

Self-cleaning cotton textiles surfaces modified by photoactive SiO₂/TiO₂ coating

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Abstract

The photocatalytic activity of TiO₂–SiO₂-coated cotton textiles was investigated through the self-cleaning of red wine stains. It was shown that a TiO₂–SiO₂ species could be produced at temperatures of 100 °C with acceptable photo-activity on non-heat resistant materials. The most suitable Ti-content of the coating was found to be 5.8% and for SiO₂, the content was 3.9% (w/w). The discoloration of red wine led to CO₂ evolution that was more efficient for TiO₂–SiO₂-coated cotton for samples than of TiO₂-coated ones. The reasons for these results are discussed. The textile surface did not show any change after several consecutive light-induced discoloration cycles of a red wine stain. By high-resolution transmission electron microscopy (HRTEM), the TiO₂–SiO₂ layer thickness on the cotton fibers was detected to 20–30 nm. The TiO₂ and SiO₂ were both observed to have particle sizes between 4 and 8 nm. Further electron microscopy work coupled with energy dispersive spectroscopy (EDS) showed that the Ti-particles were always surrounded by amorphous SiO₂ and never alone by themselves. Infrared spectroscopy revealed that no modification of the cotton could be detected after photo-discoloration processes with TiO₂–SiO₂, taking a wine stain as model compound. The mixed TiO₂ and SiO₂ colloids lead during the dip-coating and subsequent thermal treatment on cotton to an organized structure of highly dispersed TiO₂ particles always surrounded by amorphous silica.

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1. Introduction

The development of permanent self-cleaning cotton textiles with a life cycle of 25–50 washings or more is an objective sought by the textile industry in the framework of new products classified as intelligent textiles [1,2]. Such a product could have applications in the EU market of about 14 million meters of textiles/year. The cost saving on cleaning using these fabrics, presenting a total or partial self-cleaning properties, is one benefit. The other is to prolong the lifetime of the textile due to the continuous self-cleaning taking place at the fabric surface under daylight irradiation. Such an innovation comprises TiO₂ nano-clusters thin films deposited on the textile surface, in our case, a cotton textile. TiO₂ was shown in the last decade to be the best candidate for a photocatalytic

applications [3–5]. Nano-sized TiO₂ particles show high photocatalytic activity because they have a relatively large surface area per unit mass and volume, which facilitates the diffusion of the surface, generated charge carriers under light irradiation [6,7]. Sol–gel TiO₂-based thin layers require a high temperature treatment >300 °C treatment to produce thin films with a defined crystallographic phase. This limits the possibility of achieving well-crystallized TiO₂ films, to supports with reasonable thermal stability such as glass or ceramics [1–6].

We have found only three prior reports on TiO₂ thin films prepared from sol–gel TiO₂ at relatively low temperatures. The first report discussed deposited TiO₂ films on silicon wafers between 60 and 180 °C by film autoclaving under water pressure [7]. The second report was related to TiO₂ deposition on polymer PMMA and polycarbonate from TiO₂ sol–gel [8]. The third and last report involved the production of TiO₂ films of alcoxides at temperatures of 100 °C [9]. Out of our laboratories, we have recently reported the coating of synthetic fabrics with

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TiO₂ by physical and chemical methods at temperatures higher than 100 °C [10–13].

The first objective of this study was to optimize the parameters intervening in the preparation of photoactive transparent thin films of TiO₂–SiO₂ on cotton knowing that this substrate has a poor heat resistance. The maximum exposure that cotton can take without being damaged is 180 °C for 10 min and somewhat lower temperatures for longer time periods. The experimental conditions were screened for the preparation of photocatalytic active TiO₂–SiO₂ layers in the thermal range compatible with the cotton heat stability. The photocatalytic activity of TiO₂ strongly depends on the size, specific surface BET area, porosity and structure of the layers deposited on the textile surface. The specific surface area of the TiO₂ coating is favored by low temperature preparation. No sintering of the TiO₂ occurs decreasing the porosity of the film, as is the case for TiO₂ films calcined on heat-resistant substrates at a few hundred degrees. The second objective is to report in detail the SiO₂–TiO₂ morphology, responsible for the observed photoactivity, by HRTEM and EDS. The third objective of this study was to characterize and assess the surface changes on the cotton textile during the self-cleaning process by elemental analysis (EA), X-ray diffraction (XRD) and infrared spectroscopy (ATR-IR).

