratory [19], an alternative approach to the RF plasma and vacuum UV attachment of TiO_2 is presented using a spacer to attach TiO_2 on the alcoholic –OH groups of the cellulose making up the cellulose units of the cotton by chemical means (Scheme 1). This spacer should have two free carboxylic groups to bind to cotton on one hand and TiO_2 on the other hand. The chemical stability of the spacer is warranted by the single bond species selected for this function. The carboxylic groups are known to bind efficiently TiO_2 by strong electrostatic interactions. The objective for the use of the chemical spacer is presented in Fig. 7.

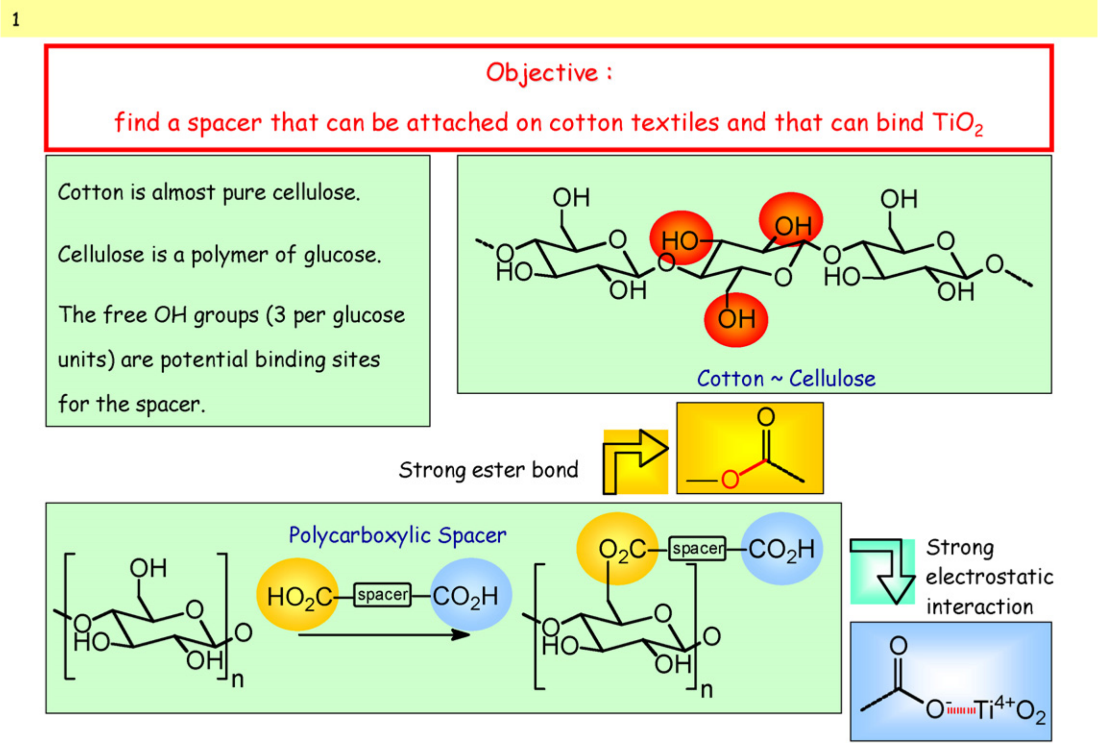
The cellulose in Fig. 7 shows that cotton is a multiple polysaccharide, with a high number of free hydroxyl groups on which the spacer can be introduced by formation of a covalent bond due to the esterification of the carboxylic group.

In order to test the feasibility of this new approach, we used first low cost (10 SFr/100 g) commercial saturated di-, tri-, tetra-carboxylic acids a spacers (Scheme 2).

The C2 white cotton after only bleaching with ammonia was immersed in an aqueous solution of **1**, **2** or **3** (6%, w/w) in presence of NaH_2PO_2 as catalyst (4%, w/w) for 1 h. After drying (3 min at 80 °C < T < 90 °C), the textiles were cured at high temperature (2 min at 115 °C < T < 210 °C). TiO_2 was subsequently introduced on the free carboxyl groups of the spacer that has been previously attached to the textiles by immersion of the textiles into an aqueous suspension of TiO_2 (5 g/L solution of TiO_2 Degussa) and heated for 1 h at 75 °C. The TiO_2 was previously sonicated for 30 min. After drying (1 h at 100 °C) the unbounded TiO_2 was washed out and further sonication was applied for this purpose (5 min). The identification of the reactive intermediates that allow the binding of the spacer to cellulose were identified by mass spectrometry (CI-MS) of the acidic aqueous solution of **1**, **2** and **3** (4%, w/w, of NaH_2PO_2, 6%, w/w, of the polyacid), we could show that the carboxylic groups – that are in a 1,4-relative position – form intramolecular anhydrides, i.e. reactive intermediates towards the formation of the desired ester bonds with the free hydroxyl groups of cellulose (Scheme 3).



