

Review Article

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Cotton fibres functionalized with plasmonic nanoparticles to promote the destruction of harmful molecules: an overview

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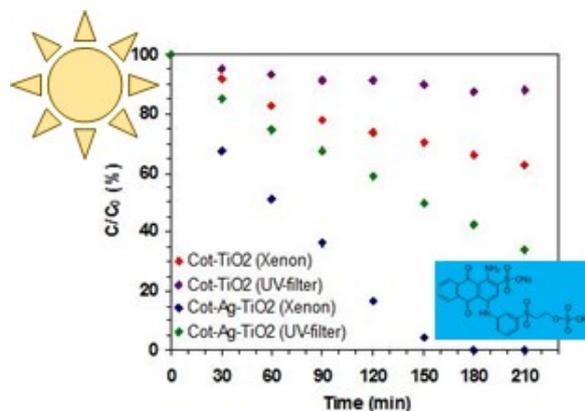
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Abstract: Self-decontaminating cotton fabrics were designed, produced and characterized aiming at the decomposition of harmful molecules namely chemical warfare agents (CWAs) by photocatalysis under day light or indoor illumination. This was achieved through the creation of a hybrid organic-inorganic nanostructured textile composed of a thin layer of TiO₂ nanoparticles (NPs) generated *in situ* and chemically immobilised on the cellulose chains of cotton fibres. TiO₂ NPs were converted into anatase by a hydrothermal procedure at low temperature around 100 °C. The fabrics covered with TiO₂ nanoparticles were examined in terms of their chemical composition, morphology, crystallinity, ageing, robustness and photocatalytic properties. In the whole preparation of the photocatalytic fabrics, only environment-friendly solvents (water or alcohol) were used. One of the important achievements in this work was providing fabrics with suitable photocatalytic activity under visible light. This was reached through plasmonic photocatalysis by generating noble metal nanoparticles (Au, Ag) and/or their halides (AgBr, AgCl) neighbouring or topping the TiO₂ NPs in the fabrics. The kinetics of degradation of the different systems were analysed and proved that the resulting fabrics could efficiently decompose, under visible light, organic dyes and dimethyl methylphosphonate (DMMP), a CWA simulant.

Keywords: Cotton, Photocatalysis, TiO₂, Plasmonic effect, Nanoparticles

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Kinetics of degradation of Remazol Brilliant Blue R by COTTON modified surfaces under Visible light or Xenon irradiation.

Graphical abstract

Abbreviation List

AFM atomic force microscopy

CWAs chemical warfare agents

DMMP dimethyl-methylphosphonate

FE-SEM field-emission scanning electron microscopy

FWHM full width at half maximum

GSDR ground state diffuse reflectance absorption spectroscopy

LIF laser induced fluorescence

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LIL laser induced luminescence
LIP laser induced phosphorescence
LSPR localized surface plasmon resonance
MONPs metal oxide nanoparticles
NPs nanoparticles
RB remazol brilliant blue R
TBT or Ti(OBu)₄ titanium tetrabutoxide
XPS X-ray photoelectron spectroscopy

1 Introduction

Chemical weapons started to be used in large scale in World War I [1]. They were also largely employed by the Nazis in World War II and, more recently, in several localized conflicts in the Middle East, in spite of the numerous conventions prohibiting their use [2–4]. The decontamination and the protection of the civilian population from exposure to hazardous chemicals, such as Chemical Warfare Agents (CWAs), is a crucial challenge nowadays. The aim of the work here reviewed is to find effective solutions to improve the protection against CWAs.

The purpose of the CATALTEX project was to contribute for an efficient personal protection for people exposed to harmful molecules, bringing a new technological contribution for decontamination through their destruction. For this purpose, time and effort were spent to develop, to design and to elaborate new “smart” textiles endowed with self-decontaminating properties based on a photocatalytic nanotechnology. These functionalized fabrics can be easily implemented in any country having a valuable industrial level to depollute infected areas invaded by toxic molecules, as CWAs, or even toxic pollution in industrial or agricultural environments or merely household products in indoor air. First attempts have been based on fibres associated to activated carbon liners [5–7]. However, most of the resulting protective clothes made of such impermeable materials, have the drawback of being heavy, not breathable and expensive. Lighter materials endowing decontaminating properties can be generated, through the combination of fabrics, for instance cotton with nanoparticles, namely those of metal oxide nanoparticles (MONPs), which exhibit a high photocatalytic activity. “Smart textiles” based on functionalized cotton fabrics have been tested, aiming the destruction of harmful compounds, such as polluting molecules, dyes, or even CWAs by degrading them to harmless products namely water and carbon dioxide through a photocatalytic procedure under day-light or indoor illumination. This paper revisits some of the results obtained in the CATALTEX project, con-

cerning the production of “smart textiles” endowing self-decontaminating properties capable of the total degradation of CWAs.

