MR. JESÚS MARCELO MORALES (Orcid ID : 0000-0003-1321-7172)

DR. CLAUDIO D. BORSARELLI (Orcid ID : 0000-0003-0120-645X)

Article type : Special Issue Research Article

SPECIAL ISSUE RESEARCH ARTICLE

Photocatalytic efficiency tuning by the surface roughness of TiO₂ coatings on glass prepared by the doctor blade method[†]

Fiorella Tulli,^{1‡} Jesús M.N. Morales,^{1‡} Esteban E. Salas,¹ Faustino E. Morán Vieyra,^{1,2} and
Claudio D. Borsarelli ^{1,2*}

¹ Instituto de Bionanotecnología del NOA (INBIONATEC), CONICET. Universidad Nacional de Santiago del Estero (UNSE), RN 9, Km 1125, G4206XCP Santiago del Estero, Argentina

² ICQ – Facultad de Agronomía y Agroindustrias. UNSE. Av. Belgrano (S) 1912. Santiago del Estero. Argentina

* Corresponding author e-mail: cdborsarelli@gmail.com (C.D. Borsarelli)

‡ Both authors contributed equally to this work

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/PHP.13320](https://doi.org/10.1111/PHP.13320)

This article is protected by copyright. All rights reserved

† This article is part of a Special Issue commemorating the XIV ELAFOT Conference held from November 11th to 14th, 2019 in Viña del Mar, Chile.

ABSTRACT

A set of opaque films were prepared with Degussa P25[®] or Hombikat UV100[®] TiO₂ powders by the doctor blade method on glass slides with different compositions of polyethylene glycol of 20 kDa (PEG20), and they were characterized by spectroscopy, microscopy, and photochemical kinetics measurements. After annealing treatment at 450 °C, about 5-7% C atom was incorporated into the films, as a consequence of the degradation of the organic complexing agents, inducing a small reduction of the energy band gap of TiO₂ (*i.e.* $3.02 \leq E_g \text{ (eV)} \leq 3.08$). All films were about $15 \pm 2 \mu\text{m}$ thick but their micro-morphological characteristics depended on the content of PEG20, showing different patterns of cracks and aggregates that produce intense light scattering and re-transmission phenomena with the result of a three-dimensional excitation of the TiO₂ particles in the thick film. Back-face excitation with UVA light ($365 \pm 42 \text{ nm}$) of the opaque films in contact with an aqueous solution produced both surface-bound and free hydroxyl radicals (HO•), as detected using a coumarin solution as a radical dosimeter. The photogeneration efficiency of HO• decreased with the surface roughness of the films, which varied between 135 and 439 nm depending on the film's composition.

KEYWORDS: Titanium dioxide films, doctor blade method, photocatalysis, surface morphology, photocatalytic quantum efficiency

INTRODUCTION

Heterogeneous photocatalysis using a semiconductor (SC) material is a field of growing interest since the early 1970's, basically by the potential use of solar radiation as driving force of photochemical conversions (1). Examples of application fields of heterogeneous photocatalysis are environment (e.g. air/water treatment by pollutant and/or microbial removal, self-cleaning, reduction of CO₂, etc.) (2–4), energy (e.g. water-splitting and hydrogen generation, solar cells, etc.) (1, 2), organic synthesis (5), health (e.g. cancer or antibacterial photodynamic therapies) (6).

The photocatalytic process starts with the absorption of a photon ($h\nu$) of enough energy to produce the excitation of an electron (e^-) from the valence band (VB) to the conduction band (CB) of the SC, remaining a positively charged hole (h^+) in the VB. These separated charges can rapidly recombine to release the absorbed energy as a photon ($h\nu_{em}$) and/or heat. However, instead of the self-back charge recombination, the transient e^- / h^+ pair can migrate separately towards the surface of the SC, where can participate in redox reactions involving organic molecules (R) [Eqs. 1-4] (1, 2, 7):

Furthermore, in aerated aqueous media, the formation of reactive oxygen species (ROS) can also be produced, [Eqs. 5-6] (7):