SiO₂ was selected as a binder since it does not decompose due to the strong photocatalytic action of TiO₂. The composite layer of TiO₂–SiO₂ should avoid as much as possible the attack on the cotton by the h_ν⁺ generated by the TiO₂ under daylight irradiation. Experiments are reported, which evaluate quantitatively the effect of the corrosion of the cotton upper layers by the action of TiO₂ under light.

2. Experimental

2.1. Materials and reagents

The cotton bleached fabrics were a gift from Cilander AG, 9100 Herisau (Ar), Switzerland. The titanium tetra-isopropoxide (TTIP), acetic acid and nitric acid were Fluka p.a. reagents and used as received. Triply distilled water was used in all experiments. The colloidal silica solution Ludox SM-30 (ex-Dupont) was used for the preparation of the mixed TiO₂–SiO₂ colloids and was a gift of Grace GmbH, 4153 Rheinach, Switzerland. These colloid particles were negatively charged having Na as a stabilizing counter-ion. The colloid contained 30 wt.% SiO₂ (specific surface area 360 m²/g) in solutions with pH 6.9. It is widely used in industry to increase the strength and abrasion resistance of treated textiles.

2.2. Preparation of TiO₂–SiO₂ colloids and coating of the cotton fabrics

After a long series of preliminary experiments, the most efficient discoloration of red wine on the cotton was observed with a TiO₂–SiO₂ layer colloid prepared as follows. The TiO₂ solution prepared from 25 ml titanium tetra-isopropoxide (TTIP), and 5 ml acetic acid were added to 500 ml of tri-distilled water. Subsequently, 3.5 ml HNO₃ was added under stirring, and the

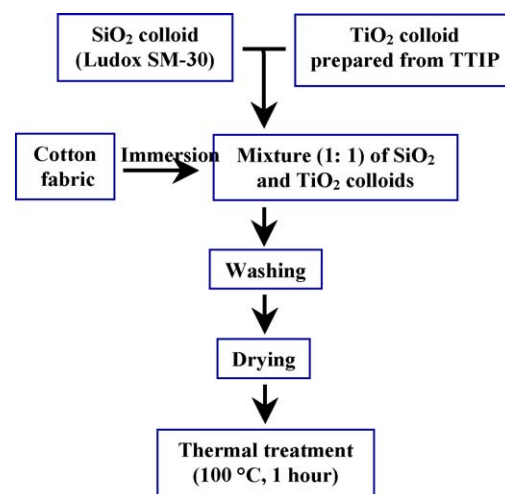


Fig. 1. Scheme of the colloid preparation and cotton loading with TiO₂- and SiO₂-colloidal mixture.

mixture was heated to 80 °C for 30 min. The resulting TiO₂ colloid was kept under stirring for 2 h. The TiO₂–SiO₂ layers on the cotton were deposited by immersing the cotton in a 1:1 volume mixture made up of the TiO₂ colloid and SiO₂ Ludox SM-30. Subsequently, the sample was dried in air and treated at 100 °C for 1 h. The process of preparing and loading TiO₂–SiO₂ on cotton textiles is schematically shown in Fig. 1.

During the preparation of diverse colloidal mixtures, the solution parameters that varied were: (a) the nature of the colloidal solutions of SiO₂, (b) the ratio of SiO₂ to TiO₂, (c) the drying temperature of the colloid on the cotton, (d) the drying time of the colloid on the cotton, (e) the dip-coating conditions of the cotton into the colloidal mixture and (f) the pH and concentrations of the mixed colloids. Preliminary discoloration experiments of wine spots showed that mixed colloids of SiO₂ and TiO₂ presented a better performance than when TiO₂ colloids were used alone for the photo-discoloration of wine stains. Also, when the SiO₂ colloid was added first to the cotton and then dried followed by the TiO₂ colloid in order to protect the textile with a layer of inert SiO₂, the photo-discoloration effect was much reduced.

When TiO₂ and SiO₂ colloids are mixed, a mixing at the molecular level is observed [14] that on heating will crosslink and gellate leading to the formation of a 3-D network. In contact with the textile surface, the condensation of the mixed colloid is higher than the crystallization rate leading to separate TiO₂ and SiO₂ loosely bound particles with a specific structure as described in Section 2.5 by HRTEM and EDS experiments.