Photocatalysis can be achieved by the production of highly reactive ions or radicals generated in the neighbourhood of the oxide surface, induced by the visible or UV radiation [8, 9]. However, these highly reactive species have too short lifetimes to be harmful. These oxides had been the subject of an intense research since the seventies and its application in CWAs degradation has also been tackled, in several papers [10, 11]. Actually, these photocatalytic reactions are fundamentally based on the absorption, by the oxide, of photons having energy higher than its gap. This is accompanied by the promotion of electrons to the semiconductor conduction band (e^-) and the consequent generation of holes (electron vacancies, h^+) in the valence band (electron-hole pairs). Mostly, oxides with shallow traps are used, where electrons can be easily promoted to higher energy levels through the action of visible or UV photons. The ensuing charge carriers h^+ and e^- are powerful oxidizing and reducing agents that react with water or atmospheric oxygen to generate highly active hydroxyl (OH^\bullet) and superoxide (O_2^-) radicals, respectively. Both of these species are powerful oxidizing agents capable of breaking down organic compounds into CO_2 and H_2O . The sensitization of the oxide layer enables the photocatalytic power to persist even with visible light.

Nowadays, photocatalysis using MONPs is regarded as a promising way to decompose harmful gases. This is due to their high specific surface, large number of highly reactive edges, corner defect sites and unusual lattice planes. Among them, some oxides, namely, Titanium dioxide, TiO_2 , are recognized to have a strong photo-oxidation power with an effective ability for decomposing a wide range of warfare agents in the presence of UV radiation [12–14].

Different strategies published in the literature can be explored to generate TiO_2 NPs on cotton fibres: in the presence or absence of molecular binders between the cotton surface and functionalized titania NPs, prepared *ex situ*, assisted by ultrasound radiation or UV light or embedded in different polymers, just to mention a few [15–19]. In the present case, a non-hydrolytic sol–gel process followed by a mild hydrothermal treatment was used. Cotton was functionalized with TiO_2 nanolayer starting from a precursor: titanium tetrabutoxide ($Ti(OBu)_4$ or TBT), presently the most cost effective precursor of TiO_2 commercially available. Cotton fabrics are dipped into a solution of TBT in tert-butanol. TBT interacts with the cotton fibres through the cellulosic OH groups in the presence of acetic acid, leading to sixfold coordinated Ti. Through a hydrothermal

treatment at low temperatures (from 80°C to 140°C), one can induce polycondensation leading to the nucleation and growth of anatase. Actually, this hydrothermal treatment enables the crystallization of the TiO₂ layer into the anatase phase.

The optimization of the photocatalytic efficiency of the hybrid system Cotton-TiO₂ is crucial because, in the amorphous state, the generated charges are promptly trapped before producing the highly reactive species at the surface [20, 21]. It is often reported in literature that a calcination treatment at a temperature over 400°C, necessary to achieve the crystallization of TiO₂ into anatase, will greatly improve the photocatalytic properties of the oxide [22, 23]. However, at these temperatures the cotton would be burned. In this study, it was shown that hydrothermal treatment at lower temperatures can lead to crystallization of TiO₂ NPs into the anatase phase [24]. Here, the charges generated under radiation on the anatase surface can be more easily exchanged to create highly active ions without being trapped. Actually, TiO₂ has a good photocatalytic activity under ultraviolet radiation; however, due to its high gap ($E_g = 3.2$ eV) [25] its activity under visible light, lower than that under ultraviolet, will not be sufficient for self-decontamination.

To extend the photocatalytic activity of the functionalized fabrics Cotton-TiO₂ to the visible domain, the usual method is doping the TiO₂ with non-metals such as nitrogen, carbon or halogens, or transition metals, rare earths [26], or, even other semiconductors such as CdS [27]. Plasmonic photocatalysis can be a good strategy [28]. This consists in the inclusion of NPs of different nature such as Ag⁰ [29, 30], Au⁰ [31, 32], Cu⁰ [33], Pt⁰, Pd⁰ [34] or their halides such as AgBr [35] or AgCl [36] dispersed in the semiconducting TiO₂ layer. This allows two prominent effects to take place: the formation of a Schottky junction and of a localized surface plasmonic resonance (LSPR). The first one delays the recombination of electrons and holes, promoting the generation of the highly reactive species; the second one, extends the light absorption domain to the visible range. The case of silver NPs will be referred here [24]. In this case, visible radiation contributes to the photocatalysis, even if the photons have energy lower than the gap of the semiconductor. Hybrid Cotton-anatase samples prepared under a hydrothermal treatment temperature of 130°C have a gap of 3.2 eV [24], which impedes the excitation of the electrons located at the top of the valence band to the bottom of the conduction band. However, photons have energy enough for the excitation of the surface plasmon of silver. The excited electrons have enough energy to cross the junction to the conduction band of the semiconducting TiO₂ NPs. Consequently, electrons result-

ing from the excitation of surface plasmon of the metal NPs by visible light nourish the conduction band of the oxide, promoting its photocatalytic activity [37, 38].