Titanium dioxide (TiO_2) is the most popular SC material used in heterogeneous photocatalysis due to its low cost and abundance, redox ability, large chemical and photochemical stability in a wide range of pH and in various solvents (1, 8). TiO_2 can be found in three crystalline phases made up of an octahedron of oxygen atoms around the titanium atom, but with different network organizations: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Rutile is the most abundant form, but anatase shows the larger photocatalytic activity than the other crystalline phases of TiO_2 (1, 8). Unmodified TiO_2 has an energy band gap $E_g = 3.2 \text{ eV}$ (1) and it can be excited with UVA light (320-400 nm), which represents about 7% of the incident solar radiation in the Earth. Taken advantage of this, TiO_2 has been immobilized in films on several solid supports, since this methodology provides certain advantages for technological applications compared to the typical problems obtained with colloidal suspensions, such as filtration stages, particle aggregation, etc.(9–13).

The degradation efficiency of organic pollutants and microorganisms in water by a photocatalytic surface mainly depends on the yield and mechanism of generation of hydroxyl radical ($\text{HO}^\bullet$) (7), since this reactive oxygen species (ROS) reacts with diffusion controlled rate constants ($10^9\text{-}10^{10} \text{ M}^{-1}\text{s}^{-1}$) with most inorganic and organic molecules (14). In this regard, structural and morphological factors of TiO_2 films supported on inert solids, *e.g.* as crystal structure, particle size, materials defects, porosity, roughness, thickness, among others, can be determinant in their final photocatalytic performance, and many of these factors can be tuned depending on the preparation method of the surfaces (1, 7, 9, 15).

The increased worldwide demand for drinking water, particularly in isolated rural areas, as occurs in Argentina's countryside (16), requires of new decontamination strategies for diverse water sources, *e.g.* rainwater, well water, creeks, etc. Hence, TiO_2 -based heterogeneous photocatalysis technologies could satisfy this demand in an economical and practical fashion (4). In this regard, the preparation of TiO_2 -based films by the doctor blade method is one of the most widely used technique to produce thin films on large-area surfaces, whereby a TiO_2 slurry can be spread on flat surfaces in a simple, fast, uniform, and economical manner, generating modified surfaces with promising both electro- and photocatalytic activities (11, 17).

In this work, we reported the preparation of photocatalytic films supported on glass slides by the doctor blade technique followed by an annealing treatment at 450°C using Degussa P25 or Hombikat UV100 TiO_2 powders, which are common commercially available SC materials for the

development of photocatalytic devices (9, 13, 18), combined with different proportions of polyethylene glycol of 20 kDa (PEG20), sodium dodecylsulfate (SDS), and acetylacetone (AcA) as complexing agents (CA) to modify the morphology of the films (19, 20) .

The TiO₂ films were characterized by UV-vis reflection and Raman spectroscopy, optical and scanning electron microscopy, and the photocatalytic efficiency was evaluated by measuring the generation of hydroxyl radicals (HO•) using coumarin (CM) as actinometer (21, 22). The results indicated that the incorporation of different amounts of PEG20 modifies the micro-size morphological properties of the annealed films, finally impacting in a continuous decrease of the photocatalytic efficiency with the increases of surface roughness of the film.

MATERIALS AND METHODS

Materials. Titanium dioxide (TiO₂) Degussa P25[®] was acquired from Degussa-Hüls and Hombikat UV100[®], coumarin (CM), sodium dodecyl sulfate (SDS, 98.5%), and acetylacetone (AcAc, 99%) were purchased from Sigma-Aldrich Argentina. Polyethylene glycol of 20000 MW (PEG20) was acquired from Merck Argentina, absolute ethanol (99.6% for HPLC) from Sintorgan S.A. (Argentina), and potassium ferrioxalate and sodium hydroxide (pro analysis ≥ 97 %) from Cicarelli Laboratorios (Argentina).

TiO₂ film's preparation. Table S1 in the Supporting Information shows the mass and percentage composition of each component in the starting paste for the film preparation. Briefly, the pastes were prepared in a porcelain mortar by adding approximately 2 g of TiO₂ together with an aliquot of 200 µL AcAc ($\delta = 0.975$ g/mL). After mixing during several minutes, the final pastes were homogenized adding the different amounts of PEG20 dissolved in 2 mL of ultra-pure water and 100 µL of 35 mM SDS solution. The pastes were spread with a dipstick glass by the doctor blade method onto clean glass slides, with thickness spacers made of Scotch[®] adhesive tape forming a lane of approximately 9 mm wide, covering a rectangle of 6.75 cm². The films were dried at room temperature for 30 minutes before annealing at 450 °C for 2 h in a muffle furnace. Glass slides with catalyst loadings ranging from 0.9 to 9.0 mg/cm² were obtained (Table S1), as determined by gravimetric analysis.