2.3. Irradiation procedure and evaluation of the textile cleaning action

The photochemical reactor consisted of 80 ml cylindrical Pyrex flasks each containing a strip of textile of 48 cm² positioned immediately against the wall of the reactor. 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 5–6% of the photons in the 290 and

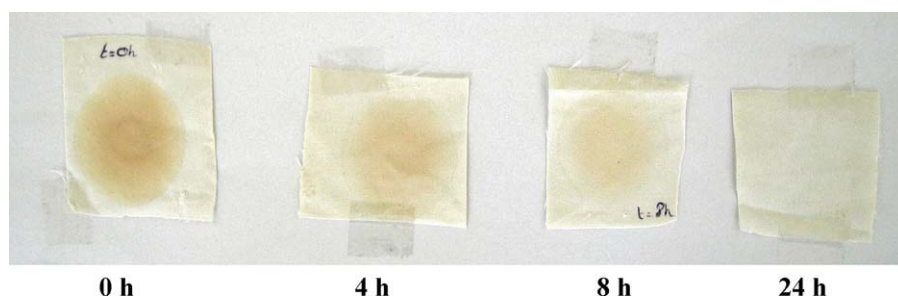


Fig. 2. Discoloration of bleached cotton samples stained with wine on $\text{TiO}_2\text{-SiO}_2$ -coated cotton textiles irradiated after 0, 4, 8 and 24 h in a solar light simulator with 90 mW/cm^2 .

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.

2.4. Elemental analysis

Elemental analysis of the $\text{TiO}_2\text{-SiO}_2$ loaded on the textile fabrics was carried out by atomic absorption spectrometry using a Perkin-Elmer 300 S unit.

2.5. High-resolution transmission electron microscopy (HRTEM)

A Philips CM 300 (field emission gun, 300 kV, 0.17 nm resolution) HRTEM microscope and a Philips EM microscope 430 (300 kV, LaB_6 , 0.23 nm resolution), both provided with an energy dispersive spectrometer (EDS) were used to measure the particles sizes of the titania clusters coating the textile fabrics. The textiles were embedded in an epoxy resin (Embed 812) and cross-sectioned with an ultra-microtome (Ultracut E, Reichert-Jung) to thin sections of 50–70 nm. Magnification from about 1000 up to $450\,000\times$ was used to characterize the samples. In this way, it was possible to provide image resolution from overview to the scale of atomic planes.

2.6. X-ray diffraction measurements (XRD) of TiO_2 -loaded textiles

The crystallinity and phase of the titanium oxide loaded on the textile surface was studied with a Siemens X-ray diffractometer using $\text{Cu K}\alpha$ radiation.

2.7. Attenuated total reflection infrared (ATR-IR) spectroscopy

The ATR-IR spectra were measured in a Portman Instruments AG spectrophotometer equipped with a Specac attachment (45° one pass diamond crystal), and were the results of 256 scans

with 2 cm^{-1} resolution in the spectral range between 4000 and 500 cm^{-1} .

3. Results and discussion

3.1. Photo-induced discoloration of red wine stains on $\text{TiO}_2\text{-SiO}_2$ -coated cotton textiles: visual evidence

Fig. 2 presents the discoloration of a wine stain, which was added on to the bleached cotton surface, after various irradiation times with simulated sunlight from a Suntest solar simulator with a dose of 90 mW/cm^2 . The intensity of the UV(A) light between 315 and 400 nm is 45 mW/cm^2 . A complete discoloration is observed after 24 h light irradiation with a light intensity that is 90% of the solar full intensity (AM1) as shown in Fig. 2. The practical significance of such a discoloration is that daylight irradiation of the wine stain will make the stained fabric more prone to the action of detergents used in the household washing. This allows the washing of cotton textiles to be further spaced with the consequent cost saving in energy and materials. Herrmann [15] had proposed that the superior photoactivity of the $\text{TiO}_2\text{-SiO}_2$ photocatalyst with respect to TiO_2 as observed in our case is due to the light that is not absorbed by TiO_2 being reflected at the SiO_2 surface if the film thickness is small enough. This is the case of the films prepared in this study as will be described in Section 3.2. Interactions leading to a more favorable photocatalysis would then occur in the film through a multi-reflection mechanism.

When depositing the $\text{TiO}_2\text{-SiO}_2$ on the cotton (as described in Section 2) the Ti-content on the cotton was found to be $5.8 \pm 0.3\%$ (w/w) by elemental analysis at time zero. After 48 h photo-discoloration of the red wine spot, the Ti-content was observed to remain almost constant and within the experimental error of the determination. The Si-content of the coating was found to be $3.9 \pm 0.2\%$ (w/w) at time zero and no change in the amount of Si was found after 48 h irradiation with a Suntest solar simulator.