The whole process was followed by several analytical tools and microscopies such as Raman spectroscopy [39], Field-Emission Scanning Electron Microscopy (FE-SEM) and Atomic Force Microscopy (AFM). Also X-ray photoelectron spectroscopy (XPS), a powerful technique for the analysis of the surface layer, as it can give extended information on the elements there present, as well as their oxidation state and their neighbourhood [40, 41], was extensively employed for characterizing the chemical composition of the cotton sample, before and after the NPs generation. UV-Vis absorption spectroscopy and time-resolved laser induced fluorescence (LIF) and phosphorescence (LIP) were mainly used to provide lifetimes and the nature of the interaction between the NPs and the substrate. Finally, the evaluation of the photocatalytic activity for the different hybrid systems was done following the discoloration of aqueous solutions of organic dyes, such as the Remazol Brilliant Blue R (RB) under a sunlight simulator equipped with selective filters. RB is a toxic anthraquinone-based dye used in the textile industry. Results obtained for Cotton-Ag-TiO₂ and the comparison with Cotton-TiO₂ will be presented here as a paradigmatic example. Some tests performed using CWAs simulant will be also referred here.

This paper reports the results obtained with the hybrid systems based on cotton/titania. Actually, instead of cotton, different types of natural textiles could be employed as silk, wool, line or even synthetic ones like polyester, acrylic or nylon as these fabrics dispose of reactive organic functions where NPs could be generated. Also ceramic NPs (inorganic non-metallic solids) can be applied to photocatalysis and dyes photodegradation [42]. Magnetic NPs (e.g. Fe₃O₄, magnetite) are also of importance for the use in environmental remediation, such as water decontamination, biomedicine [42] and also as drug carriers for photodynamic therapy of cancer [43].

The textile treatment here used was already successfully applied to chitosan [44] and can be extended to other fabrics used, namely, in military or firemen uniforms, protection blankets or tent canvas. The originality of this work relies mainly in the fact that the active photocatalytic layer is grown from the fabrics surface using the cellulose hydroxyl groups instead of being pre-synthesized and then just physically applied on the surface. This methodology intends to improve the fastness of the layer.

2 Materials and methods

2.1 Materials

Common gauze bandages (with a cellulose content exceeding 98%) were used as cotton fabrics models. All reagents of analytical grade were from Aldrich and used without further purification, including RB, AgNO₃, NaBH₄, glacial acetic acid and tert-butanol (99.7%) and Ti(OBu)₄.

2.2 Sample preparation

To remove the adsorbed water, cotton samples were dried at 70°C for 4 h. Next, they were directly dipped into a 0.5, 1 or 1.5 (w/v)% solution of Ti(OBu)₄ in a mixture of acetic acid and tert-butanol (10/90 wt%) for 12 h. After drying at 60°C for 2 h in an oven to liberate the solvent and next, samples were transferred into a 200 mL stainless steel autoclave, half-full of water, placed in an oven maintained at different hydrothermal treatment temperatures ranging from 80 to 140°C during 3 h. Samples were dried at the end of the preparation.

Samples containing TiO₂ and Ag NPs, having sizes of the order of tens of nanometres, were produced by first generating Ag NPs on the cotton fabrics surface by selective reduction of Ag⁺ species and, then, by grafting, on the fabrics surface, the TBT following the non-hydrolytic sol-gel route described above. After a mild hydrothermal treatment (around 100°C), a nanostructured TiO₂ anatase layer, firmly bound to the surface, was formed with uniform TiO₂ NPs, 20-30 nm in size. The generation of metallic Ag NPs and/or crystalline TiO₂ was proved by GSDR, XPS and Raman analysis. Using AgBr aqueous suspensions, instead of AgNO₃ solutions, and following similar protocols, hybrid systems of Cotton-Ag-TiO₂@AgBr could be formed.

In all preparations, green chemistry principles were followed.

2.3 Raman spectroscopy

A LabRAM Analytical Raman micro-spectrograph (Jobin-Yvon, Horiba group, France) using, as exciting radiation ($\lambda = 632.8$ nm), a He-Ne laser source and an air cooled CDD detector (acquisition time of 100 s) was used for recording Raman spectra.

2.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were acquired with a XSAM800 XPS dual anode spectrometer from KRATOS, irradiating the samples with non-monochromatic Mg K α radiation ($h\nu = 1253.6$ eV). Details on operating conditions of the spectrometer, acquisition parameters, and data treatment were published elsewhere [12, 24].

2.5 Field-emission scanning electron microscopy (FE-SEM)

Images of Cotton-TiO₂ were obtained with a Field-Emission Scanning Electron Microscopy (FE-SEM), a ZEISS SUPRA40, microscope completely controlled from a computer workstation. The electron source, a tungsten filament coated with a ZrO layer, is a hot cathode producing electrons by Schottky effect. Samples were attached on a carbon adhesive and coated with a 1 nm thin layer of Pt sputtered under an inert gas.