Scheme 1. Attachment of TiO_2 to cellulose by chemical means.



1

Objective :

find a spacer that can be attached on cotton textiles and that can bind TiO_2

Cotton is almost pure cellulose.

Cellulose is a polymer of glucose.

The free OH groups (3 per glucose units) are potential binding sites for the spacer.

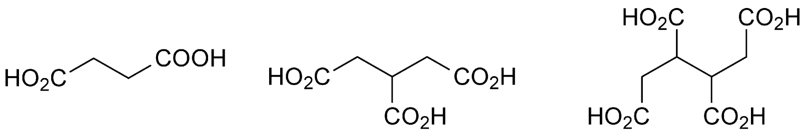
Cotton ~ Cellulose

Strong ester bond

Polycarboxylic Spacer

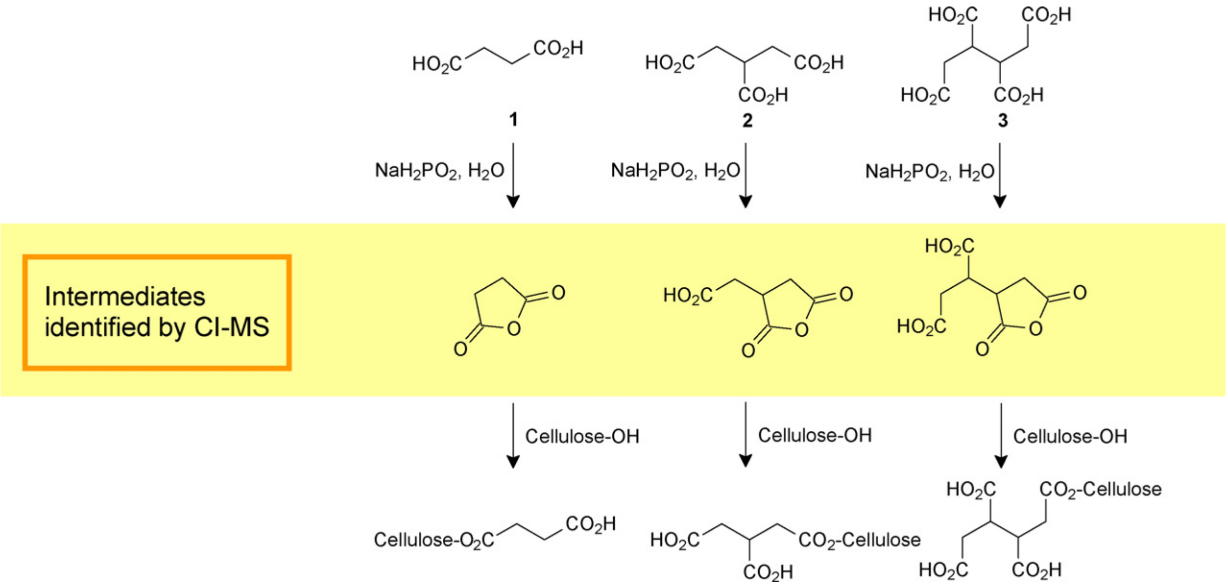
Strong electrostatic interaction

Fig. 7. Diagram showing the spacer attachment to cotton and to TiO_2. Objectives of the chemical spacer use.



1 **2** **3**

Scheme 2. Spacers tested: (**1**) succinic acid, (**2**) tricarballyc acid and (**3**) 1,2,3,4-butanetetracarboxylic acid.



Scheme 3. Anhydrides observed by CI-MS.

