Photocatalytic self-cleaning of modified cotton textiles by TiO$_2$ clusters attached by chemical spacers

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Abstract

Insights are provided into the attachment of TiO$_2$ on cotton surfaces using chemical spacers. The spacers are attached on the cotton by formation of an ester-bond. The TiO$_2$ binds to the cotton by chemical means and the textiles present self-cleaning properties. The method to prepare TiO$_2$ coated cotton surfaces did not employ toxic compounds or solvents. The deposition of TiO$_2$ on the cotton textile surface is non-homogeneous due to the irregular surface of the cotton fabrics used. The TiO$_2$ coating consisted of transparent layers t and did not change the ATR-IR spectra of the spacers used to attach the TiO$_2$ on the cellulose hydroxyl groups. The increase of the curing temperature during the esterification of the spacer by the cellulose-OH is shown to increase the amount of spacer that could be bound to the cotton textile, but curing at higher temperature did not always produce the coated cotton textiles with the best self-cleaning properties. The limit of the heat treatment was 210 °C applied for a few minutes. Above this temperature a slight yellowing of the cotton occurred. The self-cleaning activity of the cotton loaded titania was evaluated for two cotton samples using different spacers within a 24 h light irradiation period. Stains of wine, make-up, perspiration and coffee were deposited on the textiles for this purpose. Electron microscopy was able to show the details for the coverage of TiO$_2$ Degussa P25 on two types of cotton. The self-cleaning action makes possible to space at bigger intervals the cleaning of cotton tissues used in the aircraft, clothing and health industry since the self-cleaning is only partially effective in abating completely the dirt.
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1. Introduction

Cotton is almost pure cellulose (~98%), flax contains about 80% cellulose and wood contains cellulose up to 40–50%. Cellulose is the most abundant naturally occurring organic substance, being found in the cell walls of higher plants and it is not water soluble. Upon acid hydrolysis the glucose units of cellulose were shown to be *beta* (1–4) linked. Light scattering methods reveal that the cellulose is made up from 5000 to 10,000 glucose units. The unique properties of cellulose result from its ability to form long-chain fibers called micro-fibrils. The *beta*-glucose links allow an extended rigid conformation. Another consequence of the alternating top/bottom glucose alignment is that OH-groups of adjacent chains allow an extensive H-bonding between chains. This extensive inter-chain H-bonding provides a rigid *beta*-conformation making the cellulose fibers resistant to the action of concentrated NaOH solutions.

This study focuses on the introduction of a spacer onto a cotton textile by chemical means. This spacer needs to have at least two free carboxylic groups to be able to bind both the cotton and the TiO$_2$. The spacer should also have an acceptable chemical and thermal stability. Cotton–cellulose is a polysaccharide with many free hydroxyl groups on the surface. The spacer will be introduced by formation of a covalent ester-bond (Scheme 1). This implies esterification of one carboxylic group of the spacer by a hydroxyl group
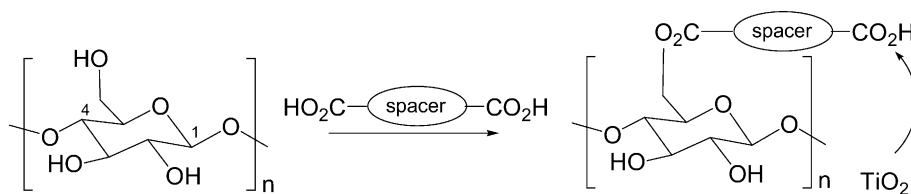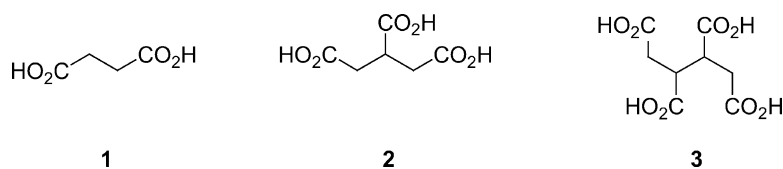

Scheme 1.

of cellulose. The second spacer carboxylic group is meant to anchor TiO_2 by electrostatic interaction [1,2]. Previous work in our laboratory showed that TiO_2 presents a strong electrostatic interaction with carboxylic groups [3].

TiO_2 has been shown to generate highly oxidative radical species ($HO_2^{\bullet-}$, $HO^{\bullet}$) and oxidants (H_2O_2) from oxygen and water vapor under band-gap light irradiation. These reactive species are able to discolor partially or totally organic stains like wine, coffee and make-up. The spacer sought should be resistant to the oxidative radical species generated by the photo-activity of TiO_2 during the self-cleaning over long periods. Additionally, the spacer should present good thermal stability, since temperatures of up to 200 °C are used during the linking of the spacers to cotton. In this way an effective degradation of the stains deposited on the cotton textiles can be achieved.