2.6 Ground state diffuse reflectance absorption spectroscopy (GSDR)

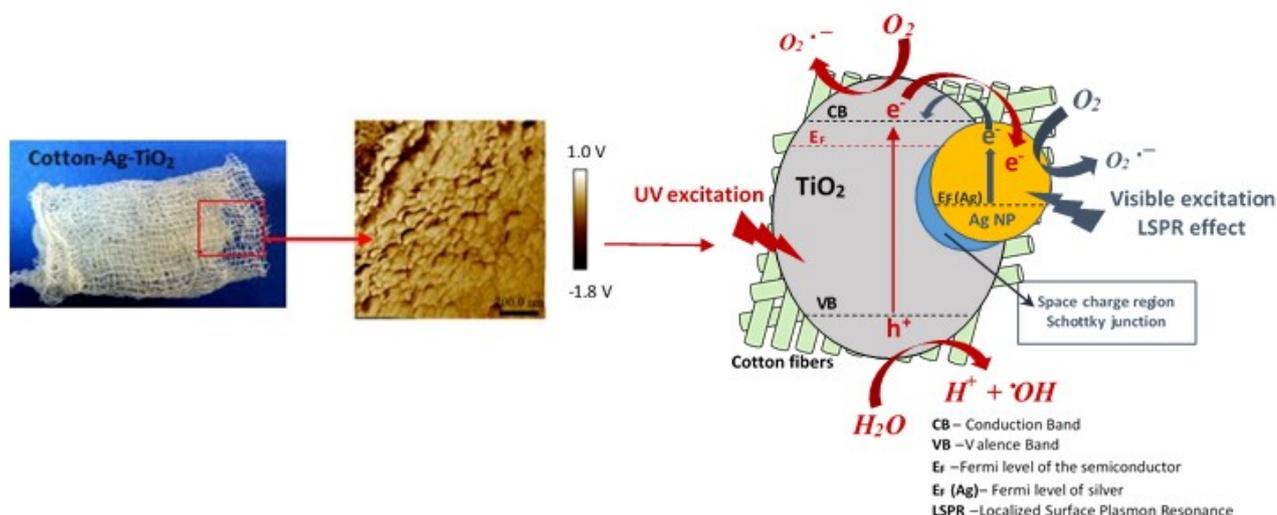
Ground-state absorption studies were performed using a homemade diffuse reflectance laser flash photolysis set-up. Details regarding the data treatment can also be found in the literature [45].

2.7 Time resolved laser induced luminescence studies (LIF and LIP)

The set-up for time resolved luminescence LIL (laser induced fluorescence, LIF, and laser induced phosphorescence, LIP) was also described in the literature [12]. Time-resolved emission spectra were performed in the nanosecond to second time range with a N₂ laser (excitation wavelength = 337 nm, PTI model2000, ca 600 ps FWHM, about 1 mJ per pulse) and with the use of an ICCD with time gate capabilities (i-Star from Andor, model 720). Emission spectra were obtained at 77 K, due to the fact that, at room temperature, luminescence intensity is negligible for the anatase form of TiO₂.

2.8 Photocatalytic tests

Photocatalytic tests were performed for the hybrid system Cotton-TiO₂-Ag by immersing a piece of the modified fabric



Scheme 1: TiO₂ functionalized cotton from concept to mechanism of action [30]. Reprinted (adapted) with permission from Elsevier

(5 cm × 5 cm) in beakers containing 50 mL of RB solution (10⁻⁴ M). The beaker was then irradiated by a Xenon lamp placed at 10 cm from the beaker top. A fixed amount of solution was withdrawn at regular time intervals and the concentration of RB was monitored by UV/Vis absorption measurements (Lambda 35 Perkin-Elmer Spectrophotometer). Prior to irradiation, beakers were kept in the dark for at least 1 h in order to reach adsorption-desorption equilibrium.

Tests using a SARIN simulant, dimethylmethylphosphonate (DMMP) were also performed in the Laboratory of Chemical Safety and Defence of the Portuguese Army in Lisbon (Portugal). The hybrid fabrics TiO₂-Ag@AgBr was chosen to investigate its ability to degrade DMMP. The setting of the protocol for the experiments was established taking into account the illumination and the dark conditions, as well as the extraction methods. Basically, a drop is deposited on the textile and the extraction of the resulting products was accomplished, before and after illumination, using an appropriate solvent.

3 Results

The whole strategy and the different steps used in this study until the final elaboration of self-decontaminating textile can be summarized, as follows:

- Immobilization and characterization of a thin layer of TiO₂ NPs, chemically bound to the cotton fibres endowing photocatalytic activity;

- Extending the photocatalytic activity to the visible light region through a plasmonic effect by including NPs of noble metals and/or their halides into the Cotton-TiO₂ fabrics;
- Characterization of the products obtained in each preparation step;
- Implementing the fabrication of “smart textiles” using an environmentally friendly approach without the use of expensive chemicals;
- Testing the ability of the hybrid systems to degrade CWA simulants, via photocatalytic oxidation, under day light and indoor illumination.