3.2. Transmission electron microscopy of $\text{TiO}_2\text{-SiO}_2$ -coated cotton textiles efficient in red wine stains' discoloration

Fig. 3 shows the electron micrograph-coated cotton sample before light irradiation presenting a continuous coating of

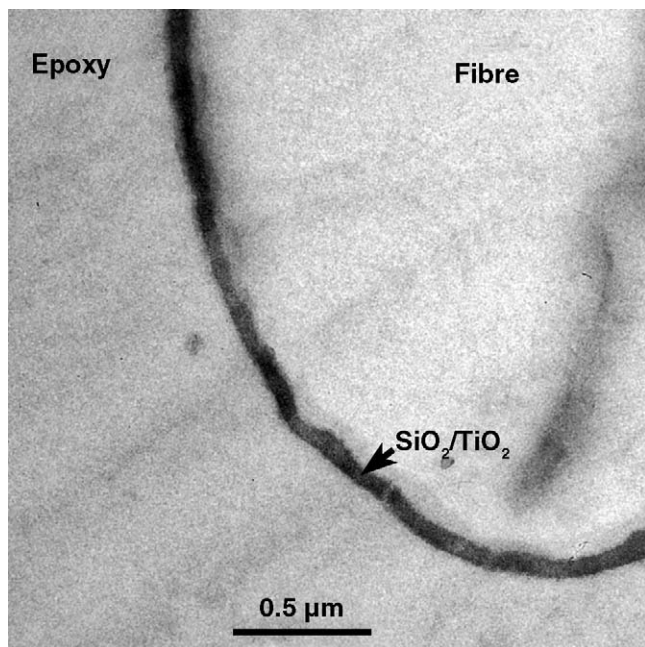


Fig. 3. Transmission electron microscopy of a TiO_2 - SiO_2 -coated cotton textile fiber at time zero (scale of $0.5 \mu\text{m}$).

TiO_2 - SiO_2 on the perimeter of the cotton fiber. A more detailed electron microscopy with a higher magnification is presented in Fig. 4. The particles of SiO_2 and TiO_2 in Fig. 4 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 size of the particles is small enough to produce transparent films. The average

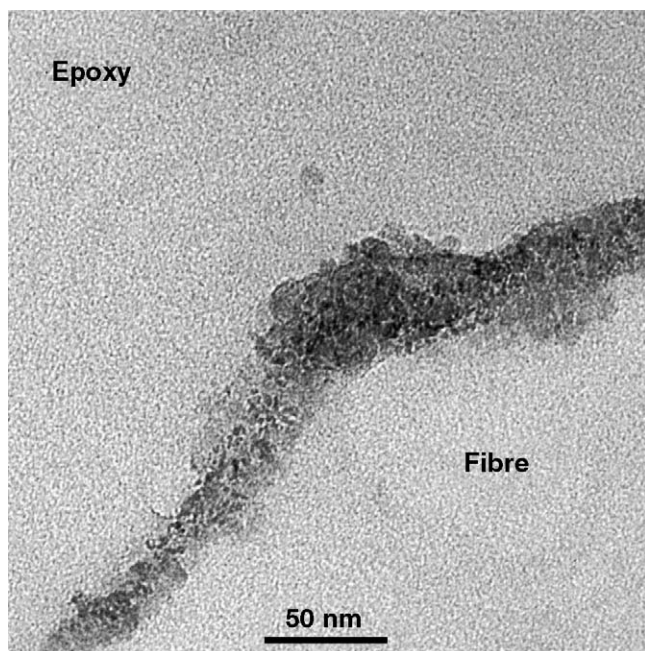


Fig. 4. Transmission electron microscopy of a TiO_2 - SiO_2 -coated cotton textile fiber at time zero showing in a more detailed way the TiO_2 and SiO_2 crystallites (scale of 50 nm).

thickness of the TiO_2 - SiO_2 layer on the cotton taken over many samples was found to be $\sim 25 \text{ nm}$. 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 [6,8,9]. The small crystallite size attained is beneficial for the photocatalytic induced discoloring of the red wine in Fig. 2 in two ways: (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 is one of the main factors limiting the efficiency of photocatalytic reactions [1,16]. 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 carried out on these samples since the cotton surface was too rough and non-uniform to be investigated by AFM methods.

Fig. 5a shows the EDS images of the cotton samples. The arrows in Fig. 5a (on the left hand side) show the individual particles of Si and Ti_1 and Ti_2 . The rectangle shows the low-resolution view of the sample. The surface C-particles are shown in Fig. 5a. 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. 5a and are observed to be everywhere on the cotton surface. The figure of Ti shows a much higher resolution of the Ti_1 and Ti_2 particles. The Ti particles were seen to be covered by amorphous SiO_2 (white areas).