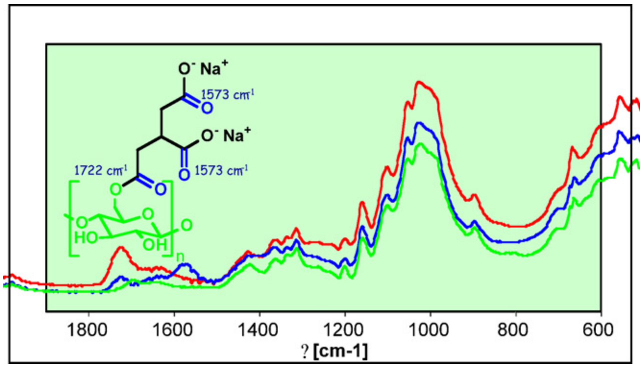


Fig. 8. Characterization of the ester bond between the spacer and cellulose by ATR-IR. Green: C2 textile, cotton bleached with ammonia); red: after immersion in a solution of 6% of (2) and 4% of NaH_2PO_2 in H_2O, followed by drying (3 min at 90 °C) and curing (2 min at 175 °C) and final treatment in a 0.1N solution of HCl; blue: same as red, but final treatment in a 0.1N solution of NaOH; grey: same as red and a final treatment with TiO_2 (1 h at 75 °C, 1 h drying at 100 °C and washing). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

By attenuated total reflection infrared spectroscopy (ATR-IR) of the textile samples, the formation of the ester bonds could be confirmed. The observations are presented in Fig. 8. As the characteristic stretching vibration of esters (R**C**O**O**R) and acids (R**C**O**O**H) are in the same region (1800–1600 cm^{-1}), the textiles where further treated in a diluted acidic solution (HCl 0.1N) and a diluted basic solution (NaOH 0.1N). By acidic treatment the complete protonation of the carboxylic groups was ensured and the basic treatment applied allowed their complete deprotonation. The deprotonation was expected to shift the stretching vibration of the cabonyl function (R**C**O**O**$^-$) down to 1550 cm^{-1}. Hence, the newly formed ester bonds could be identified with the peaks at 1724 cm^{-1} of carboxylates at 1575 cm^{-1} (blue line). This work shows that it is possible to bind TiO_2 to cotton by chemical means and that the TiO_2–cotton presents stable self-cleaning properties. The details of the binding of TiO_2 to cotton C2 (white fabric after only bleaching with ammonia) are reported in Table 1.

The experiments showed that curing at higher temperature does not always give the highest loading of TiO_2. In fact, a slight yellowing was observed when the textiles are submitted to temperatures around 200 °C. An efficient treatment at lower temperature therefore allows to preserve the textiles.

During this work it was also observed thatt he chemical treatment of the bleached cotton prior to the binding of the spacer and TiO_2 decreases the number of available OH groups decreases the amount of the spacer on the textile surface. The self-cleaning properties did not increase with the number of carboxylic groups on the spacer used.

3.5. Self-cleaning cotton textiles surfaces using SiO_2/TiO_2 coating

This study [20] aimed to protect the textile from the attack by the h_{vb}^+ generated by the TiO_2 layer under light irradiation on the textile surface. SiO_2 was selected as a binder since it does not decompose due to the strong photocatalytic action of TiO_2. The TiO_2–SiO_2 composite layer was applied on the cotton following the procedure outlined in Fig. 9.The composite layer of TiO_2–SiO_2 should avoid the attack on the cotton by the h_{vb}^+ generated by the TiO_2 under daylight irradiation. The SiO_2 layer (s) are applied therefore on the textile before the topmost layer of TiO_2. Experiments are reported which evaluate quantitatively the effect of the corrosion of the cotton upper layers by the action of TiO_2 under light.

The photocatalytic activity of TiO_2–SiO_2 coated cotton textiles was investigated through the self-cleaning of red wine stains. The most suitable Ti-content of the coating was found to be 5.8% and for SiO_2, the content was 3.9% (w/w). The discoloration of red wine led to CO_2 evolution that was more efficient for TiO_2–SiO_2 coated cotton for samples than of TiO_2 coated ones. The textile surface did not show any change after

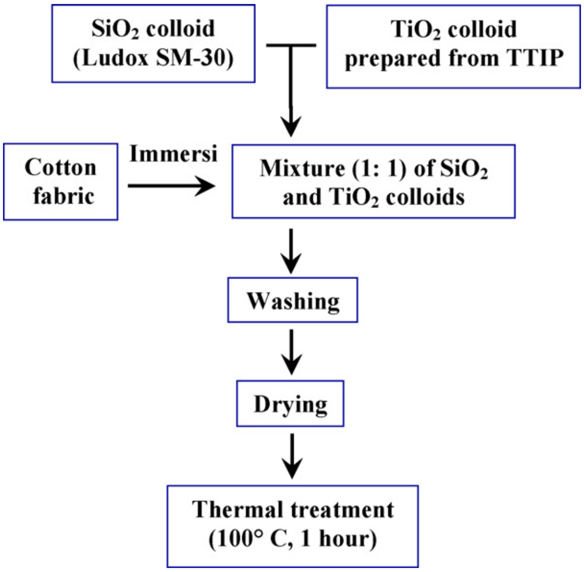


Fig. 9. Scheme of the colloid preparation and cotton loading with TiO_2 and SiO_2 colloidal mixture.