The idea of associating Ag NPs as heterojunction to TiO₂ was motivated by the low photocatalytic efficiency of TiO₂ functionalized cotton for the degradation of organic molecules under sunlight and visible light. This phenomenon is expected given the wide gap of TiO₂ anatase, which is around 3.2 eV, making the visible range photons are not energetic enough to promote the excitation of the appended TiO₂. The inclusion of Ag NPs in the form of tiny NPs well dispersed and effectively bound to the TiO₂ layer alleviates this shortcoming benefiting from the Ag LSPR. However, the process of Ag generation should be well controlled to i) avoid saturation of the TiO₂ layer; ii) control the size of Ag NPs with sizes lower than 20 nm and ensure effective dispersion within the immobilized TiO₂ layer.

The concept and the mechanisms involved in the preparation of the final functionalized cotton (Cotton-Ag-TiO₂) are presented on Scheme 1. The middle image is an AFM image of the hybrid system. Last diagram shows the energy levels of the valence and the conduction band of TiO₂, where interband transitions are available by the ab-

sorption of ultraviolet radiation, resulting in a free electron and a hole. Before their recombination, electrons and holes can give rise to highly active species such as $O_2^{\bullet-}$ and OH^{\bullet} . These radicals created from air, water molecules or aqueous species can efficiently destroy organic molecules under visible light, thanks to the plasmonic effect. The presence of the silver nanoparticle enables the formation of the Schottky junction and opens the possibility for the excitation of a LSPR.

To accomplish the aim of the project, characterization is needed at different stages of the “smart fabrics” preparation. For instance, crystallinity of the TiO_2 NPs could be well established by Raman spectroscopy or even by X-ray diffraction. Most important vibrational modes of anatase phase E_g , B_{1g} , A_{1g} and E_g are located at 145, 397, 515 and 640 cm^{-1} respectively. Figure 1 presents a set of Raman spectra showing that the anatase peak appears for temperatures equal to or higher than 80°C at 153 cm^{-1} displaying, then, a red shift when compared to 145 cm^{-1} , the corresponding value for the bulky anatase. This shift is here assigned to a phonon confinement effect [24, 46]. The anatase peak intensity evolution is compared to the cellulose region located at 1098 cm^{-1} in terms of the hydrothermal treatment temperature. One can, then, infer that anatase is created at quite low temperatures, much lower than that of the cotton calcination, which allows the anatase crystallization, without destruction of the organic material.

The morphology of the cotton fibres and the degree of coverage of the TiO_2 layers can be perceived in the image obtained by FE-SEM, presented in Figure 2. The image exhibits the cotton gauze surface after the hydrothermal

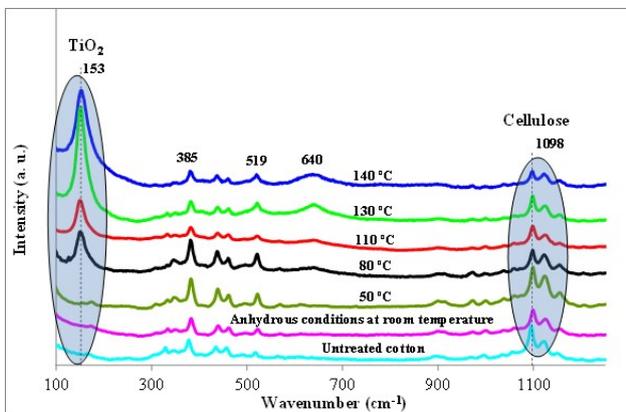


Figure 1: Raman spectra of cotton- TiO_2 samples showing the evolution of the characteristic peak of anatase (at 153 cm^{-1}) as a function of the hydrothermal treatment temperature; cellulose peaks are located around 1098 cm^{-1} [24]; reprinted (modified) with permission from Royal Society of Chemistry

treatment at 130°C . In the insert, with higher resolution, one can observe that the gauze is covered by a thin layer of TiO_2 NPs of a few tens of nanometres of diameter.

A scheme showing the formation of the cotton-anatase hybrid structures through the hydrothermal treatment from the initiator TBT is presented in Figure 3. The mechanisms leading to the formation of the cotton-anatase structures were described in a former publication [24].