Fig. 5b presents another view of the embedded Ti-particles by the amorphous SiO_2 . The SiO_2 is shown in the clear areas of Fig. 5b. The Ti-particles were always found to have amorphous SiO_2 always surrounding them.

3.3. Infrared spectroscopy of TiO_2 - SiO_2 -coated samples

Fig. 6a shows the IR spectrogram of a red wine drop deposited on a glass plate. The prominent peak at $\sim 1026 \text{ cm}^{-1}$ corresponds to the lycopene, tannin and carotenoid pigments in red wine. Fig. 6b shows the experimental IR-spectra for a control sample of bleached cotton up to 48 h light irradiation with a solar simulator. It is readily seen that light irradiation affect to a small extend the amplitude of the peak at $\sim 1026 \text{ cm}^{-1}$ within the initial 8 h, but the peak remains stable afterwards. No yellowing of the cotton or degradation of the cotton polysaccharide peak at $\sim 1026 \text{ cm}^{-1}$ [17] indicates that the cotton textile is stable under daylight irradiation.

Fig. 6c shows the IR-spectra of samples in traces (a)–(d) for cotton samples with TiO_2 - SiO_2 irradiated under solar-simulated light for up to 48 h. The IR-spectral results within this period are the same as reported in Fig. 6b for cotton alone. Therefore, we cannot differentiate the stretching vibration of Si–O–Si at ~ 800 [18] or the stretching SiOH bond at 970 cm^{-1} [19]. Fig. 6c shows that the prominent peak height does not change with the time of irradiation, and also that the TiO_2 coating does not affect the cellulose cotton groups under daylight irradiation.

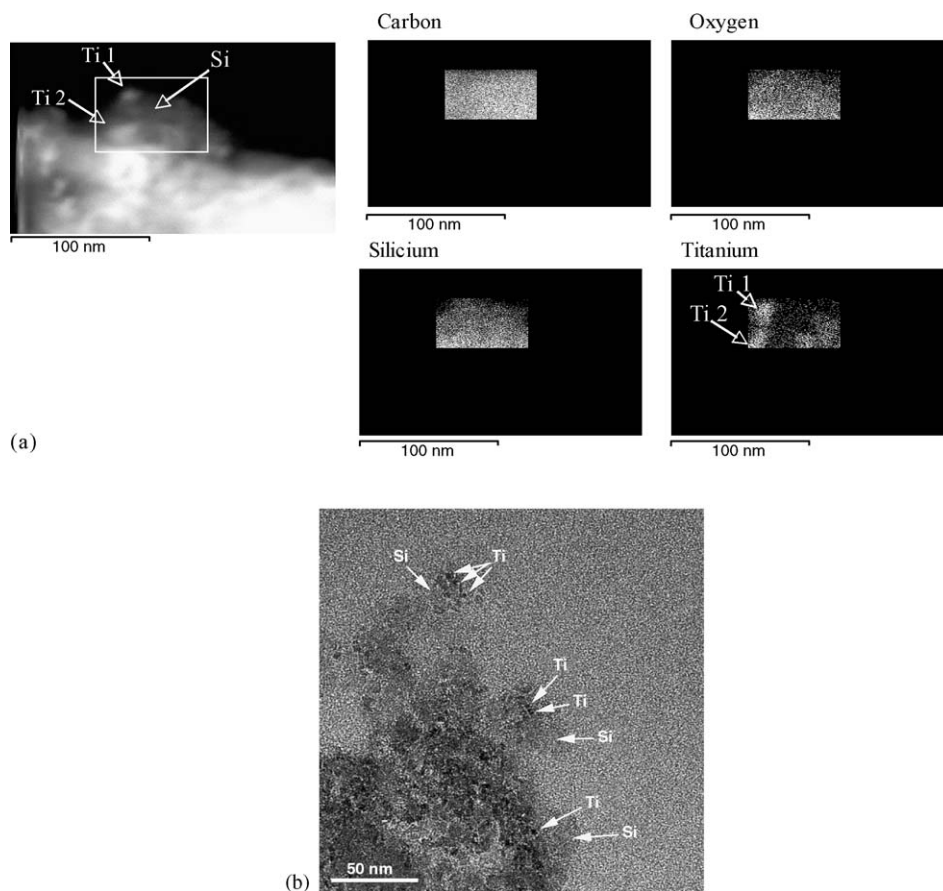


Fig. 5. (a) Energy dispersive spectroscopy (EDS) of the cotton TiO_2 - SiO_2 sample. Elements Mapp INCA Oxford. For other details see text and (b) EDS spectroscopy of the cotton TiO_2 - SiO_2 sample showing the Si and Ti particles present on the textile surface.