TiO₂ film's characterization. The mechanical stability or adherence of the TiO₂ films on the glass slides was estimated as a percentage of losing mass, by weighting the dried films before and after contact with 20 ml of ultrapure water in a Petri dish under orbital shaking for 135 minutes.

Diffuse reflectance properties of the films were evaluated with a CCD spectrometer (Ocean Insight, USB2000) coupled with a bifurcated angled reflection/backscatter fiber optic probe (Ocean Insight R400-ANGLE-UV, 330-1100 nm). Barium sulfate was used as 100% reflectance standard.

Fourier-transform infrared spectrophotometry (ATR-FTIR) was performed with a Jasco 4600 apparatus containing a single reflection monolithic diamond crystal, with spectral resolution of 4 cm⁻¹ between 500 and 3500 cm⁻¹. Spectral handling and analysis was performed using Spectra manager CFR software of Jasco. All measurements were carried out under N₂ atmosphere provided by a Parker-Balston 75-45 gas purge.

Raman spectra were recorded with the confocal Raman microscope LabRAM Horiba HR Evolution, using as excitation source the beam of a HeNe excimer laser (633 nm, 17.4 mW, 50% intensity), focused with 50× objective High stability Olympus BX41 microscope).

Optical micro-images of the TiO₂ films on the glass slide were obtained with the Carl Zeiss Axio-Observer Z1 fluorescence inverted microscope equipped with an HBO Xe lamp as illumination source, working in the bright-field transmission mode using a 40× objective and detected with AxioCam 506 mono camera (4.54×4.54 μm, 6 megapixels).

Micro and sub-micro morphology of the films were analyzed with a Phenom ProX desktop scanning electron microscope (SEM) (ThermoFisher Scientific). Surface roughness and film thickness values were obtained employing the 3D Roughness Reconstruction application software (Phenom ProX), and element identification was performed with the fully integrated Energy Dispersive Spectrometer (EDS), applying a potential of 5 and 15 kV, respectively.

Photocatalytic experiments. Photocatalytic experiments were performed with a home-built stirred tank reactor (STR) as it is shown in Figure S1, using as solution container a black-painted Petri dish, with a transparent window of 8×70 mm at the bottom. An illuminator system (Spectroline ENF-260C/FE) equipped with UVA lamp (Phillips, 6 W, $\lambda_{\text{max}} = 360$ nm, FWHM = 42 nm) was fixed below the Petri dish to obtain a back face irradiation set-up (Figure S1). The full device was placed on an orbital shaker with a soft swing (70 rpm) to ensure the complete mixing of the solutions. The photonic flow across the STR containing a clean glass slide placed at the center of the optical axis of the transparent window was calculated as $4.12 (\pm 0.04) \times 10^{-9}$ einsteins.s⁻¹ using a potassium ferrioxalate solution (23). The UVA light intensity across clean glass slide and with

deposited TiO₂ films was measured using the Ocean Insight USB2000 spectrometer coupled with an optical fiber with a cosine corrector attached to the surface of the samples.

Photocatalytic efficiency of the TiO₂ films were determined using 20 mL of 9 μ M coumarin (CM) aqueous solution as probe of the hydroxyl radical (HO $\cdot$) (7, 21, 22, 24). The degradation of CM and the formation of the fluorescence reaction product 7-hydroxycoumarin (HCM) in the supernatant solution were monitored with an Agilent 8453 spectrophotometer and Agilent Cary Eclipse spectrofluorometer, respectively. Formation of HCM at the surface of the TiO₂ films was evaluated with the Carl Zeiss Axio-Observer Z1 fluorescence inverted microscope with a 40 $\times$ objective and excitation/beam splitter/emission filter set of 365/395/450 nm and a HAL 100 (UV – Vis) illuminator as the excitation source.