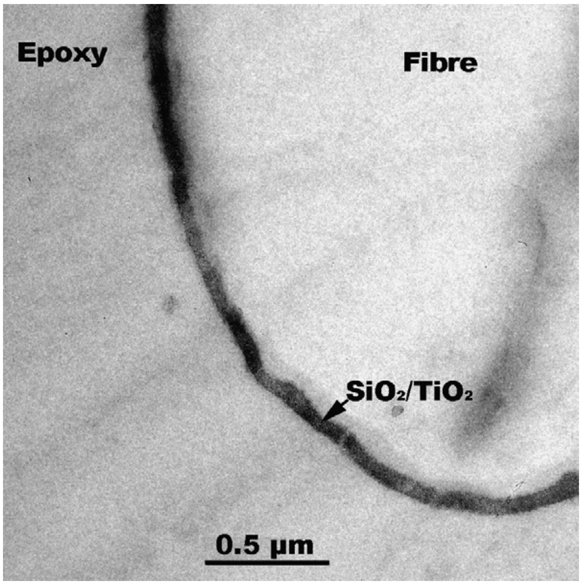


Fig. 10. Transmission electron microscopy of a TiO_2 and SiO_2 coated cotton.

several consecutive light induced discoloration cycles of a red wine stain. Infrared spectroscopy revealed that no modification of the cotton could be detected after photo-discoloration processes with TiO_2–SiO_2, taking a wine stain as model compound. The mixed TiO_2 and SiO_2 colloids lead during the dip-coating and subsequent thermal treatment on cotton to an organized structure of highly dispersed TiO_2 particles always surrounded by amorphous silica (Fig. 10).

3.6. Transmission electron microscopy and energy dispersive spectroscopy of TiO_2–SiO_2 coated cotton textiles efficient in red wine stains discoloration

Fig. 10 shows the electron micrograph coated cotton sample before light irradiation presenting a continuous coating of TiO_2–SiO_2 on the perimeter of the cotton fiber. The particles of SiO_2 and TiO_2 in Fig. 11 were identified by high-resolution electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS). The particles observed on the cotton had sizes between 4 and 8 nm. The particles were small enough to produce transparent films. The average thickness of the TiO_2–SiO_2 layer on the cotton taken over many samples was found to be ~25 nm. This is the equivalent of 3–6 layers of TiO_2–SiO_2 particles on the cotton surface. Small TiO_2 size particles of TiO_2 were obtained due to the peptization of the colloid in acid media. The small crystallite size attained is beneficial for the photocatalytic induced discoloring of the of red wine since: (a) it provides a large specific surface area of the particles facilitating an improved contact to the red wine stain that is photocatalytically decomposed and (b) it reduces the probability of bulk electron-hole pair recombination. This recombination limits the efficiency of photocatalytic reaction. The TiO_2–SiO_2 layers on the cotton after 24 h irradiation presented by HRTEM have the same structure as the TiO_2–SiO_2 layers as observed at time zero. This is the proof of the stable nature of the TiO_2–SiO_2 layers deposited on the cotton. No atomic force microscopy (AFM) could be

