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2 **Ultrasonic effect on the photocatalytic degradation of Rhodamine 6G**
3 **(Rh6G) dye by cotton fabrics loaded with TiO₂**

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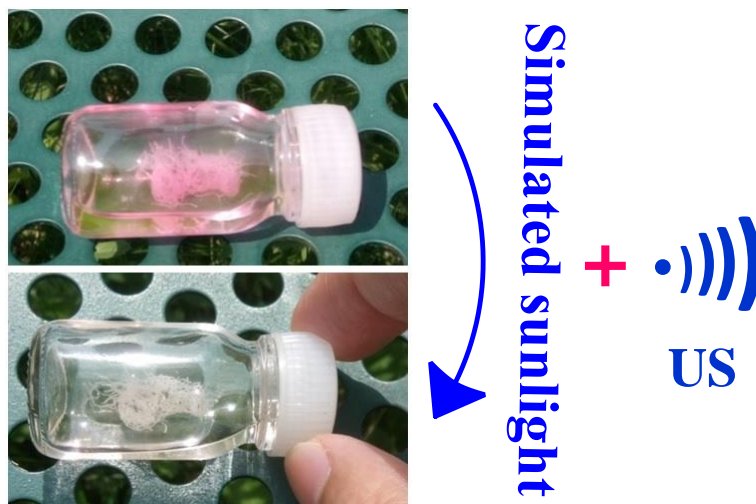
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21
22 [The Authors declare no conflict of interest.](#)

24 GRAPHICAL ABSTRACT

25



26

27 ABSTRACT

28 The effect of sonication on the photodegradation of Rhodamine 6G (Rh6G, a fluorone
29 dye) using woven cotton fabrics decorated with TiO₂ nanoparticles (NPs) has been
30 investigated. TiO₂ NPs were synthesized in situ by sol-gel method in the presence of cotton
31 textile and then hydrothermally treated. TiO₂-loaded fabrics were treated ultrasonically to test
32 adhesion to- and properties of the NPs on the fabrics. We demonstrate good adhesion and a
33 good stability of the NPs of TiO₂. Moreover, sonication substantially improved the
34 distribution on the surfaces and hence enhanced the fabrics catalytic activity. Either under UV
35 or simulated sunlight, ultrasonicated fabrics were found to have a high photocatalytic activity
36 towards Rh6G, used as a model dye. SEM, XPS, UV-Vis and FTIR spectroscopy, as well as
37 ground state diffuse reflectance (GSDR) and laser induced luminescence (LIL) were used to
38 characterize fabrics/TiO₂ samples in terms of topography, surface composition, influence of
39 hydrothermal treatment on photocatalytic activity, stability of TiO₂ NPs, electro-optical
40 properties of the modified fabrics, as well as the effect of ultrasonication on the
41 photodegradation of Rh6G. This work paves the way to a larger scale improvement of the
42 photocatalytic performances of TiO₂-loaded cotton fabrics by post-sonication.

43

44 **Keywords:** cotton fabrics, TiO₂ nanoparticles, adhesion, sonication, Rhodamine 6G,
45 photodegradation of dyes.

46 **Introduction**

47 Currently, there is a growing demand for imparting textiles a technical property in
48 addition to their intrinsic function of clothing. Indeed, functionalized textiles (**Horrocks and**
49 **Anand 2000; Blaser et al. 2008**), are used for different applications such as comfort (odour
50 elimination) (**Yuranova et al. 2006; Chen et al. 2010**), biomedical (prostheses, implants,
51 bandages ...) (**Li et al. 2015**), civil engineering (composites, geotextile...) (**Fangueiro 2011**)
52 and protection of individuals (protective clothing (**Scott 2005**), clothes for military (**Wilusz**
53 **2008**) or firemen (**Hristian et al. 2014**). Protection can also be provided for public ready-to-
54 wear clothes using textiles with protective TiO₂ nanoparticles. These nanomaterials protect
55 the skin from the UV-B (290-320 nm) and UV-A (320-400 nm) regions of the solar spectrum
56 (**Popov et al. 2005**), which consists of three ranges: UV-A, UV-B and UV-C (**McKinlay**
57 **1987; Diffey 1991**) (100 to 290 nm) being almost completely absorbed by the ozone layer in
58 the upper part of the Earth atmosphere.

59 To these above-mentioned remarkable features, one can also design textiles that possess
60 photocatalytic properties imparted by immobilized TiO₂ nanoparticles (**Bozzi et al. 2005;**
61 **Meilert et al. 2005; Xue et al. 2008; Abidi et al. 2009; Abid et al. 2016**) for the elimination
62 of dyes, fats, bacteria and viruses (**Bozzi et al. 2005**). It is well-known that titanium dioxide in
63 its crystalline anatase form is considered as the semiconductor oxide having the highest
64 photocatalytic activity and the best quantum yield (reaction rate in moles per second)
65 (**Hadjiivanov and Klissurski 1996**). The photocatalytic activity of TiO₂ rests on its excitation
66 with light the energy of which $h\nu \geq E_g$ (band gap energy) to create an electron pair (e⁻)/hole
67 (h⁺) by the transfer of an electron of the valence band to the conduction band. This electron
68 can be ejected and will react with oxygen adsorbed on the surface of TiO₂, while the hole h⁺
69 created can react with surface water, forming highly oxidizing hydroxyl radicals (OH[•])
70 responsible for the degradation of pollutants (**Min et al. 2007; Salvador 2007; Tariq et al.**
71 **2008; Ochiai and Fujishima 2012**). In addition to these salient chemical reactivity features,
72 TiO₂ is industrially employed due to its chemical stability, non-toxicity and low cost.

73 Either dyes or pigments employed in the textile industry undergo numerous testing;
74 probably the most important one is colour fastness (**Mohammad 2015; Rehman et al. 2017**).
75 It is thus important to investigate the adhesion of TiO₂ NPs to cotton textile in order to
76 understand the shelf life of the textile and its long-term use to catalyse the degradation of
77 dyes. Dealing with technical textile loaded with TiO₂ immobilized for photocatalytic purpose,

78 we have envisioned testing the stability of the immobilized nanocatalysts in terms of their (i)
79 adhesion, and (ii) photoactivity. In an academic laboratory scale, ultrasonication remains a
80 simple procedure to test the shaking off of the nanoparticles away from the textile support.
81 However, it was also necessary to investigate the reminiscent photoactivity of the textiles
82 after the adhesion testing.