General experimental conditions and data analysis. Solutions were prepared with aerated ultra-pure water (MiliQ system, 0.05 μ S/cm, pH = 6.1 $\pm$ 0.3), and all experiments were carried out by triplicate at 25 $^{\circ}$ C. The results were expressed as the average value with its respective standard errors. Data analyses were processed with OriginPro[®] 9.0 software from OriginLab Corporation.

RESULTS AND DISCUSSION

TiO₂ film's characterization

The effect of the annealing treatment at 450 $^{\circ}$ C for 2 h on the composition of the TiO₂ films prepared by the doctor blade method was evaluated by ATR-FTIR and Raman spectroscopies, Fig. 1. The ATR-FTIR spectrum of the starting paste containing the mixture of TiO₂ with the complexing agents (CA), *i.e.* AcAc, SDS and PEG20 (dotted orange line in Fig. 1a), shows bands at 2920 and 2850 cm⁻¹ corresponding to the stretching of the alkyl chain of PEG20, while the bands at 1340 and 1097cm⁻¹ are associated to C–H bending and C–O stretching vibration, respectively; and the band at 1240 cm⁻¹ corresponds to C–H twisting vibrations (25). Vibrational bands associated to AcAc can be found in the 1170–1600 cm⁻¹ range (26), but probably overlapped with the PEG20 absorptions, and the deformations of –CH₃ (1465 cm⁻¹) and stretching vibrations of S–O at 1240 cm⁻¹ of the –SO₄ group of SDS (27). The intense broad absorption below 900 cm⁻¹ is assigned to the stretching vibration of Ti–O– Ti backbone bonds in the anatase phase with a maximum at 500 cm⁻¹ (28), as also confirmed by the spectrum of the neat TiO₂

powder (solid black line in Fig. 1a). In the ATR-FTIR spectrum of the sample after annealing treatment (dashed blue line in Fig. 1a) all bands above 900 cm^{-1} disappeared, remaining only the strong absorption band of the catalyst. This result indicates the complete degradation of the CA during the calcination of the paste.

> FIGURE 1 <

Figure 1b shows the Raman spectrum of Degussa P25 TiO_2 powder (solid black line), dominated by the bands at 143 , 197 , 398 , 519 and 630 cm^{-1} , which are typical of the anatase crystalline phase (29), as this trade mark contains around 76% of anatase and 22% of rutile (13). After annealing at $450\text{ }^\circ\text{C}$, the Raman spectrum remained almost unmodified (dotted orange line in Fig. 1b), but after calcination at $750\text{ }^\circ\text{C}$ new bands at 448 and 612 cm^{-1} corresponding to the rutile phase were also observed (dashed blue line in Fig. 1b), in agreement with the fact that TiO_2 powders of high purity show a phase transformation equilibrium at $\sim 650\text{ }^\circ\text{C}$ (30). A similar ATR-FITR and Raman spectroscopic behavior was observed for the pastes prepared with Hombikat UV100 TiO_2 powder (data not shown).

Therefore, the previous results prove that the thermal treatment only degrades the CA added in the starting paste without modification of the intrinsic crystalline structure of each type of TiO_2 powder.

The example photograph inserted in Fig. 2a illustrates that opaque TiO_2 films on the glass slides were obtained under the high loading conditions utilized (0.9 to 9.0 mg/cm^2), suggesting that reflection and scattering effects are dominant. Figure 2a also compares the diffuse reflectance spectra, both plotted as $(1-R)$, of a clean glass slide (blue line) with that of the TiO_2 film deposited on the glass slide (orange line), both monitored with the bifurcated reflectance/backscatter fiber optic probe. It can be observed that the diffuse reflectance spectrum of the TiO_2 film is distorted at the blue edge due to the intrinsic optical density of the material of reflection/backscatter probe, and hence the reflectance spectra were analyzed above 350 nm (Figure S2). According to the experimental set-up used, the reflectance spectra were collected over the entire half-space above the illuminated surface, and hence it can be related with the modified Kubelka-Munk (K-M) remission function $F(R)$, eq. 7, assuming an isotropic excitation (31).

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{4R} \quad (7)$$

$F(R)$ also represents the ratio between the absorption and the scattering coefficients (K/S) and it is proportional to the absorption coefficient (α) of the material, an indication of the sample absorbance at a particular wavelength (31).