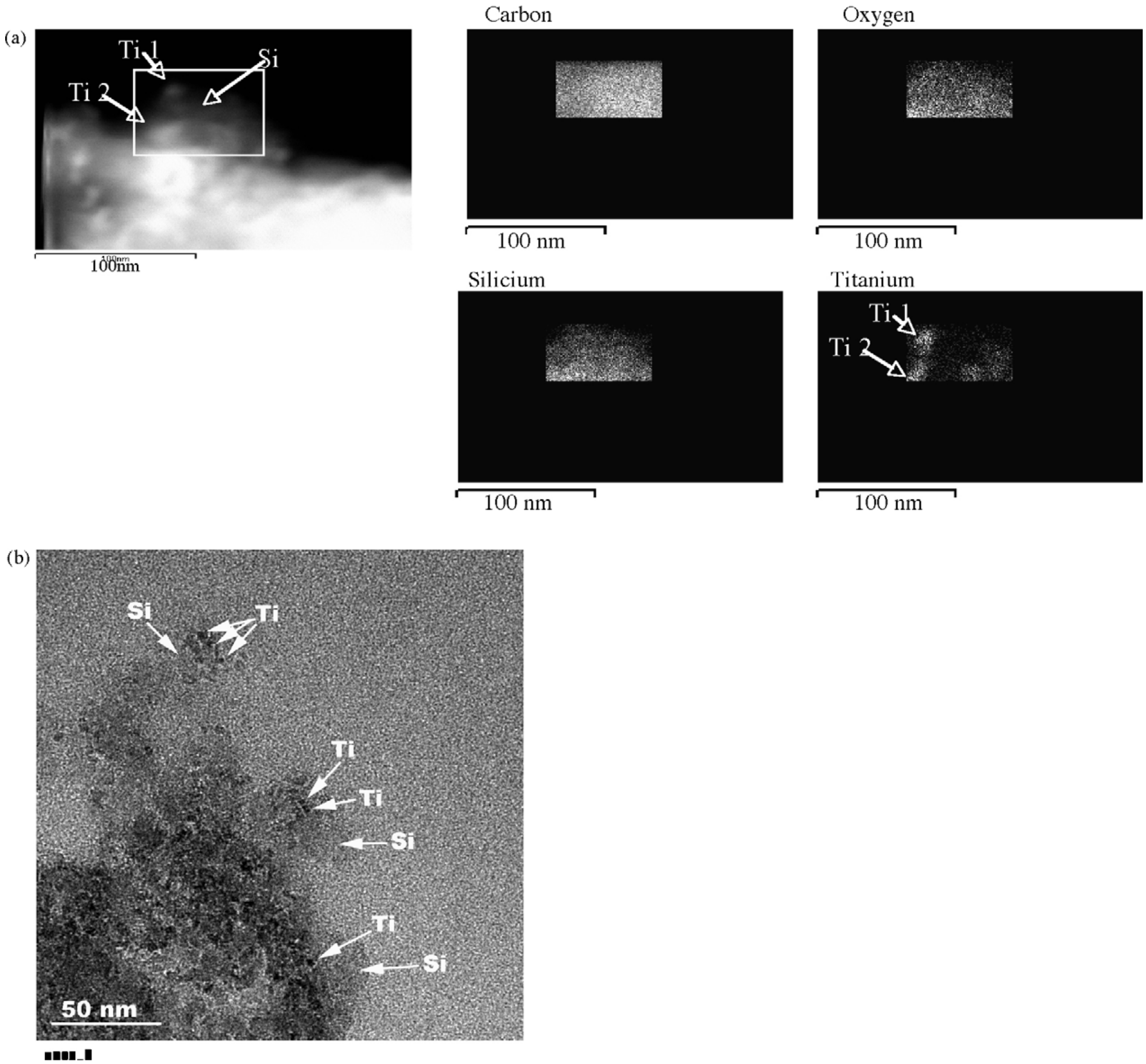


Fig. 11. (a) Energy dispersive spectroscopy (EDS) of the cotton TiO_2–SiO_2 sample. Elements Mapp INCA Oxford. For other details see text. (b) EDS spectroscopy of the cotton TiO_2–SiO_2 sample showing the Si and Ti particles present on the textile surface.

carried out on these samples since the cotton surface was too rough and non-uniform to be investigated by AFM methods.

Fig. 11a shows the EDS images of the cotton samples. The arrows in Fig. 11a (on the left hand side) show the individual particles of Si and Ti1 and Ti2. The rectangle shows a low-resolution view of the sample. The surface C-particles are shown in Fig. 11a. The high amount of C comes from the C of the grid used for the EDS observation and also from the epoxy-resin applied during the sample preparation. Si and Ti are also shown in Fig. 11a and are observed to be everywhere on the cotton surface. The Figure of Ti shows a much higher resolution of the Ti1 and Ti2 particles. The Ti particles were observed to be covered by amorphous SiO_2 (white areas).

Fig. 11b presents another view of the embedded Ti-particles by the amorphous SiO_2. The SiO_2 is shown in the clear areas of Fig. 11b. The Ti-particles were always found to have amorphous SiO_2 always surrounding them.

4. Conclusions

Three different pretreatment methods of synthetic textiles have been studied that allow the TiO_2 coatings able 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 nanoparticles 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. The sol–gel preparation of transparent photoactive coatings of TiO_2–SiO_2 is possible at low temperatures not damaging the cotton structure. The TiO_2–SiO_2 coating showed a high photocatalytic activity, superior to a TiO_2 coating alone due to the high dispersion and the structural effects of the amorphous silica present.

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