During this study commercially available non-toxic and low cost saturated poly-carboxylic acids **1–3** were used as spacers to attach TiO_2 to the cotton (Scheme 2). Succinic acid (**1**), 1,2,3-propanetricarboxylic acid (**2**) and 1,2,3,4-butanetetracarboxylic acid (**3**) have been previously reported to be able to bind to cotton [4]. These spacers have in common a saturated carbon framework and ester functions resistant to radical and oxidative species.

Recently, several studies reported the nucleation of anatase at relatively low temperatures (a) from sol–gel coated substrates exposed to boiling water [5], (b) from sol–gel exposed to water vapor [5], (c) from TiO_2–SiO_2 films exposed to water vapor [6] and (d) from titania tetra-isopropyl orthotitanate (TTIP) rendering particle sizes of anatase of ~20 nm. The anatase phase was attained on the cotton textile surface by boiling the textiles in water for 3 h [7]. 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 [8,9]. Cotton presents moderate heat resistance and can be heated for a few minutes up to 210 °C. In this study we will show that partial discoloration of the natural pigments found in red wine is possible by the TiO_2 attached through chemical spacers to cotton textiles.

2. Experimental

2.1. Materials and reagents

The white cotton textiles were supplied by Cilander AG, Herisau, Switzerland. Two types of cotton textiles have been used throughout this work. The first type, cotton C_2, with a minimal chemical treatment and the second one cotton E, which had undergone an extensive chemical treatment. The C_2 type cotton: refers to the cotton that was bleached with H_2O_2 using NaOH to discolor the natural pigments and stains of the cellulose fibers. Afterwards this cotton is washed and finally a treatment with ammonia is applied and the ammonia eliminated by evaporation. The E type cotton: was networked with an adequate cross-linking agent, followed by softener and a brightener in the last step. Due to the additional treatment, the OH-groups of the cellulose are partially blocked for reaction with a spacer.

Succinic acid (**1**), 1,2,3-propanetricarboxylic acid (**2**) and 1,2,3,4-butanetetracarboxylic acid (**3**) from Fluka, Acros Organics and Lancaster were p.a. reagents and used as received. The TiO_2 Degussa P25, having BET area 55 m^2/g, was provided by Degussa AG (Hanau, Germany).

The cotton samples of wine, coffee, make-up and perspiration have been stained with 50 μL of red wine, hot concentrated coffee and a make-up solution provided by Cilander AG. In the case of the perspiration, the standard testing solution was been used (Standarization of Textiles Tests Leipzig, 1981, p. 148, paragraph 36.3.2). A solution of 50 μL having a composition close to human perspiration made of L-histidine-chloride (0.5 g/L), NaCl (5 g/L) and $Na_2HPO_4 \cdot 12H_2O$ (5 g/L) were used to monitor the discoloring on the textile.

2.2. Attachment of the spacer to the cotton surface

Samples of cotton E or C_2 were immersed in an aqueous solution of the spacer **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

Scheme 2.

at $80\,°C < T < 90\,°C$), the textiles were cured at different temperatures (2 min at $115\,°C < T < 210\,°C$).

2.3. Loading of TiO$_2$ on the cotton surface

A TiO$_2$ suspension (5 g/L TiO$_2$ P25 Degussa) was sonicated for 30 min. The cotton textiles with loaded compounds **1**, **2** or **3** were immersed into this aqueous suspension of TiO$_2$ and heated for 1 h at $75\,°C$. After drying (1 h at $100\,°C$), the unbounded TiO$_2$ was washed out under sonication in distilled water for 5 min.

2.4. 1Irradiation procedure and evaluation of the textiles cleaning performance by gas chromatography (GC)

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 irradiation of the samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air-cooled at $45\,°C$ for 24 h. The Suntest lamp had a wavelength distribution with 7% of the photons between 290 and 400 nm and was provided for with a cut-off filter at 310 nm. The profile of the photons emitted between 3100 and 800 nm followed the solar spectrum with a light intensity of 50 mW/cm^2 corresponding to 50% of AM 1, the light intensity of the mid-day equatorial solar radiation. The CO$_2$ produced during the irradiation was measured in a GC (Carlo Erba, Milano) provided with a Poropak S column.