> FIGURE 2 <

Figure 2b shows that the $F(R)$ spectra of the TiO_2 films overlap almost completely with the emission spectrum of the UVA lamp, assuring the photo-excitation of the semiconductor.

According to the solid-state theory, the energy band gap of a semiconductor E_g can be estimated using the Tauc's plot (32), which correlates α (*i.e.* $F(R)$) with the excitation energy $h\nu$, eq. 8; where A is constant and n is a coefficient associated with the type of electronic transition of the semiconductor, with values of $1/2$, 2 , $3/2$, and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transition, respectively (33).

$$[F(R)h\nu]^{1/n} \approx A(h\nu - E_g) \quad (8)$$

Inset of Fig. 2b shows the typical Tauc's plots obtained for the Degussa P25 TiO_2 films considering $n = 2$ (33). The E_g value is calculated by extrapolating the linear portion of the graphic to the photon energy axis. For unmodified TiO_2 , $E_g = 3.21$ eV is expected (1, 2), but in the present case values between $3.02 \leq E_g$ (eV) ≤ 3.08 were obtained, with a slight decrease as the amount of PEG20 was increased (Table S2 in the Supporting Information).

Energy-dispersive X-ray spectroscopy (EDS) results of the annealed TiO_2 films are shown in Figure S3 and Table S3 in the Supporting Information, indicating that all films are mainly composed of Ti ($\approx 17\%$) and O ($\approx 77\%$), but also contain between 5% and 7% of C atoms. This result together with the slight reduction of E_g , suggests that the CA utilized in the paste preparation were mineralized during the annealing treatment and a fraction of C atoms was incorporated into the TiO_2 films. It has been reported that typical CA molecules, in particular PEG

derivatives, could stabilize the anatase phase in the films after calcination at high temperature (19, 20).

Micro-morphological analysis of the surface of the TiO_2 films was performed by SEM with several magnification levels. At $350\times$ magnification, it was observed that the cracking pattern of the film surface changes with the PEG/ TiO_2 % wt ratio in the starting paste, with a strong reduction of the crack density for paste composition with approximately 20% wt PEG20/ TiO_2 ratio, but with more cracking and potholes at larger PEG20/ TiO_2 ratios (Fig. 3a). The film cracking and other mechanical imperfections at the surface are produced in the drying and sintering steps during the annealing process, and it is related to the internal and external stress of the film and tends to result in film decohesion (34). A similar morphological behavior was also observed for the formation of TiO_2 films on open-celled aluminum foams, where cracking was also inhibited at relatively low PEG concentrations (*e.g.* < 10 mM) (35), an equivalent polymer molar concentration used in the preparation of the current films with 20% wt PEG20/ TiO_2 ratio.

SEM images obtained with a larger magnification of $13000\times$ were utilized to calculate the surface roughness (SR) with the software provided by the equipment, by averaging up to five linear trajectories in a region of the surface free of cracks and other imperfections (Fig. 3b). The SR values calculated for all TiO_2 films are reported in Table 1, and it can be observed that the SR changed between 135 nm and 440 nm depending on the PEG20 amount and type of commercial powder of the starting paste for the film preparation. The SR values for the present TiO_2 films without the addition of PEG20 were slightly larger than those estimated by AFM measurements for thin films prepared by sol-gel method with the same commercial powders (13). For the films prepared with Degussa P25 TiO_2 , the SR value tends to increase with the polymer concentration, probably by the adhesion of small TiO_2 aggregates to form larger clusters as the PEG content increases (35). Instead, the SR value for the TiO_2 films prepared with Hombikat UV100 showed an opposite dependence with the PEG20 amount, with the larger SR for the film prepared with the smaller PEG20/ TiO_2 ratio (Table 1). This complex behavior can be understood in terms of the strength balance between TiO_2 particle self-aggregation and TiO_2 interactions with the polymer occurring in the course of the annealing process. The surface area (m^2/gr) of TiO_2 particles of Hombikat UV100 is about seven-times larger than for Degussa P25, and hence contains larger surface energy favoring particle self-agglomeration, as it was confirmed by dynamic light scattering measurements in aqueous dispersions (13). The present results suggest that during the annealing of the films with Hombikat UV100 powder, a low amount of the polymer exerts the

agglomeration of the TiO₂ aggregates, but at higher PEG20 concentration, the excess of polymer favors the disruption of the aggregates. A similar effect was observed for ZnO porous thin films prepared by sol–gel, where the film without PEG was compact, becoming more porous and aggregated with an intermediated PEG amount, but the porosity disappeared gradually at larger polymer content (36).