83 In the recent literature, laboratory scale adhesion testing experiments, or in technical
84 wording, “colour fastness” were conducted by (i) light exposure (**Hinsch and Robinson**
85 **2018**), (ii) washing and flexibility (**Monzavi et al. 2017**), and (iii) rubbing (**Zou et al. 2018**).
86 In this context, we wished to contribute to this topic by bridging the gap between adhesion
87 phenomena and photocatalysis. In the course of the investigation of adhesion of TiO₂ to the
88 textiles by an ultrasonic test (“ultrasonic colour fastness”), we surprisingly discovered that the
89 ultrasonic waves increased the photocatalytic activity of TiO₂ NPs. This good example of
90 serendipity has encouraged us to deepen the study of the ultrasonic effect on the
91 photocatalytic properties of TiO₂-immobilized textiles.

92 In this paper, we describe the use of a cotton fabric that has been coated with TiO₂
93 nanoparticles for the photocatalyzed destruction of Rhodamine 6G (Rh6G) taken as model
94 organic dye as well as the frequently investigated Methylene Blue. **The rationale for choosing**
95 **these model compounds for testing textile photocatalyst is the following: Rhodamine 6G is a**
96 **product with well-known toxicity. Its LD50 lethal dose is 89.5 mg/kg for rats. Rh6G is**
97 **specifically used as a tracer dye in water to determine volumes, flow rates and directions of**
98 **flow and transport. Methylene Blue is most often used as a disinfectant and can be found in**
99 **natural waters through medical discharges. The presence of these two compounds in the**
100 **aquatic environment can be harmful for the environment (Budavari et al. 1989; Program**
101 **1989; Djaneye-Boundjou et al. 2001; George and Kishen 2007).**

102 The TiO₂ NPs were prepared *in situ* in the presence of cotton fabric and activated by a
103 hydrothermal treatment. The resulting hybrid textile has shown good photocatalytic activity
104 for the degradation of Remazol Brilliant Blue R (**Abid et al. 2016**). This method of
105 preparation of such specific fabrics is reliable and easy to produce. Although, much progress
106 has been made in the production of TiO₂-modified smart textiles, the examination of the
107 photocatalytic properties of the final product after adhesion test of TiO₂ remains sparse
108 despite the technological interest of this kind of investigation to the textile industry, hence the
109 motivation for this in-depth study.

110 Nanostructured cotton samples were characterized by several techniques (SEM, XPS,
111 UV-Vis and FTIR spectroscopy, GSDR and LIL). The final fabric/TiO₂ was used to degrade
112 Rhodamine 6G. The photodegradation of the dye molecules in fabric/TiO₂-containing
113 solutions exposed to a sun simulator was monitored by the colour change, observed by naked
114 eye and UV/Vis absorption spectroscopy.

115 **Experimental**

116 **Chemicals**

117 Chemical reagents were provided by **Sigma Aldrich were of analytical grade** and used
118 without further purification: Ti(OBu)₄, glacial acetic acid, Rhodamine 6G (~95%), tert-
119 butanol 99.7%. Cotton fabrics were common gauze bandages with more than 99% of cellulose
120 (purchased from Mega, Médicale Gaze S.A.).

121 **Preparation of cotton fabrics/TiO₂**

122 The cotton fabrics/TiO₂ samples were prepared as previously reported (**Abid et al.**
123 **2016**). It is a non-hydrolytic sol-gel process followed by a mild hydrothermal treatment at a
124 temperature below 140 °C. We used samples prepared at different temperatures (50, 110, 120
125 and 140 °C).

126 **Sonication of cotton fabrics**

127 The samples were placed in vials containing deionized water and subjected to
128 ultrasonication in a sonocleaner (Bandelin, Sonorex Digitec model; 860 W, 35kHz) for 5, 15
129 or 30 min. After sonication, they were washed with water, and dried for further studies.

130 **Characterization**

131 Scanning electron microscopy images were recorded using a Field Emission Scanning
132 Electron Microscope (FE-SEM) ZEISS SUPRA40, previously described (**Abid et al. 2016**).

133 X-ray photoelectron spectroscopy (XPS) measurements were recorded using a K Alpha
134 system (Thermo Fisher Scientific) fitted with Al X-ray source (hν=1486.6 eV; spot
135 size=400 μm) and an electron flood gun. Surface composition was determined using the
136 manufacturer's sensitivity factors.

137 FTIR spectra were acquired using a Bruker Tensor 27 IR spectrometer in the range of
138 400-4000 cm^{-1} spectral region. Samples were first washed 3 times with distilled water and
139 dried before analysis.

140 Ground state diffuse reflectance (GSDR) absorption spectra were recorded using an
141 OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given
142 elsewhere (**Vieira Ferreira and Ferreira Machado 2007; Errokh et al. 2016**).

143 The set-up for the laser induced luminescence (LIL) was described in the literature
144 (**Errokh et al. 2016**). Time-resolved emission spectra were performed in the nanosecond to
145 second time range with a N_2 laser (excitation wavelength=337 nm, PTI model 2000, ca.
146 600 ps FWHM, about 1 mJ per pulse). Emission spectra were obtained at 77 K, due to the fact
147 that, at the room temperature, luminescence intensity is negligible for the anatase form of
148 TiO_2 .

149 **Photocatalytic measurements**

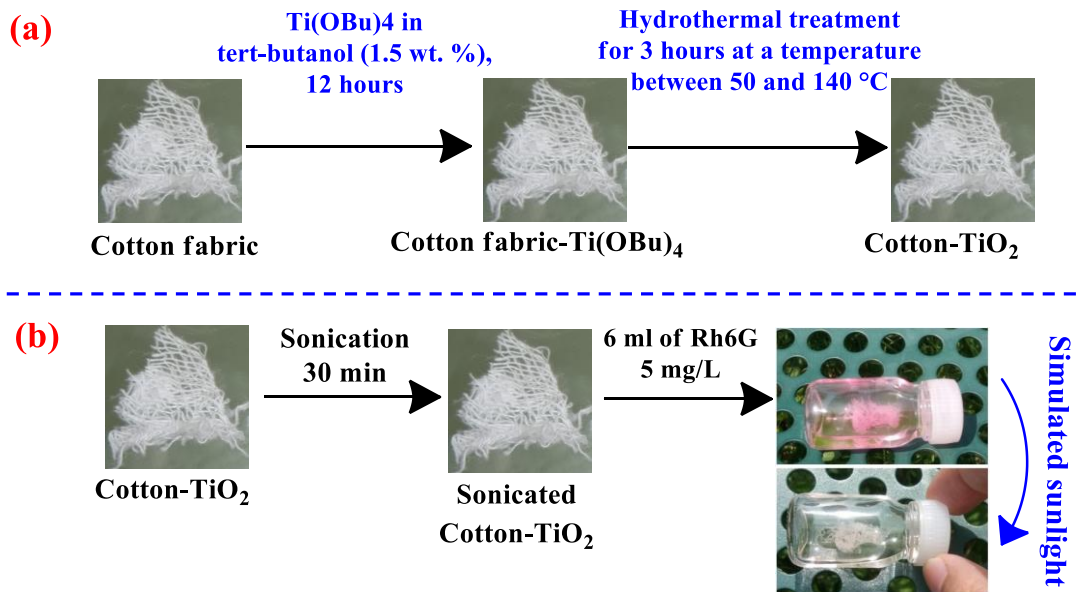
150 The irradiation tests were carried out using UVACUBE400 photoreactor, producing a
151 simulated sunlight; this device was used to test the photocatalytic activity of the cotton
152 fabrics/ TiO_2 samples. All measurements were performed with 30 mg (per step) of fabric/ TiO_2
153 in 6 ml of a Rh6G solution (5 mg/L) stored in the dark for 45 min to reach the adsorption
154 equilibrium. The absorbance of the Rh6G solution was monitored using a Varian Cary 50 Bio
155 UV-visible spectrophotometer controlled by the CaryWinUV software.