2.5. 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). Spectra were the results of 256 scans with a resolution of 2 cm^{-1} in the spectral range 4000–500 cm^{-1}.

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), both provided for with energy dispersive spectrometer (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× up to 450,000× were used

to characterize the samples. In this way, it was possible to provide overview images up to images in the range of resolution of atomic planes.

2.8. Chemical ionization mass spectrometry (CI-MS) analysis of the reactive intermediates involved in the binding of the spacer to cellulose

Intermediate identification of the acidic solutions of each spacer was performed by CI-MS and the mass spectra were recorded on a Nermag R 10-10 instrument in chemical ionization mode.

3. Results and discussion

3.1. Identification of the reactive intermediates present in the solutions used for the binding of the spacers to cellulose

By CI-MS of the acidic aqueous solutions of **1**–**3** (4%, w/w of NaH$_2$PO$_2$, 6%, w/w of polyacid) that were used to bind the spacer on the textiles, it was possible to show that the carboxylic groups in 1,4-position form intra-molecular anhydrides (Scheme 3). These anhydrides are more reactive than the corresponding carboxylic acids towards the formation of esters with the hydroxyl groups of cellulose. Similar observations have been reported previously [10–12].

3.2. Characterization of the ester link between the spacer 1–3 and cellulose by attenuated total reflection infrared spectroscopy (ATR-IR): effect of the curing temperature

ATR-IR spectroscopy of the textile samples confirmed the formation of ester bonds between the hydroxyl groups of cellulose and the spacers **1**–**3**. The textiles used for ATR-IR analysis were prepared according to Section 2.2 and further treated with a diluted solution of HCl (0.1N), to ensure complete protonation of the carboxylic groups. Whereas the characteristic stretching vibrations of the carbonyl functions in esters (RCOOR) and acids (RCOOH) are both in the same range between 1800 and 1650 cm^{-1}, the stretching vibration in the sodium carboxylates (RCOO$^-$Na$^+$) was significantly shifted to 1610–1560 cm^{-1}. This difference was used to show that the spacer was bound to the cotton and that some free carboxylic groups remained available to bind to the TiO$_2$.

The infrared spectrum of the C$_2$ cotton shows mainly a wide band at 1000 cm^{-1} due to the vibrational levels of the oligosaccharide units (Fig. 1, spectrum A). A similar spectrum was obtained from the E cotton textile. Spectrum B (Fig. 1) shows the vibrational band at 1739 cm^{-1} of the carbonyl function of the ester formed between the spacer **2** and the cotton after treatment. Spectrum C (Fig. 1) shows the effect of a basic treatment with a diluted solution of NaOH (0.1 N) on the cotton loaded with spacer **2**. The base addition
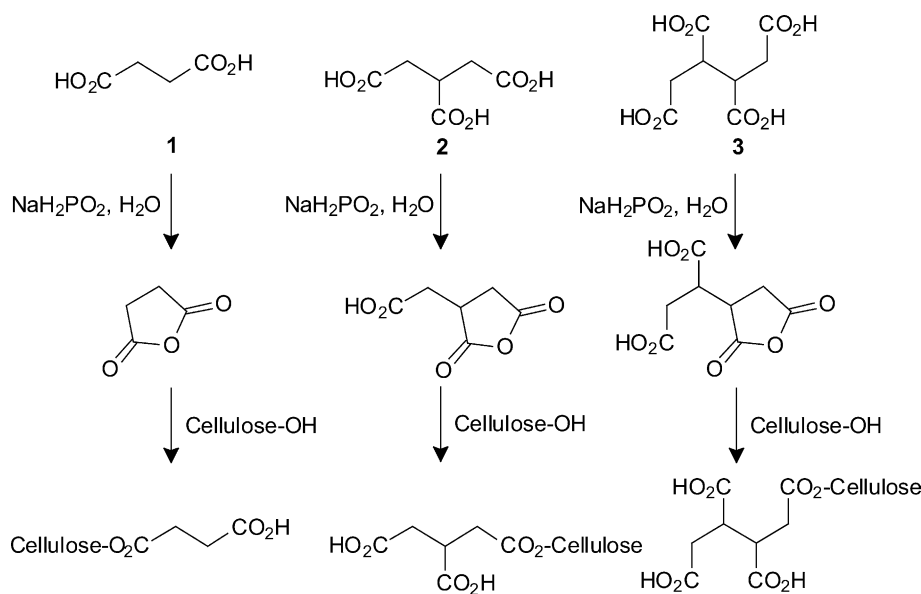
Scheme 3.

leads to complete deprotonation of the carboxylic groups of the spacer in the reaction $RCOOH \rightarrow RCOO^-Na^+$. The carbonyl functions of the $RCOO^-Na^+$ salt on the cotton were identified by their characteristic stretching vibration bands at $1585\,cm^{-1}$ with a peak that is different to the one coming from the ester stretching vibration. Similar shifts of the IR-bands were obtained for the three spacers **1–3** on the E and C_2 cotton samples. These results show that the spacer is bound to cellulose and that each spacer has some free carboxylic acid groups to bind TiO_2.