Finally, Fig. 6d shows the IR-spectra of samples in traces (a)–(d) for cotton samples of TiO_2 - SiO_2 stained with red wine irradiated under solar-simulated light for up to 48 h. This last run shows that there is no peak deterioration of the cellulose (polysaccharide), which makes up the cotton fiber within the irradiation period. But at the same time, it is not possible to detect the peaks related to the photodegradation of the red wine pigment(s) in a differentiated way. Both peaks overlap as reported previously in Fig. 5a at $\sim 1026\text{ cm}^{-1}$. In another set of experiments, we varied the intensity of the solar simulator by increasing the applied light intensity to 90 mW/cm^2 . This corresponds to 90% of maximum solar light intensity. The results obtained were the same as the ones reported in Fig. 6d for TiO_2 - SiO_2 red wine-stained cotton samples. Odenbrand et al. have shown that for coprecipitated silica-titania mixtures, isolated SiO_4 -tetrahedra and exposed Ti^{4+} -tetrahedra were formed in mixtures consisting of amorphous silica and anatase phases [20].

3.4. X-ray diffraction measurements

The crystallinity of the TiO_2 formed on the textile surface of the TiO_2 - SiO_2 -coated cotton textile was investigated. The cotton immersed once in the mixture of both colloids by the procedure outlined in Section 2. The bulk of the X-ray sig-

nal originated from the cotton underlying substrate. Since the amount of TiO_2 was low as determined by elemental analysis ($1.5\text{ mg of TiO}_2/\text{cm}^2$ or 5.8%, w/w) and the particles presented sizes between 4 and 8 nm as detected by TEM, TiO_2 did not show a crystalline phase. This indicates that the coating of TiO_2 - SiO_2 is predominantly amorphous. But if the cotton is immersed four times in the mixtures of TiO_2 and SiO_2 colloids and dried successively after each immersion before the final thermal treatment at 100°C , small peaks at $\theta = 25^\circ$, 37° and 48° were observed. These are associated with broad diffraction peaks corresponding to anatase crystallites. The observed film was predominantly amorphous with a small content of anatase.

The anatase formation originates from the hydrolyzed- TiO_2 species in the colloidal mixture leading to nucleation and growth of TiO_2 -anatase crystals under very mild heat treatment. Since amorphous TiO_2 is only expected at temperatures of 100°C , the cotton must have a structure-forming function on the amorphous TiO_2 colloid. The texture of the cotton loaded TiO_2 - SiO_2 changes significantly after several immersions in the two colloid mixture and becomes considerably more rough and less flexible. This is not desirable in the manufacture of cotton textiles, since it changes the cotton texture and handling which is an essential property for the cotton use. Therefore, no more experimental

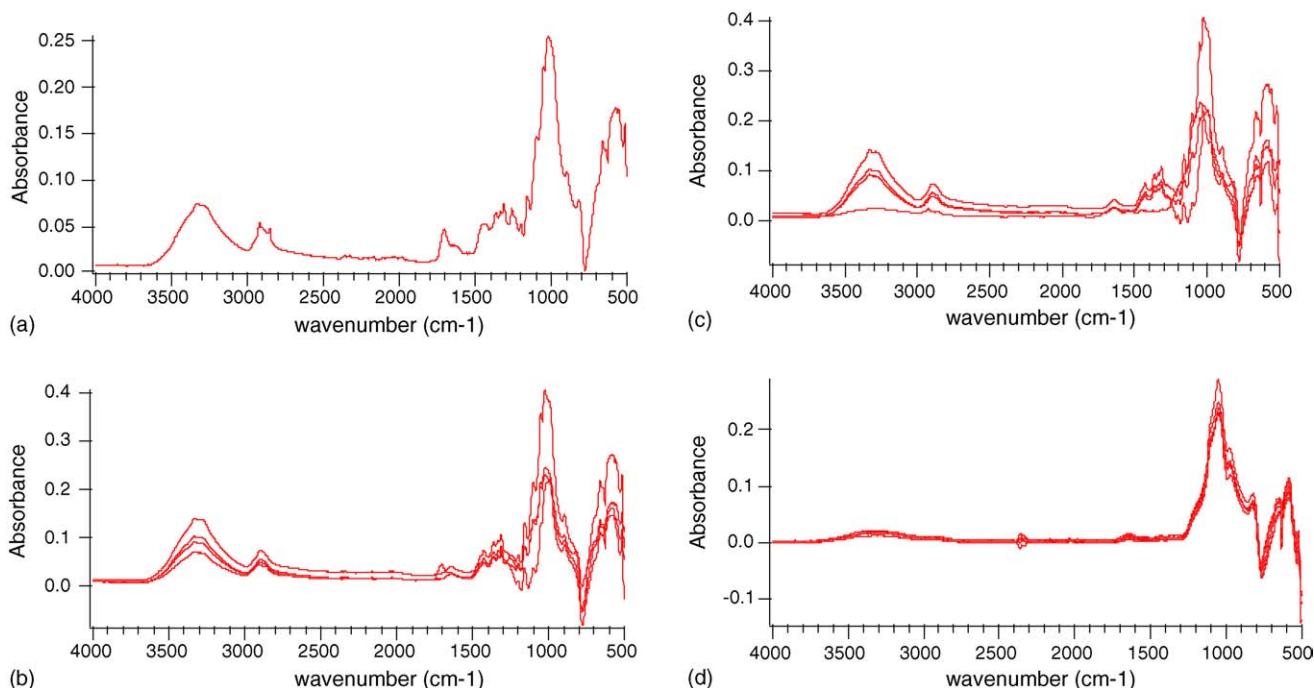
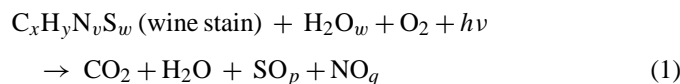