156

157 **Results and discussion**

158 The sequential steps of the work are presented in Fig. 1. In the first step of the
159 preparation of cotton- TiO_2 , woven cotton samples were immersed in a solution of $\text{Ti}(\text{OBu})_4$ in
160 tert-butanol for 12 hours at room temperature. Then, after drying, the cotton fabrics were
161 subjected to mild hydrothermal treatment for 3 hours at indicated temperature to crystallize
162 the TiO_2 layer generated on the surface of the cotton fibers (**Abid et al. 2016**). These samples
163 have been tested to determine optimal conditions for high performance photocatalytic activity.

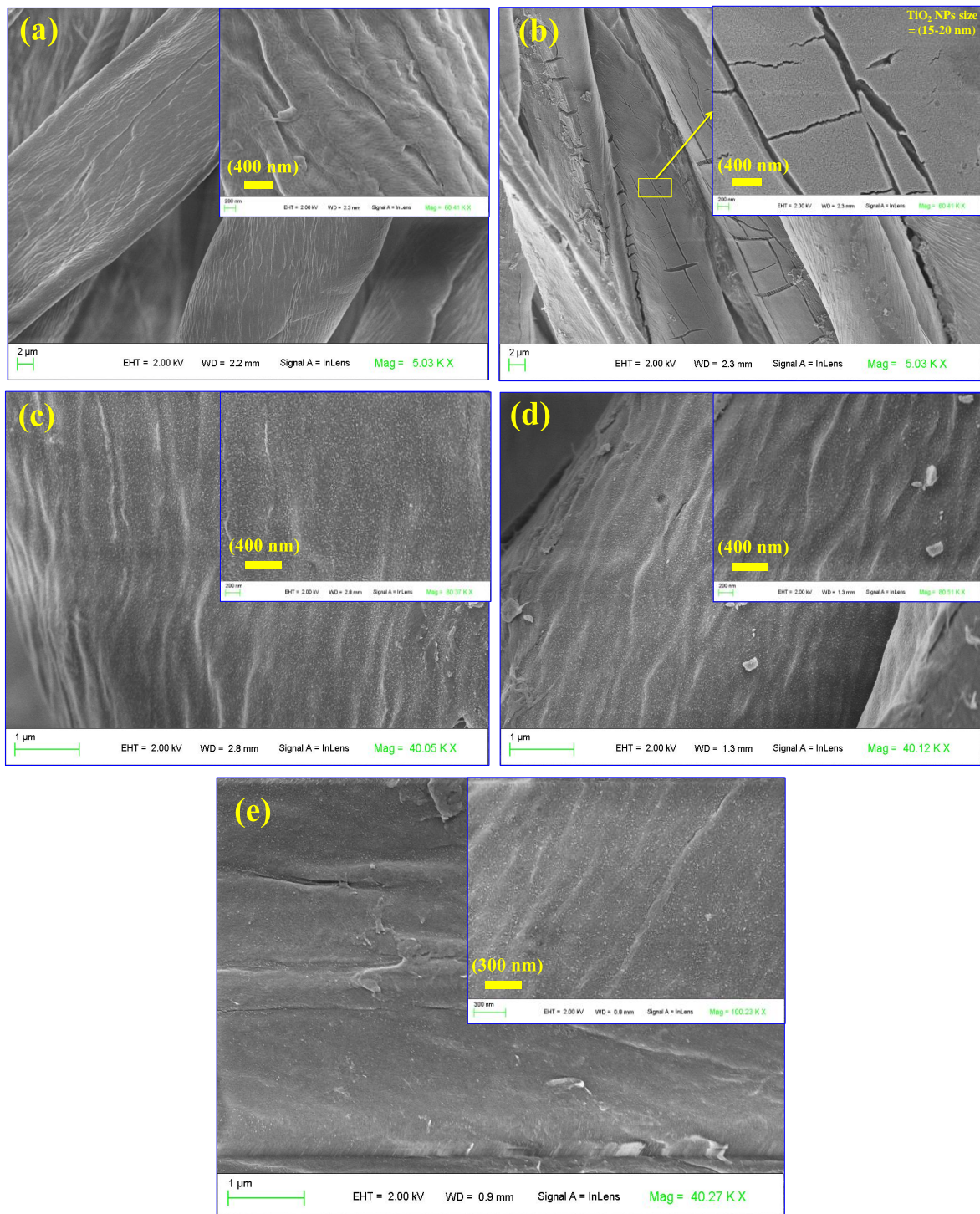
164 Cotton- TiO_2 samples were then sonicated at room temperature (Fig. 1(a)). 30 mg of
165 each sample was placed in a beaker containing 10 ml of distilled water and sonicated for 30
166 minutes.



167
 168 **Fig. 1** Illustration of the different steps followed to : (a) prepare different cotton-TiO₂ NPs samples
 169 and (b) sonication and photodegradation of Rh6G.

170 **Scanning electron microscopy (SEM)**

171 The SEM images of the different cotton samples are shown in Fig. 2. The morphology
 172 of cotton cellulose fibres prior to hydrothermal treatment is shown in Fig. 2(a). *In situ*
 173 synthesis of TiO₂ nanoparticles the latter for a very thin layer that is topping the cotton fibres.
 174 The mean size of the TiO₂ NPs is less than 20 nm for the hydrothermal treatment at 120 °C.