The surface of the band found in the $1700\,cm^{-1}$ region is proportional to the amount of ester-bonds formed between spacer **1** and the cotton surface. Fig. 2 shows the ATR-IR spectra of two textile samples E loaded with the same spacer
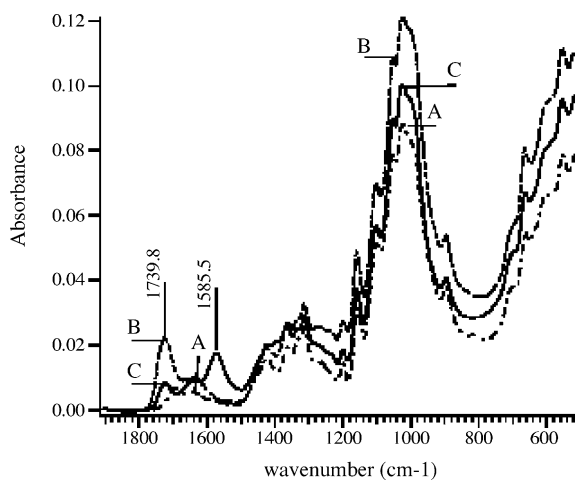
1, but cured at different temperatures (entry 1 (trace A) and entry 2 (trace B), Table 2). Trace B shows a ester band at $1717\,cm^{-1}$ about three times higher compared to the ester band observed at $1701\,cm^{-1}$ in trace A, indicating that the amount of spacer bound to the cotton increases with the curing temperature ($115–230\,°C$). This trend was observed with spacers **2** and **3** as well for both the E and C_2 textile. The curing temperature was limited to $200\,°C$, as at temperatures above this limit, the cotton becomes slightly yellow upon heating.

One can expect the esterification yield to increase with the curing temperature by shifting the equilibrium towards the ester, i.e. the binding of the spacer. Our results are in agreement with recent reports suggesting that the amount of spacer bound to cotton textiles increases with the curing temperature [12,13]. On thermodynamic grounds a higher curing temperature should allow a higher loading, but it has to be taken in account that the formation of multiple ester bonds

Fig. 1. Traces: (A) spectra of the untreated C_2 cotton textile; (B) spectra of the C_2 cotton textiles loaded with spacer **2** and washed with HCl (Table 1, entry 3); (C) spectra of the C_2 cotton textiles loaded with spacer **2** and washed with NaOH (Table 1, entry 3).
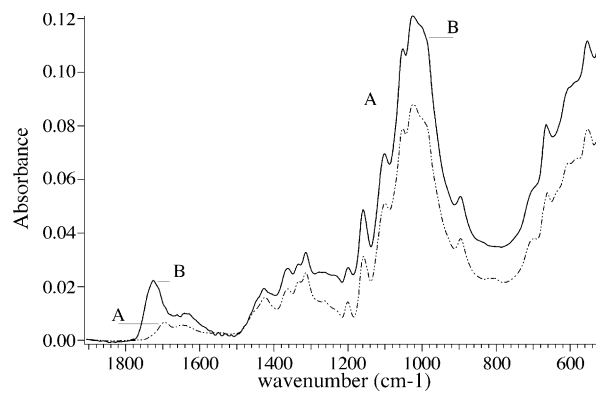

Fig. 2. ATR-IR spectra of entries 1 and 2 of Table 2 showing that the amount of spacer **1** bound to cellulose increases with the curing temperature. The peak surface at $1724\,cm^{-1}$ is proportional to the amounts of ester bonds.

with the same spacer molecule and cellulose are possible as well. In particular with spacers **2** and **3**, as after formation of a first ester bond, at least two COOH groups remain to form an intramolecular anhydride that undergoes esterification. Only a few temperatures were tried but no optimization was carried out during this study.