Lifetimes of the charges generated on the layer surface by radiation (visible or ultra-violet) are important factors to tailor the photocatalytic properties of the layer, as they can generate active ions responsible for the destruction of the organic molecules present around. GSDR spectra can

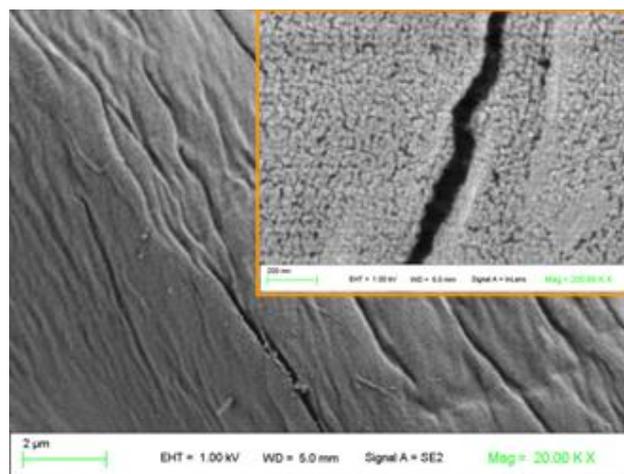


Figure 2: FE-SEM images of cotton fibres covered by a layer of TiO_2 NPs after a hydrothermal temperature of 130°C ; in the inserted window, a more resolved image shows a thin layer of TiO_2 NPs covering the whole cotton surface [24]; reprinted (modified) with permission from Royal Society of Chemistry

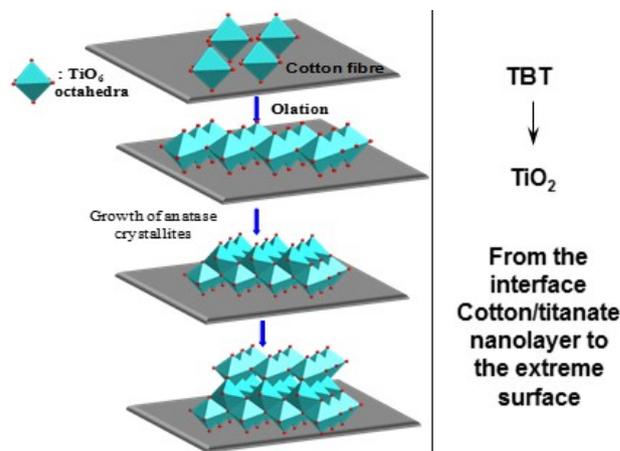


Figure 3: Schematic nucleation and growth of octahedral anatase crystals during the hydrothermal treatment, leading to Cotton- TiO_2 hybrid structures [24]; reprinted (modified) with permission from Royal Society of Chemistry

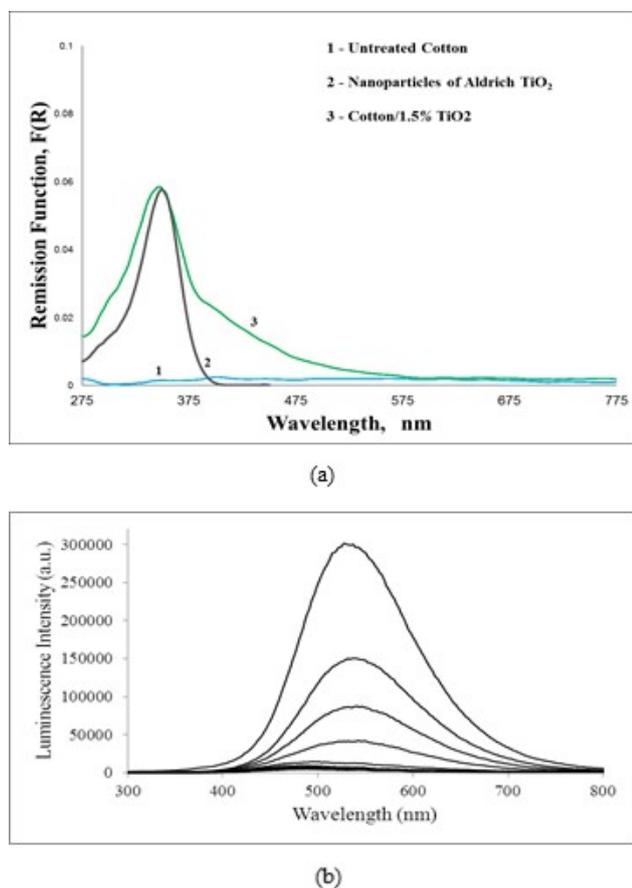


Figure 4: a) GSDR of untreated cotton, commercial TiO_2 nanoparticles and Cotton impregnated with 1.5% TiO_2 ; b) Time resolved Laser induced luminescence of cotton impregnated with 1.5% TiO_2 at 77 K; the time interval between curves is 1 μs

reveal and measure the photo-physical properties of the layer. In some samples, TiO_2 is most probably in an amorphous form and the luminescence spectra is difficult to obtain, even at 77 K. Figure 4a compares the absorption spectra of two samples: commercial TiO_2 NPs and 1.5% TiO_2 adsorbed onto cotton fibres treated by the hydrothermal method. The time resolved luminescence of TiO_2 at 77 K is presented in Figure 4b. A half-life of about 1.5 μs was obtained for the emission of the adsorbed crystalline TiO_2 , at 77 K, peaking at approximately 530 nm. The results confirm that with suitable experimental conditions, crystalline forms of anatase can be obtained, covering the cellulose cotton fibres. Moreover, luminescence studies lead to lifetimes of the excited TiO_2 (at 77 K) about 2 μs , which largely corroborates the photocatalytic properties of the cotton- TiO_2 system.