175

176 **Fig. 2** SEM images: (a) top view of pristine cotton substrate; (b) cotton fabric/TiO₂-120 °C; (c) sonicated cotton fabric/TiO₂-
 177 120 °C/5 min; (d) sonicated cotton fabric/TiO₂-120 °C/30 min and (e) cotton fabric/TiO₂-120 °C after 4 hours and 30 min
 178 exposure to simulated sunlight

179 Fabric/TiO₂ samples were sonicated for 5, 15 and 30 minutes to test the adhesion
 180 between the TiO₂ NPs layer and the woven cotton surface. Fig. 2(c) shows Fabric/TiO₂-
 181 120 °C after 5 minutes of sonication; one can note that the TiO₂ NPs layer withstands
 182 sonication even after 30 minutes of sonication. Another important observation concerns the

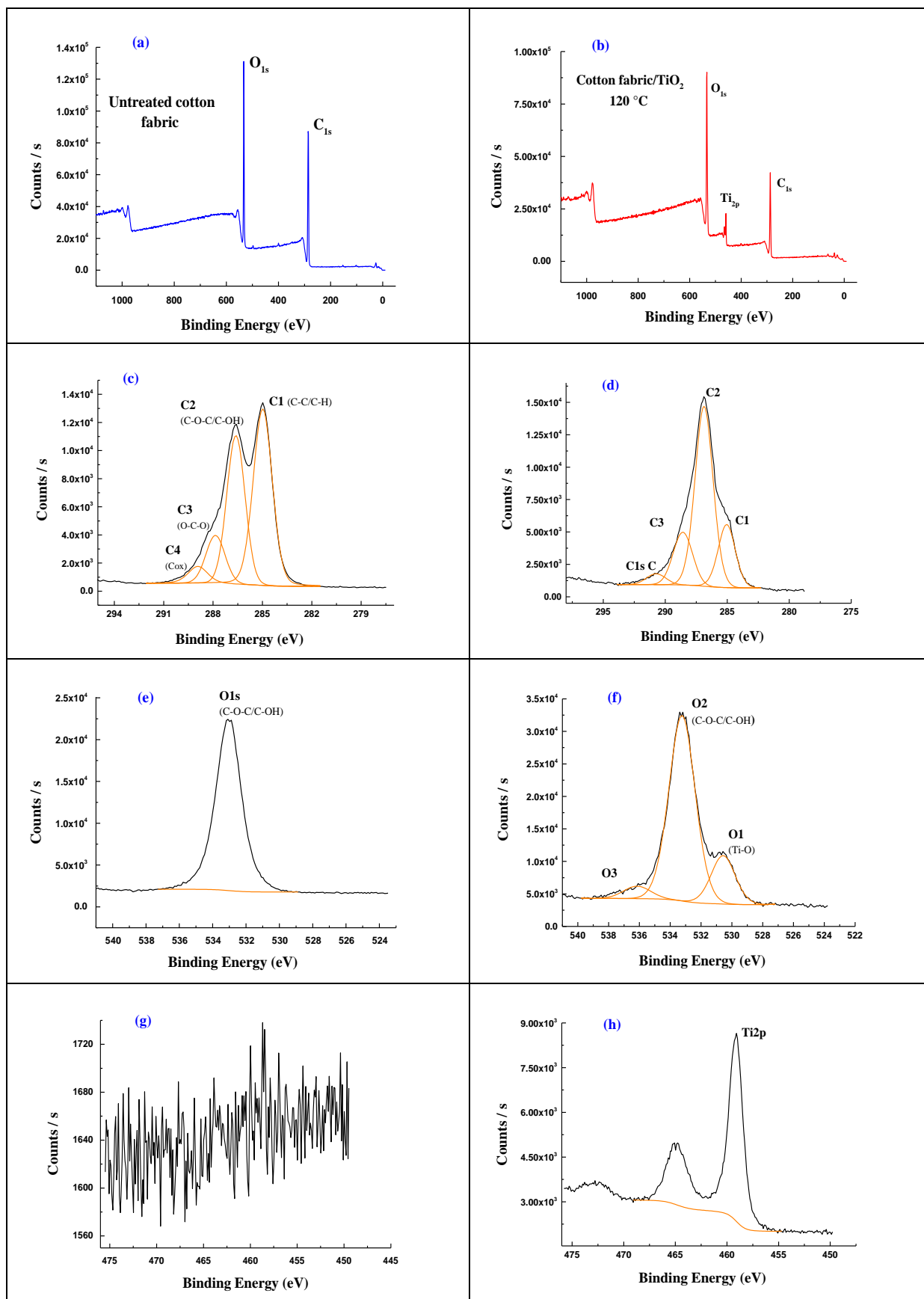
183 homogeneous spreading of TiO₂ NPs over the entire cotton fabrics (Figs. 2(c-d)) compared to
184 the surface shown in Fig. 2(b). To study the robustness of the catalytic property of the TiO₂-
185 containing fabric relatively to the irradiation of the simulated sunlight, a UVACUBE400
186 reactor was used. Indeed, the exposure of fabric/TiO₂ for one hour in the sun simulator
187 corresponds to about 9 days and 2 hours of exposure to the sun. The fabric/TiO₂ sample is
188 introduced in a tube and stays under insolation for 4 hours and 30 min in the photoreactor,
189 corresponding to 40 days and 9 hours of day light exposure. SEM image shown in Fig. 2(e)
190 confirms that the simulated sunlight treated surface remains identical to the sonicated one
191 (image (d)).

192 X-ray photoelectron spectroscopy (XPS)

193 Fig. 3 displays XPS spectra of untreated cotton (Fig. 3 (a, c, e, g)) and TiO₂ loaded
194 cotton fabric-120 °C (b, d, f, h). Survey regions are displayed in Fig. 3 (a (untreated cotton)
195 and b (Fabric/TiO₂-120 °C)); and the main peaks are C1s (285 eV), Ti2p (459 eV) and O1s
196 (532 eV). The untreated cotton does not contain TiO₂ NPs, which was confirmed by the shape
197 of Ti2p line obtained in Fig. 3(g), whereas fabric/TiO₂-120 °C spectrum exhibits a peak at
198 459 eV corresponding to Ti2p (Fig. 3(h)), which proves that the immobilization step of TiO₂
199 NPs on cotton samples was successfully accomplished. The C1s region presented in Fig. 3(c,
200 d) was fitted with four components centred at 285.0, 286.6, 288.3 and 289.5 eV, assigned to:
201 C-C/C-H bonds derived from the hydrocarbon contamination or treatment of cotton fabrics
202 (sizing); C-O-C/C-OH, O-C-O bonds corresponding to the hemi-acetal group characteristic of
203 cellulose; and finally, an oxidation peak which corresponds to an ester or an adsorbed
204 carbonate. Since a cellulose unit has only one hemiacetal carbon atom, we will choose this
205 atom as a marker element for cellulose in the following (Belgacem et al. 1995; Attia et al.
206 2013).