3.3. TiO₂ loading of C₂ and E cotton textiles loaded with spacers 1–3

The C₂ textile samples were loaded with the spacers **1–3** according to the drying and curing temperatures shown in Table 1. These modified C₂ cotton textiles were then loaded with TiO₂ according to the procedure described in Section 2.3. Additionally, three samples were prepared with higher concentrations of spacer (entries 7–9, Table 1). The TiO₂ loadings obtained for all samples were around 1% as the concentration of spacers were the same (entries 1–6). All solutions contained 6% (w/w) of spacer, corresponding to a molar concentration of 0.50 M for spacer **1**, 0.34 M for spacer **2** and 0.25 M for spacer **3**. Therefore, relative to the number of carboxylic groups, the normal concentration was observed to be the same (1N [–COOH]). The highest TiO₂ loadings were obtained with spacer **1** (1.34%, entry 7) and spacer **2** (1.36%, entry 4). These results show that the highest TiO₂ loading was not always obtained with the spacers that have the most carboxylic groups, but that the loading depends only on the amount of available carboxylic groups. Additionally, no clear correlation between the curing temperatures used to bind the spacer and the TiO₂ loading could be observed. The formation of more then one ester-bond between cellulose and the spacer molecule explains that even if a higher curing temperature favors greatly the esterification reaction, i.e. binding of more spacer, it does not always provide significantly more free carboxylic groups to bind TiO₂ and therefore similar loadings where obtained (entries 1 versus 2 and 5 versus 6). Formation of more than one ester bond are most likely with spacers **2** and **3**, since after formation of the first ester-bond they can still form intramolecular anhydrides. Somehow inconsistent loadings of TiO₂ (entries 3 versus 4), are caused by the non-homogenous surface of the cotton surface. These assumptions

Table 1
Loading of TiO₂ on the C₂ cotton textile with spacers **1–3**

Entry	Spacer	Concentration[a]	Drying (3 min) (°C)	Curing (2 min) (°C)	[TiO₂] (%)
1	**1**	0.50 (1.00)	85	115	0.96
2	**1**	0.50 (1.00)	90	200	1.06
3	**2**	0.34 (1.02)	90	175	0.47
4	**2**	0.34 (1.02)	90	200	1.36
5	**3**	0.25 (1.00)	85	110	0.93
6	**3**	0.25 (1.00)	90	200	0.82
7	**1**	1.01 (2.00)	90	200	1.34
8	**2**	0.68 (2.04)	90	200	0.76
9	**3**	0.51 (2.00)	90	200	1.09

[a] Molar concentration M (mol/L) of spacer for 6% (w/w) solutions of spacer (normal concentration N [(# COOH groups) × M].

Table 2
Loading of TiO₂ on the E cotton textile with spacers **1–3**

Sample	Spacer	Concentration[a]	Drying (3 min) (°C)	Curing (2 min) (°C)	[TiO₂] (%)
1	**1**	0.50 (1.00)	85	115	1.00
2	**1**	0.50 (1.00)	90	210	1.26
3	**2**	0.34 (1.02)	90	175	1.09
4	**2**	0.34 (1.02)	90	210	0.81
5	**3**	0.25 (1.00)	90	175	1.08
6	**3**	0.25 (1.00)	90	210	1.19

[a] Molar concentration M (mol/L) of spacer for 6% (w/w) solutions of spacer (normal concentration N [(# COOH groups) × M].

were confirmed by transmission electron microscopy (TEM) analysis of the textile samples (see Section 3.6).

The TiO₂ loadings on the modified E cotton are shown in Table 2. Two samples were prepared with each of the spacers **1–3** and subsequently cured at different temperatures. The loadings used were similar to the ones used on the C₂ cotton textiles (1%). The best loading of TiO₂ (1.26%) was obtained using spacer **1** (Table 2, entry 2). Again, higher curing temperature allowed only a slightly higher spacer loading and therefore a higher TiO₂ loading, except for the entries 4 versus 3. For C₂ cotton textiles, a higher curing temperature allows in principle a higher spacer loading on the cotton, but the non-homogeneous nature of the cotton surface in conjunction with the binding procedure used, does not allow the formation of an homogeneous distribution of TiO₂ clusters on the cotton surface. Even higher spacer concentrations (entries 7–9) were not conducive to higher TiO₂ loadings, since apparently saturation of the solution was reached.

The TiO₂ on the spacer loaded C₂ or E cotton samples did not modify the ATR-IR spectra (Figs. 1 and 2). The transparent TiO₂ coating allows using TiO₂ on colored textiles without modifying its optical properties.