The thickness of the TiO₂ film was evaluated from SEM images with a magnification of 1200× (Fig. 3c). By using the software facility of the SEM apparatus, several trajectories crossing the film edge with the glass surface were selected for the estimation of the average thickness value, as reported in Table 1. In average, a film thickness of $15 \pm 2 \mu\text{m}$ was obtained, independently on the initial paste composition and type of TiO₂ powder utilized for the film preparations. This thickness value is in the range of those reported for TiO₂ films prepared by the doctor blade method (37), and its relative low dispersion ($\pm 10\%$) confirms the very good reproducibility of the film's preparation method.

> FIGURE 3<

Finally, the mechanical stability (MS) or adherence of the TiO₂ films on the glass slides was calculated as $\%MS = 100 \times (1 - m_{\text{after}}/m_{\text{before}})$, where m_{before} and m_{after} is the mass ($\pm 0.1 \text{ mg}$) of the dry TiO₂ coated glass slide before and after the orbital shaking of the films in water during 135 min, respectively (Figure S4). In all cases, the film's adherence was superior to 99% indicating that the combination of the doctor blade technique followed by high-temperature annealing produces an appropriated sintering of the TiO₂ films on the glass support.

Photocatalytic behavior

The hydroxyl radical HO• is the most reactive ROS towards both inorganic and organic molecules (14). Hence, the photocatalytic efficiency of SC materials is typically evaluated by the reaction of HO• with target molecular probes (7), as it is the case of coumarin (CM) to yield the highly fluorescent 7-hydroxy-coumarin (HCM), Scheme 1 (7, 21, 22, 24).

> SCHEME 1<

The photocatalytic efficiency of the prepared TiO₂ films on glass slides was evaluated using the home-built stirred tank reactor (STR, Figure S1) containing 20 mL of approximately 9 μM CM aqueous solution. Before the UVA photolysis, the CM solution was kept in the dark with orbital stirring until the adsorption-desorption equilibrium of the dye on the film surface was reached. The blue circles of Fig. 4a show a typical kinetic profile for the CM concentration decreases in the supernatant solution due to the adsorption process, as calculated by absorbance changes at 278 nm using the molar extinction coefficient of $\epsilon_{278} = 10820 \text{ M}^{-1}\text{cm}^{-1}$ (21). The fraction of adsorbed CM on the TiO₂ films is reported in Table 1, and it was calculated as $f_{\text{ad}} = (1 - [\text{CM}]_{\infty}/[\text{CM}]_0)$, where $[\text{CM}]_0$ and $[\text{CM}]_{\infty}$ is the initial and final concentration of the dye in the supernatant solution, respectively. For the TiO₂ film prepared with Degussa P25 and in the absence of PEG20, the f_{ad} value was similar to that reported for aqueous suspensions of the same material (38). Nevertheless, in presence of PEG, a larger adsorption of the dye was observed probably by specific interactions exerted by the polymer and the inhomogeneous micro-topography of the films (Fig. 3). After the adsorption equilibrium was achieved, the TiO₂ films were back-face irradiated with the UVA source, and the photodegradation kinetics of the CM in the supernatant solution was also monitored by absorbance measurements (orange squares in Fig. 4a). The full-width half-maximum (fwhm) of the UV-final absorbance spectrum became broader compared with that before photolysis, suggesting the presence of more than a molecule that absorbs light in the supernatant solution (Fig. 4b). In order to confirm the photocatalytic formation of the fluorescent derivative HCM (Scheme 1), the excitation-emission matrix (EEM) spectra of an aliquot of the supernatant CM solution in contact with the TiO₂ film before and after UVA photolysis were compared. Prior to UVA irradiation, the EEM spectrum shows a weak fluorescence band at $\lambda_{\text{ex}} = 278 \text{ nm}$ and $\lambda_{\text{em}} = 385 \text{ nm}$, characteristic of CM (39), Fig. 4c. After UVA photolysis, the EEM spectrum of the supernatant solution shows now an intense and red-shifted fluorescence with a maximum at $\lambda_{\text{ex}} = 325 \text{ nm}$ and $\lambda_{\text{em}} = 455 \text{ nm}$, typical of HCM (21, 39), Fig. 4d. The time-dependent increment of the fluorescence intensity at 455 nm with the UVA-photolysis in the supernatant solutions of CM was only observed in the presence of the TiO₂ films (Figure S5), confirming the photocatalytic formation of HCM by the reaction of CM with HO[•].