207 The O1s XPS region presented in Fig. 3 (e) reveals an asymmetric peak at 533.0 eV
208 attributed to C-O bonds in cellulose and other organic compounds. While for fabric/TiO₂-
209 120 °C, there is an additional contribution centred at 530.5 eV, which is characteristic of
210 metallic oxides and herein assigned to Ti-O bond (Atashbar et al. 1998).

211



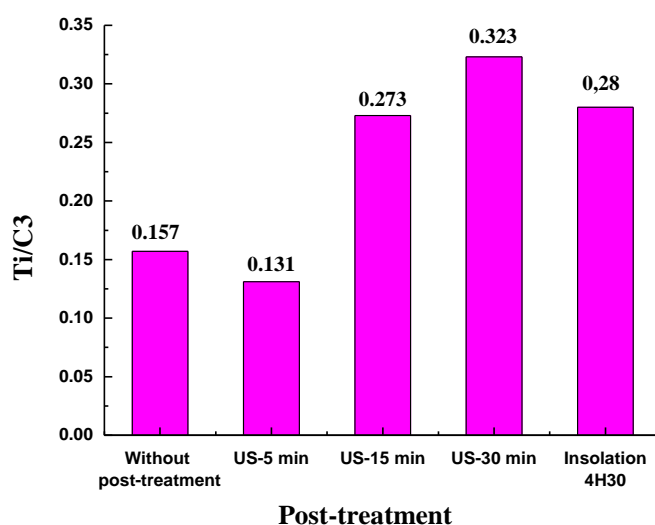
212 **Fig. 3** XPS spectra of untreated cotton fabric (a, c, e, g) and cotton fabric/TiO₂-120 °C (b, d, f, h)

213 XPS spectra were recorded for fabrics/TiO₂-(50, 110 and 140 °C). Table 1 shows the
 214 chemical composition of the untreated and TiO₂ loaded cotton fabrics. The cotton fabric used
 215 is contaminated even if it is a sterile sample. In fact, hydrocarbons contribute 33.2% to the
 216 composition of untreated cotton (regardless of hydrogen). Once TiO₂ has been deposited, this
 217 contribution is substantially reduced. We note also that the atomic percentage of TiO₂ is
 218 higher for the refluxed cotton fabric sample at 120 °C; this variation may be due to the
 219 difference in reflux temperatures.

220 **Table 1** Surface chemical composition of untreated and TiO₂ loaded woven cotton fabrics.

Samples	C1 (C-C/C-H)	C2 (C-O-C/C-OH)	C3 (O-C-O)	C4 (CO _x)	O1 (TiO ₂)	O2 (org)	Ti
Untreated cotton fabric	33.20	25.90	8.86	3.51	-	28.60	-
Fabric/TiO ₂ -50 °C	11.23	29.75	12.74	2.52	3.72	38.11	1.92
Fabric/TiO ₂ -110 °C	14.64	30.16	10.06	2.13	7.56	33.10	2.45
Fabric/TiO ₂ -120 °C	11.01	32.89	10.20	2.10	7.42	12.30	3.14
Fabric/TiO ₂ -140 °C	18.75	25.34	9.54	3.11	6.24	34.10	3.01

221 In order to study the effect of the adhesion test (sonication) on the fabric/TiO₂ as well as
 222 the effect of the exposure to simulated sunlight on the stability of the photocatalytic activity of
 223 TiO₂ NPs, 4 samples of 30 mg of cotton fabric/TiO₂-120 °C were taken for post-treatment
 224 under ultrasonic waves for 5, 15 and 30 min, respectively; and the 4th sample was placed in
 225 the photoreactor for an insolation of 4h30. These samples were then analysed in XPS, and the
 226 ratio Ti/C3 (Fig. 4) was compared, Ti being the marker element of titanium oxide and C3 that
 227 of cellulose. One can remark that the atomic percentage of Ti increases from a non-post-
 228 treated fabric/TiO₂-120 °C to a sonicated sample and the sonication time. This may be due to
 229 the fact that sonication leaves the distribution of TiO₂ NPs more homogeneous on the surface
 230 of the cotton fibres, improving the screening of the fabric. The ratio Ti/C3 for the insolated
 231 sample for 4 hours 30 min still reveals a high percentage of Ti, confirming that titanium oxide
 232 remains on the fabric surface despite the long treatment in the photoreactor.

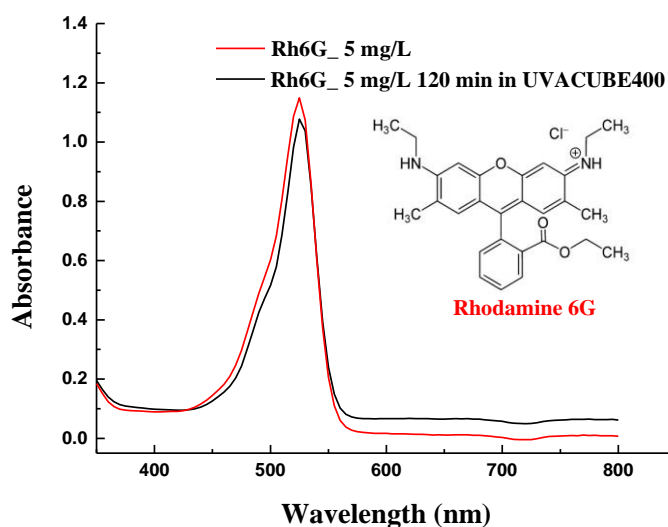


233
 234 **Fig. 4** Atomic ratios (Ti/C3) of samples untreated or treated (sonication and insolation) undergone by a fabric/TiO₂-120 °C
 235 sample

236 **Effect of fabric/TiO₂ treatment on the catalysed photodegradation of**
 237 **Rhodamine 6G**