These results show that hybrid organic-inorganic nanostructured layers, owning photocatalytic properties, can be produced on cotton at temperatures lower than

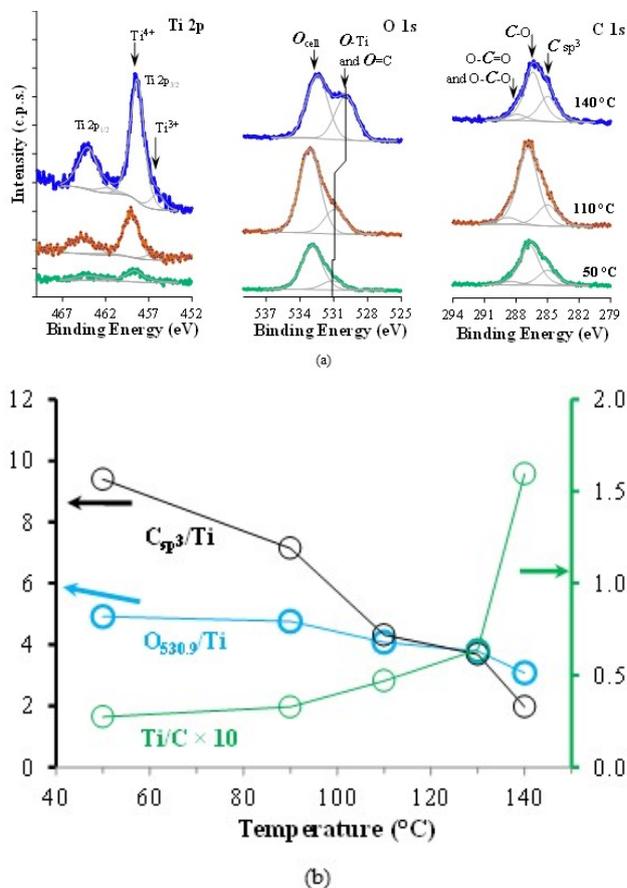


Figure 5: a) XPS Ti 2p, O 1s and C 1s regions, for Cotton- TiO_2 samples submitted to hydrothermal treatment at different temperatures; b) XPS atomic ratios as a function of the hydrothermal temperature [24]; reprinted (modified) with permission from Royal Society of Chemistry

150°C, preventing any risk of thermal degradation or chain scission of the cellulose chains, while using environmentally friendly approaches and water or alcohol, as sole solvents.

XPS results have shown (Figure 5) the presence of carbon and oxygen typical of the cellulose, as well as the presence of aliphatic carbon existing just in the TBT, the TiO_2 precursor. Figure 5a) shows that the titanium could be well detected through its most intense region, the Ti 2p, exhibiting two different oxidation numbers: Ti^{4+} and a small fraction of Ti^{3+} . A detailed qualitative and quantitative data analysis presented in Figure 5b) suggests that the transformation of the precursor into crystalline TiO_2 NPs progresses from the interface cotton/titanate nanolayer to the extreme surface, justifying the relative increase of the Ti 2p signal with the increase of the thermal treatment temperature.

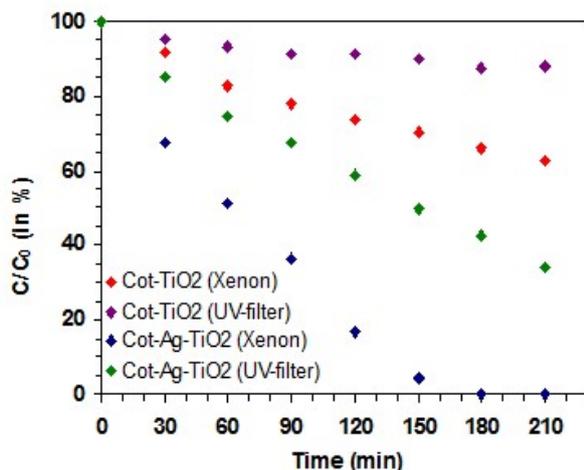


Figure 6: Evolution of the RB concentration of an aqueous solution in presence of a piece of modified cotton, Cotton-TiO₂ or Cotton-Ag-TiO₂ immersed in the RB solution under a Xenon lamp, in the presence or in absence of a UV-filter [30]; reprinted with permission from Elsevier