Fig. 6. (a) Reference IR-spectrum of wine on glass showing the 1026 cm⁻¹ peak of polysaccharides found in the cotton fibers overlapping with the wine pigment tannin peak; (b) IR-spectra of bleached cotton at: (a) zero time, (b) 8 h, (c) 24 h and (d) 48 h irradiation with a solar simulator (90 mW/cm²). Trace (a) is the highest one and traces (b)–(d) follow in descending order; (c) IR-spectra of TiO₂-SiO₂-coated cotton at: (a) zero time, (b) 8 h, (c) 24 h and (d) 48 h irradiation with a solar simulator (90 mW/cm²). Trace (a) is the highest one and traces (b)–(d) follow in descending order; (d) IR-spectra of TiO₂-SiO₂-coated cotton where a stain of red wine has been deposited, at: (a) zero time, (b) 8 h, (c) 24 h and (d) 48 h irradiation with a solar simulator (90 mW/cm²). Trace (a) is the highest one and traces (b)–(d) follow in descending order.

work was carried out on thick TiO₂-SiO₂-coated cotton samples.

3.5. Evolution of CO₂ from TiO₂-SiO₂-coated textiles under solar simulated light

The mineralization of the red wine stain on the TiO₂-SiO₂-coated cotton sample prepared as described in Section 2 was measured by gas chromatography (GC). The results are shown in Fig. 7. The production of CO₂ under Suntest light irradiation is attained with a light dose corresponding to 50% of the maximum sun intensity. The release of CO₂ follows reaction (1) and occurs with the concomitant formation of a small amount of cations and anions [10–13].



According to reaction (1), the release of CO₂ is proportional to the oxidative decomposition of the red wine stain as seen in trace (4). But the corrosion of the cotton due to the TiO₂ layers presence also occurs as shown in trace (3). The stained sample was irradiated for 24 h with a Suntest solar light simulator with a light intensity of 90 mW/cm² and the release of CO₂ was followed by gas chromatography (GC) for 24 h. A more efficient discoloration and CO₂ production was observed for the TiO₂-SiO₂-coated cotton compared to samples coated only with TiO₂ because SiO₂ increases the adsorption of the red wine [21–24]. Then, the surface organic compounds are degraded by

the photoactive TiO₂ in close contact with the SiO₂ surrounding layers.