238 *Stability of the dye and degradation time*

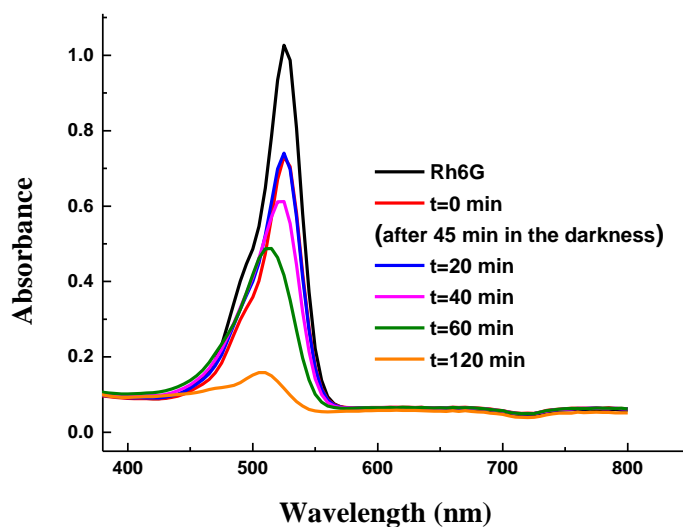
239 Prior to any photocatalytic test, a 5 mg/L aqueous solution of the model dye Rhodamine
 240 6G (Rh6G) was exposed to simulated sunlight in the absence of the fabric. Similarly, spectra
 241 of Rh6G solutions exposed to the photoreactor in the presence of fabric/TiO₂-120 °C were
 242 recorded to check the stability of the dye before and after contact with the photocatalytic
 243 textile. Fig. 5 shows the UV-vis spectra for this assay as well as the chemical formula of the
 244 Rh6G dye. It should be noted that the aqueous solution of Rh6G gives a peak at 525 nm and
 245 after exposure to the simulated sunlight, the absorbance remains the same, that is to say that
 246 the Rh6G was not degraded under irradiation at photoreactor for 120 minutes. This indicates
 247 that this dye is stable and can be used for testing the photocatalytic activity of the textile
 248 catalytic samples as it does not give any false positive result.



249

250 **Fig. 5** UV-Vis absorption spectra of Rh6G before and after irradiation in the UVACUBE400 photoreactor

251 To optimize the exposure time of the dye/textile mixture to light, several tests at
 252 different time intervals (20, 40, 60 and 120 min) were performed, considering the start time
 253 $t_0=45$ min prior in the obscurity. The different UV-vis spectra compared in [Fig.6](#), which show
 254 a progressive decrease in the maximum intensity of the initial Rh6G solution in the presence
 255 of fabric/TiO₂-120 °C from the beginning up to 2 hours of the insolation exposure. After
 256 120 min exposure of the Rh6G dye to light, the aqueous solution becomes colourless, which is
 257 here conferred to the activity of the photocatalytic textile, proving the photocatalytic activity
 258 of TiO₂ nanoparticles immobilized on the cotton fibres. However, the photocatalytic activity
 259 decreases after several operations. This may be associated to the presence of aggregating by-
 260 products on the surface of the photocatalyst (**Hamden et al. 2014**). On the one hand, Rh6G is
 261 stable after long exposure to simulated sunlight, and on the other hand the textile catalyst is
 262 active and induces bleaching of the dye.



263
 264 **Fig. 6** UV-Vis absorption spectra of Rh6G with and without fabric/TiO₂-120 °C at different time intervals under UV
 265 irradiation

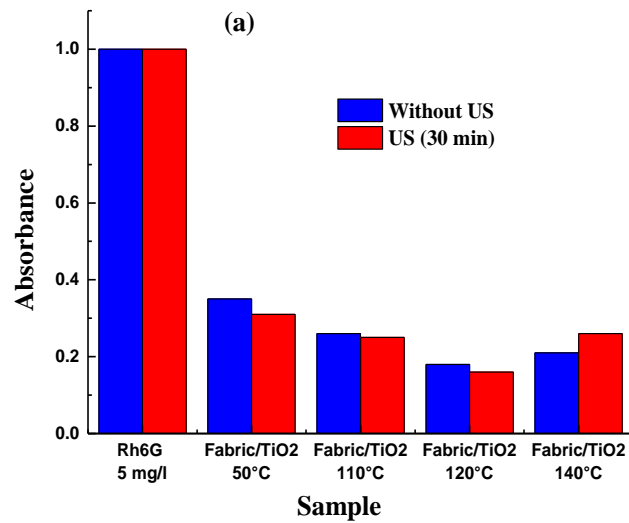
266 *Dual effects of hydrothermal and post-sonication treatments on the catalytic fabrics*

267 The treated fabric/TiO₂ hybrid nanocomposites were refluxed to 50, 110, 120 and
 268 140 °C then introduced to Rh6G aqueous solution before exposure to simulated sunlight.
 269 After sunlight irradiation for 120 minutes, all vials turned colourless which denotes the
 270 effective photocatalytic activity of the immobilized TiO₂ NPs. The sharp decrease in
 271 absorbance after exposure of the dye/textile mixtures to light in Fig. 7(a) emphasizes the
 272 successful photocatalytic degradation of Rh6G in the presence of the refluxed fabrics after
 273 being UV irradiated for 120 minutes.

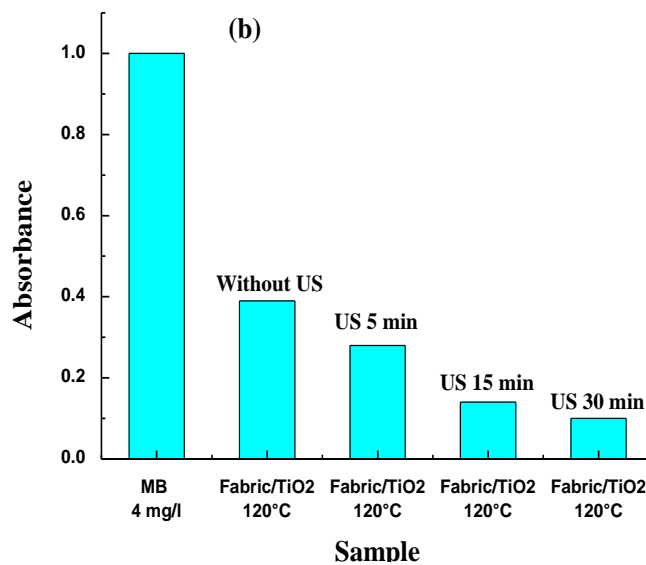
274 Furthermore, the hydrothermal treatment carried out at different temperatures
 275 undergone by the fabric/TiO₂ influences the catalytic power of TiO₂ NPs. It is noted that the
 276 optimum temperature for photodegradation of Rh6G is 120 °C (Fig. 7(a)). At higher
 277 temperature; namely 140 °C, we have a higher absorbance value than that obtained for the
 278 fabric prepared at 120 °C indicating a decrease in the photocatalytic activity at higher
 279 temperatures than 120 °C as previously reported (Abid et al. 2016).