TiO₂ NPs show to be strongly bound to the cotton fibres and after some washing tests they could be reused. Ultrasonicated fabrics undergo partial loss of nanoparticles but surprisingly exhibit excellent photocatalytic properties likely due to a better distribution of the NPs on the fabrics. Cotton-TiO₂, the first functionalized fabrics to be prepared in this study, presents a quite effective photoactivity under ultraviolet. However, its photoactivity in the visible domain is not sufficiently high for the aims here proposed. To enhance it, plasmonic photocatalysis can be the solution dispersing noble metal nanoparticles into the semiconductor photocatalysts, resulting in two effects: formation of a Schottky junction and of a localized surface plasmon resonance [47]. For this purpose, a second hybrid system was investigated, the hybrid system Cotton-Ag-TiO₂. Ag NPs were generated on cotton fibres using diluted AgNO₃ aqueous solutions, preceding the generation of the TiO₂ layer [30].

The photocatalytic activity of the two hybrid systems, Cotton-TiO₂ and Cotton-Ag-TiO₂, was compared following the discoloration of RB in water under a 40 W Xenon lamp irradiation, as described above.

Figure 6 shows the evolution of RB concentration in an irradiated aqueous solution, where a piece of modified cotton (Cotton-TiO₂ or Cotton-Ag-TiO₂) was immersed. In spite of a larger rate of discoloration when the filter is absent, a measurable rate is obtained in the presence of the UV-filter, especially in the case of Cotton-Ag-TiO₂ attesting the plasmonic effect. The Cotton-TiO₂ sample, in the presence of a UV-filter induces a very limited discoloration of

the solution, probably due to some adsorption of the dye on the piece of the cotton-TiO₂ surface.

Aiming to further enhance the photocatalytic efficiency, a third approach was used, where the TiO₂ layer was coupled with a AgBr heterojunction instead of Ag NPs alone. Here again, the method adopted is ecofriendly, easy to process and the hydrothermal treatment was kept lower than 150°C. For this purpose, a layer of TiO₂ was first generated as described above, followed by immersion of the cotton/TiO₂ in a suspension of AgBr freshly prepared by mixing a solution of AgNO₃ (5×10^{-3} M) with a solution of KBr (5×10^{-3} M). The cotton sample was then submitted to a hydrothermal treatment.

Among the different hybrid systems prepared, the TiO₂-Ag@AgBr functionalized fabrics was also characterized by Raman, XRD and XPS. GSDR analysis revealed a strong absorption in the visible region brought by the LSPR of Ag nanocrystals generated at the AgBr surface. XPS evidenced the presence of Ag⁺, Ag⁰ and bromine, suggesting that Ag⁰ formed a shell around the deposited AgBr. The immobilized TiO₂-Ag-AgBr heterostructured layer imparts a strong photocatalytic activity under visible light for the degradation of dyes in aqueous solution [35].

The tests performed using a SARIN simulant, DMMP, show that the fraction of DMMP degraded under visible light irradiation in the presence of functionalized cotton is much higher than that obtained with unmodified cotton [35].

4 Conclusions

Innovative approaches to functionalize cotton fabrics with covalently bonded nanostructured layers of TiO₂ in the anatase crystalline form were used. Here, TiO₂ NPs are generated in the cellulose hydroxyl groups instead of being pre-synthesized and spread onto the cotton fabrics. The methodology presented improves the fastness of the layer, contrarily to that where TiO₂ NPs are just physically applied onto the surface. TiO₂ NPs obtained can crystallize to anatase through mild conditions under temperatures compatible with the integrity of the fabrics. The method developed is in agreement with the *Green Chemistry* principles, easy to implement, reliable and cost-effective. TiO₂ NPs show to be strongly bound to the cotton fibres and exhibit a high photocatalytic activity under ultraviolet. The degradation of dye molecules demonstrated the high photocatalytic activity of the hybrid system Cotton-TiO₂ under UV-radiation.

In contrast, Cotton-TiO₂ hybrid systems have a low activity under sunlight illumination. However, this can be successfully improved through the plasmonic effect, by the inclusion on the fabrics of silver NPs and/or their halides, among others. The hybrid Cotton-Ag-TiO₂ enables the degradation of dyes under visible light. These hybrid systems were also ultrasonicated and no significant loss of photocatalytic properties was detected attesting the efficient binding of the monolayer to the cotton.

Samples of cotton fabrics decorated with TiO₂ and AgBr NPs were also tested, exhibiting a strong photocatalytic activity under day light illumination. The hybrid cotton, where anatase was associated to NPs of silver and silver halides, showed a good efficiency for the degradation of a CWA simulant (DMPP).

These new plasmonic photocatalysts functionalized fabrics exhibit self-detoxification properties and seem to hold promises for application in chemical protective clothes and might offer new opportunities for the design of novel functional materials for toxic chemical protection, namely against chemical pollutants in water, household products in indoor air, pollution in factory or agronomic environment and, naturally, against CWAs. This methodology is foreseen to be easily scalable to industrial processing.

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