3.4. Self-cleaning properties of the modified cotton textiles E and C₂

The self-cleaning properties of the TiO₂ loaded textiles are based on the highly oxidative intermediates generated at the cotton textile surface as shown in Fig. 3. The release of CO₂ due to wine, coffee, make-up and perspiration stains under light irradiation follows reaction (1):

$$C_xH_yN_vS_w + h\nu + H_2O_w + O_2$$
$$\rightarrow CO_2 + H_2O + SO_p + NO_q \qquad (1)$$
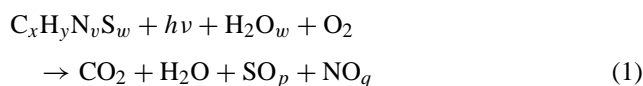
According to (1), the release of CO₂ is proportional to the oxidative decomposition of the organic stains. In this study, stains of wine, coffee, make-up and perspiration were deposited on the different TiO₂ loaded C₂ and E cotton textiles (entries 1–6, Table 1 and entries 1–6, Table 2). These samples were irradiated for 24 h with a Suntest solar light simulator (see Section 2) with a light intensity of 50 mW/cm² and the release of CO₂ was followed by gas chromatography (GC) during 24 h.
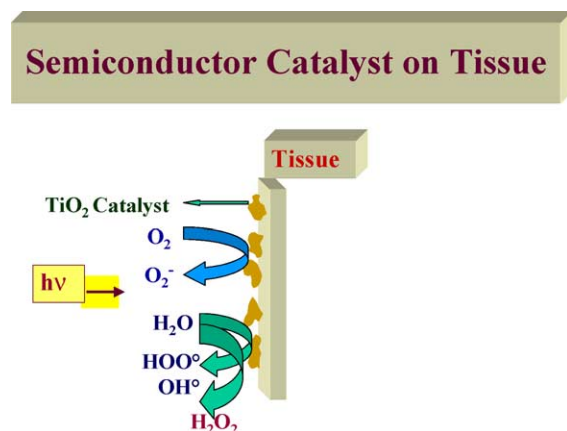
Fig. 3. Photocatalytic oxidative intermediates produced by TiO_2 on a cotton tissue in the presence of O_2 and H_2O vapor under light irradiation.

Fig. 4 shows the release of CO_2 in microliters after 24 h irradiation for stains loaded on TiO_2 coated cotton types C_2 and E. The release of CO_2 is not proportional to the loading of TiO_2 determined by elemental analysis due to the
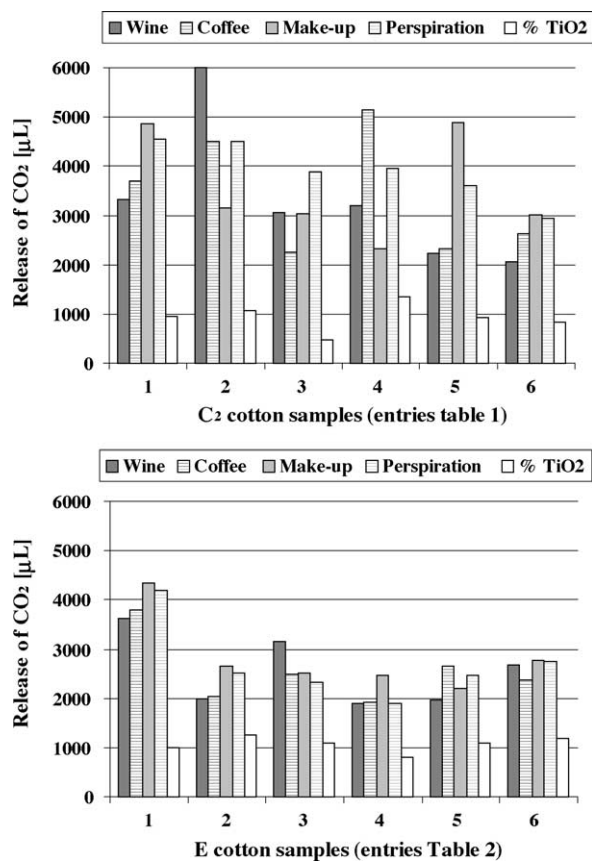

Fig. 4. Release of CO_2 from TiO_2 loaded E and C_2 cotton textiles under Suntest simulated solar light irradiation. For the different stains applied on both textile fabrics. The samples have been irradiated with a Suntest solar simulator (90 mW/cm^2) for 24 h. The stains of around 3 cm diameter were applied on the cotton spreading 50 μL of the stain solution by means of a micro-injector.

non-homogeneity in the distribution of the TiO_2 clusters on the cotton textile (see Section 3.6). The modified C_2 textiles showed better self-cleaning properties than the E cotton textiles as higher amount of CO_2 was measured (Fig. 4). As already mentioned, the main reason for this difference is that the E cotton textile had a more complete chemical pretreatment compared to the one used in C_2. This precludes the ester-link formation of the spacer with the cellulose-OH units in the case of cotton E. Elemental analysis of the samples before and after irradiation showed that the amount of TiO_2 on the textile surface did not change within 24 h under visible light irradiation during the self-cleaning process.