280 An approach by means of ultrasonication (US) has been endeavoured with fabric/TiO₂
 281 to test the adhesion of TiO₂ to the cotton fabric. Three vials; each containing (30 mg of treated
 282 fabric/TiO₂) were ultrasonicated for 5, 15 and 30 min. Then, the samples were washed 3 times
 283 with distilled water. This was followed by placing 6 ml of the prepared Rh6G solution in each

284 vial containing the ultrasonicated treated fabrics and subjecting them to simulated sunlight
285 exposure for 120 minutes. The effect of post-sonication is shown in Fig.7(a) (red bars). As
286 one can observe, there is a significant decrease in absorbance compared to non-ultrasound
287 samples. This means that despite partial removal of the catalytic nanoparticles, the fabrics
288 retain photocatalytic activity. Surprisingly, the decrease in the spectral peak intensity of the
289 dye is systematically lower for post-sonicated hydrothermally treated fabrics, up to 120 °C.
290 This difference is significant and is not contained within the error bars, therefore testifying a
291 true synergetic effect of ultrasonication on the fabric. There is an exception for the TiO₂-
292 modified fabric that has been treated hydrothermally at 140 °C: we noted slight increase of
293 absorbance, mostly due to slight adhesion loss of TiO₂ nanoparticles. Indeed, XPS analysis of
294 cotton-TiO₂ samples reported in Table 1 shows that annealed sample at 140 °C has a Ti at.%
295 of 3.01% , slightly lower compared to 3.14% for 120 °C annealing temperature. Sonication
296 does not improve the photocatalytic character of the fabric annealed at 140 °C; for this reason
297 we further examined the performances of the fabric annealed at 120 °C (see Fig. 7b).
298



300



301

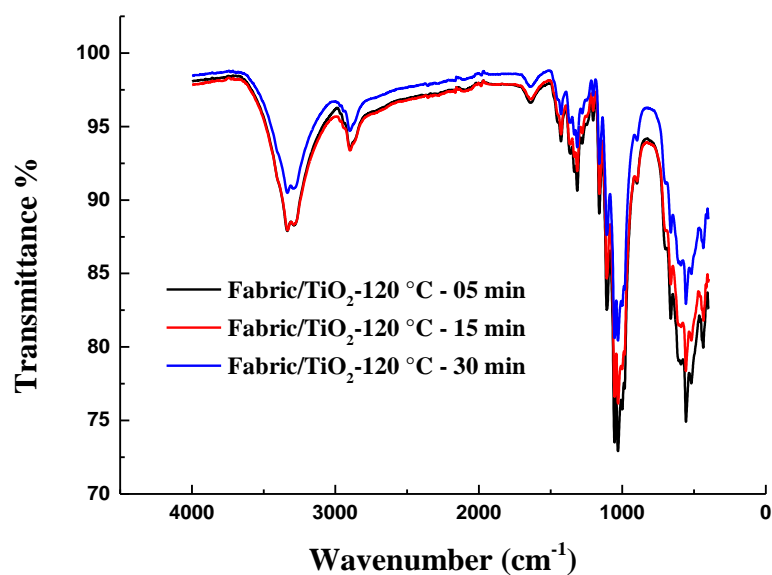
302 **Fig. 7** (a) UV-Vis absorption spectra of Rh6G after photocatalytic degradation in the presence of non-sonicated
 303 fabric/TiO₂ refluxed at (50, 110, 120 and 140 °C) subjected to UV irradiation. (b) Photodegradation spectrum of methylene
 304 blue with fabric/TiO₂-120 °C with and without sonication

305 To confirm that sonication increases the photocatalytic effect of TiO₂ NPs, we repeated
 306 a similar experiment with a fabric that has been hydrothermally treated at 120 °C. Three
 307 samples of this fabric were post-sonicated for 5, 15 and 30 min and then used to catalyse the
 308 photodegradation of Methylene Blue, MB (Fig.7(b)). It is clear that the fabric continues to act
 309 as a true photocatalyst after sonication since the maximum absorbance of the MB decreases
 310 by 60% compared to the pure MB solution (4 mg/L) after a short sonication period

311 (5 minutes). On the other hand, after a sonication of 30 minutes, one reaches to attain 90% of
312 degradation of MB.

313 The results displayed in Fig. 7 demonstrate the important improvement of the
314 photocatalytic performances of TiO₂ loaded cotton fabrics. This unexpected result, accounts
315 for the morphology displayed in the SEM images, which show that after sonication the
316 surface of the cotton becomes more homogeneous. Possibly, with an even distribution of the
317 cotton fabric, a larger specific surface was achieved by the TiO₂ NPs that remained on the
318 textile.

319 The adhesion between the cotton fabric and TiO₂ after sonication has been studied by
320 FT-IR spectroscopy in transmission mode. Hence, the treated fabrics were washed 3 times
321 with distilled water and dried before analysed by FTIRS. Fig. 8 illustrates the infrared spectra
322 of treated fabric/TiO₂, showing no changes in the wave numbers of the characteristic peaks of
323 the three treated samples after 5, 15 and 30 minutes of sonication. Cellulosic chains are
324 characterized by different bands, a broad one corresponding to the O-H stretching located at
325 3320 cm⁻¹, the C-H stretching at 2886 cm⁻¹ with the corresponding C-H bending at 1430 cm⁻¹,
326 -O-H bending at 1630 and at 1418 cm⁻¹ stretching vibrations. In addition, the peak at
327 1031 cm⁻¹ refers to symmetric and asymmetric stretching C-O-C bonds. The peak that appears
328 at 690 cm⁻¹ is assigned to Ti-O-O bond and accounts for the presence of TiO₂ after sonication.
329 These results show that despite this strong sonication test, the characteristic peak of TiO₂ NPs
330 is always present.