3.6. Photodiscoloration mechanism of red wine stains

Fig. 8 shows the proposed mechanism of discoloration of the tannin pigments of red wine on TiO₂-coated textiles under

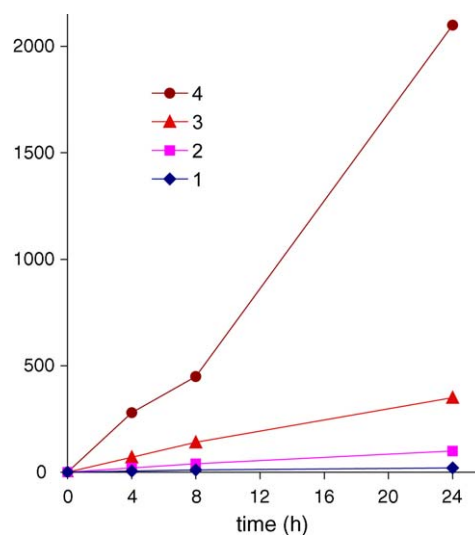


Fig. 7. Evolution of CO₂ during the irradiation of bleached-cotton textile stained with wine under solar-simulated light (50 mW/cm²) from: (1) cotton textile, (2) cotton textile with wine, (3) cotton textile-coated TiO₂-SiO₂ and (4) cotton textile-coated TiO₂-SiO₂ stained with wine.

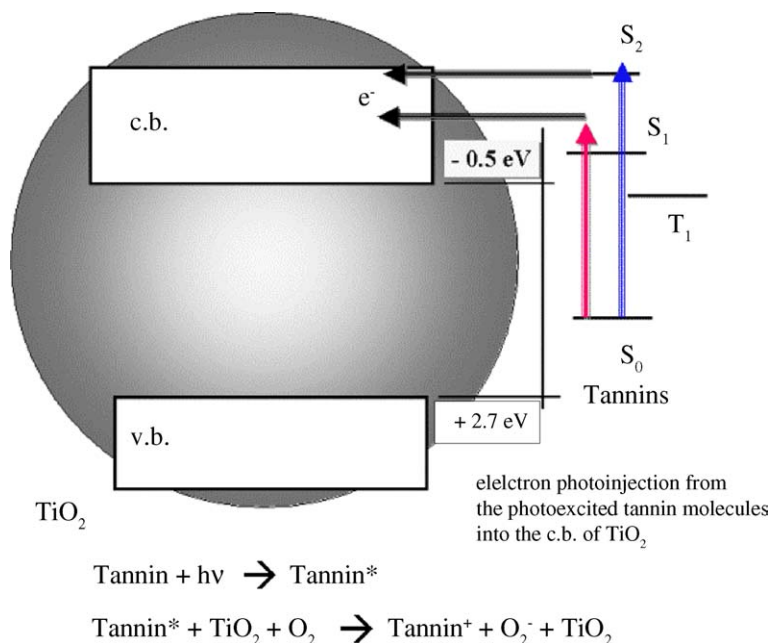
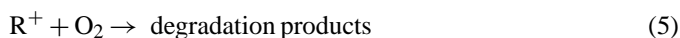
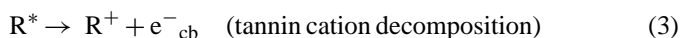
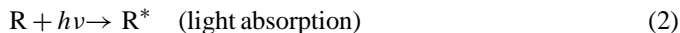


Fig. 8. Suggested mechanism for the discoloration of the red wine pigment tannin by the Suntest solar simulator.

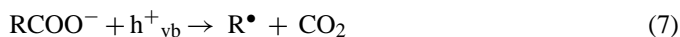
visible light. The electron photo-injection from the photo-excited tannin molecule into the conduction band of TiO_2 due to the tannin sensitization under visible light has also been reported for lycopene and carotenoids. These pigments are responsible for the coloration of red wine, tomatoes and various berries [25,26]. The wine pigment cation, injecting an electron into the conduction band of TiO_2 would allow reaction (1) to proceed inducing the sequence of reactions (2–6).



The direct reaction of the excited pigment of the organic compound (R^*) with photo-induced holes (h^+) at later stages of the discoloration is possible due to the transparent intermediates produced consisting of carboxylic acid and other colorless organic compound. At this stage, the TiO_2 absorbs the incoming UV light generating h^+_{cb}



in of reaction (6) the generated holes can then react directly with carboxylic acids generating CO_2 through a photo-Kolbe type reaction [27] as shown below.



4. Conclusions

This study reports the structure-forming function of cotton textile at low temperatures on a mixture of TiO_2 – SiO_2 colloids effective in photodiscoloration of red wine stains under solar-simulated radiation. The amorphous SiO_2 was detected by EDS

to enrobe but not continuously the Ti particles. The processing temperature at 100°C allows the procedure used to be applied to organic polymers, plastics and other non-heat resistant materials. This is the potential market application of this study. The sol–gel preparation allowed the preparation of photoactive coatings of TiO_2 – SiO_2 at low temperatures, which do not modify or damage the cotton structure. A transparent coating was obtained. The TiO_2 – SiO_2 coating has been characterized by surface techniques in regard to microstructure and composition. 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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