Without the use of any spacer, TiO_2 deposition of the C_2 and E samples was carried out by the method described in Section 2.3. The amount of TiO_2 found on the cotton surface amounted to less than 5% of the values reported in Table 1 of around 1%. For electrostatic reasons the hydroxyl groups of the cotton textiles are not able to bind the TiO_2 as the carboxyl groups are. These cotton samples under Suntest irradiation lead to almost no discoloration of wine and coffee stains. The amount of CO_2 evolved was <5% of the values obtained for wine (column 2) and coffee (column 4) in Fig. 4. Stained C_2 and E cotton samples as provided by AG Cilander with wine or coffee did not lead to any significant discoloration.

Irradiation of a cotton–spacer–TiO_2 sample showed that CO_2 was released even without stains. However, the amount of CO_2 released varied from 16% to 40% of the values observed when the same samples were stained with wine in the usual way. Over a few cycles, the CO_2 released by the stained sample showed reproducible values. The CO_2 released is due to either (i) C-containing impurities on the cotton surface introduced during the manufacturing process of the textile, (ii) slow degradation of the cotton spacer and (iii) CO_2 adsorbed from the air.

The degradation of the cotton was monitored by IR spectroscopy. Experiments were carried out taking the IR spectra of wine stained cotton sample (entry 2 in Table 1). Irradiation of the sample was carried out for 24 h and the sample was stained again with wine. The only peak that could be identified was at $1000 \, cm^{-1}$ and corresponds to the peak of the polysaccharide associated with the cotton cellulose groups. This peak did not vary during the four irradiation cycles. This suggests that no degradation of the cotton textile takes place during the four-irradiation cycles since the polysaccharide group is the most easily to degrade on the cotton surface. In view of this result, it is possible to suggest the decomposition of surface containing C-impurities or a very slow degradation of the spacer acting as the CO_2 source during irradiation of the cotton–TiO_2 samples.

3.5. Visual discoloration of the spots on the treated E and C_2 textiles after 24 h of irradiation

Fig. 5 shows the discoloration of the wine stains added to the TiO_2 loaded textiles using spacer **1** after 24 h of
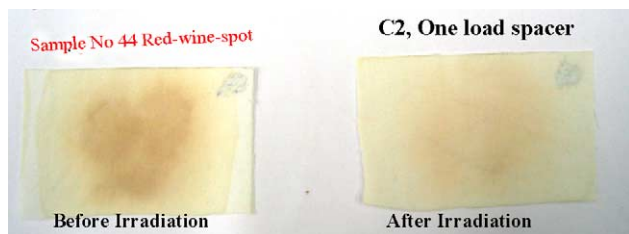
Fig. 5. Discoloration of a C_2 cotton sample stained wine (entry 2 in Table 1) after 24 h Suntest light irradiation.

irradiation. The comments below summarize the observations made during the discoloration experiments:

1. The best visual discolorations have been obtained with the samples of entry 2 (wine) and entry 4 (coffee) in Table 1. These samples are also those for which the highest release of CO_2 has been measured under light irradiation (Fig. 4). The CO_2 quantitative measurements confirm the discoloration observed by visual means.
2. The make-up stains were the most difficult to discolor. The low degree of discoloration may be due to the presence of inorganic dyes in the make-up that cannot be degraded by photocatalytic reactions. This highlights that the type of stain is a limitation to the efficiency of the self-cleaning textile.
3. The perspiration stains do not absorb strongly in the visible. They do not lend themselves for a meaningful visual inspection effect after 24 h irradiation.

3.6. Transmission electron microscopy (TEM) of TiO_2 clusters on C_2 and E loaded cotton textiles

Fig. 6a shows the irregular and non-continuous coverage of TiO_2 Degussa P25 crystallites on the surface of a C_2 cotton fiber. The middle electron microscopy picture (Fig. 6b) shows another area of the cotton C_2 in which the coating is continuous. This is a further proof of the influence of the non-homogeneity of the cotton fabric towards the deposition of TiO_2 by chemical means. In Fig. 6c, the size distribution of the TiO_2 Degussa P-25 with a dense distribution of sizes around 30 nm can be seen. Fig. 6c shows an enlargement of the clusters shown in Fig. 6a and b. The absence of TiO_2 clusters in the main body of the electron photographs presented in Fig. 6a and b are due to the microtome cutting of the cotton fiber. These pictures show that neither the cotton structure nor the nature of the spacer influences the size and non-homogeneous distribution of the TiO_2 P25 crystallites used to coat the cotton.