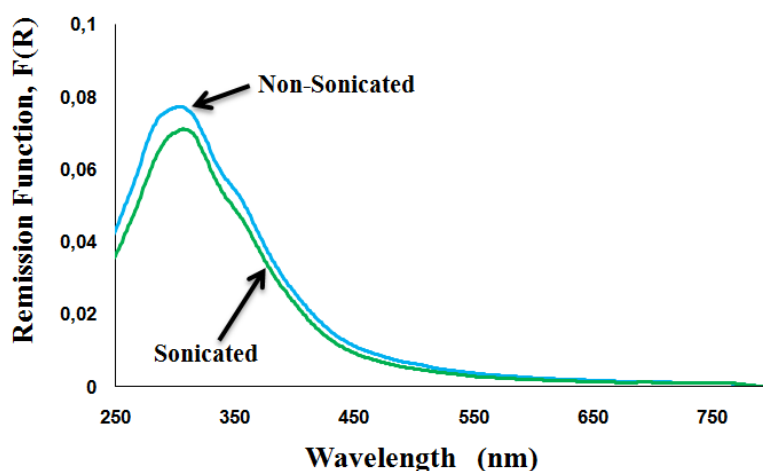


331
 332 **Fig. 8** FTIR spectra of treated Fabric/TiO₂-120 °C ultrasonicated during 5, 15 and 30 minutes

333 **Ground-state diffuse reflectance**

334 The ground-state diffuse reflectance spectra of fabric/TiO₂ before and after ultrasonic
 335 vibration are shown in Fig. 9. The UV absorption band at about 310 nm corresponding to
 336 TiO₂, already studied and reported in a previous work (Abid et al. 2016), proves the existence
 337 of TiO₂ NPs on cotton fibres.

338 The presence of the same peak at about 312 nm after sonication shows that this test does
 339 not detach the TiO₂ NPs from the cotton substrate, i.e. the bond is strong between the TiO₂
 340 NPs and cotton fibres.

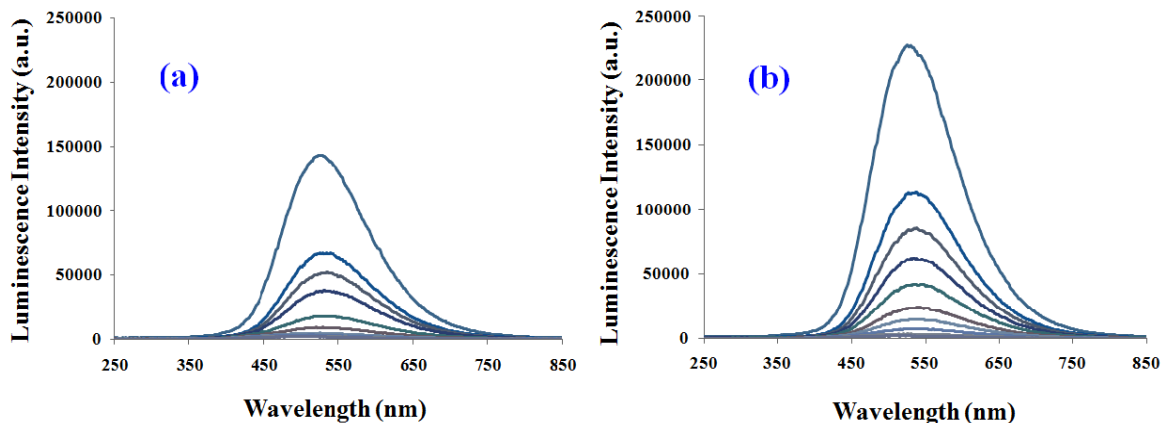


341
 342 **Fig. 9** Ground State Diffuse Reflectance (GSDR) spectra of Fabric/TiO₂ sample before and after sonication

343 However, a small amount of TiO₂ is detached from the substrate, as the decrease of the
344 remission function value for the sonicated sample clearly shows.

345 Laser induced luminescence

346 The laser induced luminescence spectra ($\lambda_{exc}=337$ nm, ~ 1.3 mJ per excitation pulse), at
347 77 K, for the fabric/TiO₂ samples are illustrated in Fig. 10(a). The initial curve was obtained
348 after laser pulse, and the following curves were obtained with the step of 1000 ns. The gate
349 width was 10 ms. The laser induced emission spectra of non-sonicated fabric/TiO₂ are
350 displayed with maxima at 533 nm. The maximum emission of non-sonicated fabric/TiO₂, was
351 obtained with a maximum of about 533 nm (Fig. 10(a)) and a luminescence intensity of about
352 150000 (a.u.). These spectra reflect a simultaneous emission of cotton and TiO₂ with a greater
353 contribution of the latter. After ultrasonic treatment with fabric/TiO₂-120 °C (Fig. 10(b)), the
354 luminescence intensity increases to about 230000 (a.u.). This large difference between the two
355 spectra is certainly due to the effect of sonication on the distribution and the organization of
356 TiO₂ NPs immobilized on the fabric. Only the better attached TiO₂ NPs remain on the surface
357 and possibly the number of surface defects decreases with sonication, meaning that the
358 number of traps for the excited TiO₂ to be deactivated by a non-radiative pathway also
359 decreases. Therefore, the luminescence intensity of TiO₂ increases for the sonicated sample
360 and also the half-life is about 1.5 μ s, while the non-sonicated sample exhibits a shorter half-
361 life, at least in the initial times of its decay. These data also support the interpretation that the
362 remaining TiO₂ NPs (after sonication) contain less defects (traps), therefore larger intensities
363 for its luminescence and larger lifetimes for the TiO₂ NPs are observed.



364
365 **Fig. 10** Laser induced luminescence spectra, obtained at 77 K, of Fabric/TiO₂-120 °C samples (a) before sonication and (b)
366 after sonication. The excitation wavelength was 337 nm and the step was 1 μ s in both cases. The used gate width was 10 ms

367 **Conclusion**

368 Woven cotton textile samples **loaded** with TiO₂ NPs were hydrothermally treated at
369 temperatures ranging from 50 °C to 140 °C. The presence of TiO₂ on the samples was verified
370 by several characterization techniques and the photocatalytic activity was found optimized for
371 a hydrothermal treatment at 120 °C, as judged from the results obtained with a model dye
372 Rhodamine 6G (Rh6G). In our quest of photocatalytic pigment fastness, we subjected the
373 samples to ultrasonication to check their ability to remain attached to the surface. In a
374 serendipitous way, we found out that ultrasonication boosted the photocatalytic effect despite
375 a slight partial removal of TiO₂ nanoparticles. The study was repeated with Methylene Blue
376 dye, and a similar effect was observed as the photocatalyzed degradation of MB led to a loss
377 of 90% after 30 min of ultrasonication of the fabric primarily hydrothermally treated at
378 120 °C. Compared to un-sonicated fabric the photocatalyzed degradation using a sonicated
379 catalytic fabric is 4 times better as the non-sonicated fabric degraded MB but left 40% of the
380 dye.

381 This work conclusively shows that ultrasonication clearly boosts up the photocatalytic
382 activity of TiO₂, and the process could be extended to other types of nanocatalysts such as
383 mixed oxides or noble metal **loaded** TiO₂. The process is simple and could be generalized for
384 pilot testing.

385

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389

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