Fig. 7a shows the non-continuous deposition of TiO_2 crystallites on the 3 μm E-cotton fiber. The middle picture (Fig. 7b) shows another section of the cotton fabric showing a continuous TiO_2 layer. The absence of TiO_2 clusters in the main body of the electron photographs presented in Fig. 7a and b are due to the microtome cutting of the cotton fiber. Finally, Fig. 7c shows about the same TiO_2 Degussa P25 particle size distribution on cotton E as previously observed for cotton C_2. Fig. 7c shows an enlargement of the clusters shown in Fig. 7a and b.
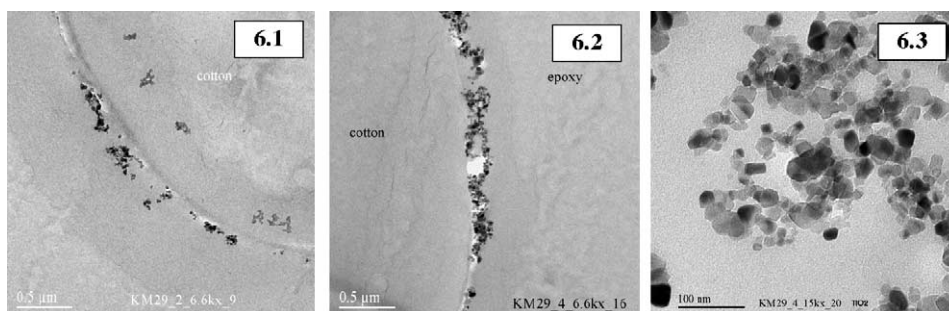

Fig. 6. High resolution electron microscopy of the TiO_2 cotton loaded sample (Table 1, entry 7).
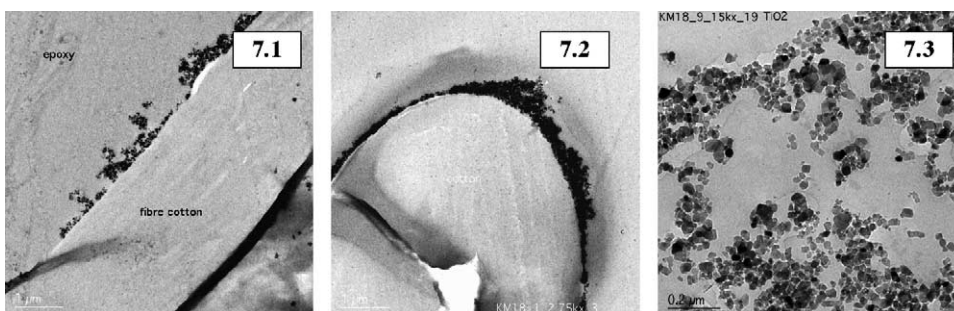

Fig. 7. High resolution electron microscopy of the TiO_2 cotton loaded sample (Table 2, entry 6).

108 K.T. Meilert et al. / Journal of Molecular Catalysis A: Chemical 237 (2005) 101–108

4. Conclusions

This study shows that it is possible to bind TiO_2 to cotton textiles through chemical spacers. Elemental analysis of the TiO_2 loadings on the cotton employing different spacers and different experimental conditions was determined to be around 1%. The coating procedure was straightforward and used non-toxic reagents. The TiO_2 loaded cotton textiles presented stable self-cleaning properties and allowed to eliminate partially the chromophore(s) of the red wine under daylight irradiation presenting long-term stable performance. ATR-IR spectroscopy shows the formation of ester bonds between the spacer and the cotton surface. Additionally, it could be shown that free carboxyl units remain available to bind the TiO_2. Without the spacer, none of the textiles binds efficiently TiO_2. The cellulose is not decomposed by the reactive species generated by the photo catalytic process within the testing period. The C_2 cotton with a much smaller degree of chemical pre-treatment than cotton E was more effective in the self-cleaning action of stains under light irradiation. As the use of higher spacer concentrations is limited by the saturation of the solutions, multilayer loading may allow a higher spacer and consequently TiO_2 loading. In this feasibility study, no optimisations have been made for the parameters reported.

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