> FIGURE 4<

Figure 4e shows the inverted fluorescent microscopy images obtained with an excitation/emission filter set of 365/450 nm for two different TiO₂ films that were kept in contact with solutions of CM in the dark during 60 min in the STR to assure the adsorption of the dye, and subsequently, the dye solution was replaced with 20 mL of ultra-pure water and the TiO₂ films were back-face irradiated with UVA during 60 min. Before UVA irradiation, blue fluorescence signal arisen from the surface of the TiO₂ films was not observed. However, after UVA photolysis, all films showed blue fluorescent spots due to adsorbed HCM (Fig. 4e and Figure S6), indicating that the photocatalytic formation of HCM also occurs on the TiO₂ film surface.

The photocatalytic generation of HO• and subsequent substrate oxidation mechanisms have been extensively discussed (15, 38, 40–43), and recently reviewed by Nosaka's group (7). It is now accepted that a fraction of the photogenerated HO• at the TiO₂ surface (HO•_{bound}) can diffuse to the bulk solution as free radical species (HO•_{free}) (41, 42). The relative amount of both types of HO• species depends on the crystalline composition of TiO₂, being anatase more prone to release HO• while rutile does not, limiting in the latter case only the oxidation reaction with adsorbed substrates (15, 38, 41).

The results presented above (Fig. 4) suggest that both HO•_b and HO•_f are responsible for the photocatalytic generation of the fluorescent HCM. In aqueous solution, the reaction between HO• and CM is a diffusion-controlled process ($k = 2 \times 10^9 \text{ M}^{-1} \text{ cm}^{-1}$, (14)), and it can be assumed that the initial rate of HO•_f generation is equal to the initial rate of CM depletion in the supernatant solution, *i.e.* $v_0 = -d[\text{CM}_f]_0/dt = [\text{HO}^\bullet_f]/dt$. The calculated v_0 values obtained within the 10% of the initial consumption of CM in the supernatant solution are shown in Table 1, and it can be observed that they correlate with the surface roughness (SR) values rather than the PEG20 composition in the TiO₂ film.

The photocatalytic quantum yield (Φ_{PC}) of a SC is defined by the quotient between the rate of the number of reactant or product molecules transformed and the rate of absorbed photons by the photocatalyst, *e.g.* $\Phi_{\text{PC}} = r \text{ (mol.s}^{-1})/I_{\text{ab}} \text{ (einstein.s}^{-1})$ (44). The accurate determination of Φ_{PC} in heterogeneous photocatalysis is a difficult task, mainly because of the uncertainties in the evaluation of the actual absorbed photon flow I_{ab} by the semiconductor particles (22, 44). In the present case, the operational quantum efficiency of HO•_f generation $Y_{\text{HO}^\bullet_{\text{free}}}$ was calculated by eqn. 9 as the ratio between the initial rate (r_0) of HO•_f generation in the total volume ($V = 0.02 \text{ L}$) of the irradiated solution and

the rate absorbed photons by the TiO₂ film (I_{ab}), which it can be assumed as a fraction of the impinging photon flow I_0 ($= 4.12 \times 10^{-9}$ einstein.s⁻¹) modulated by the area value of the $F(R)$ spectrum under the wavelength region that overlaps to the emission spectrum of the UVA lamp ($F(R)_\lambda$), Table 1.

$$Y_{HO^{\bullet}_{free}} = \frac{r_0 (\text{mol.s}^{-1})}{I_{ab} (\text{einstein.s}^{-1})} \propto \frac{v_0 V}{F(R)_\lambda I_0} \quad (9)$$

The calculated $Y_{HO^{\bullet}_{free}}$ values for the TiO₂ films ranged between 1 - 3%, Table 1, and were quite similar to those reported for semi-transparent TiO₂-anatase films deposited on SiO₂-precoated soda-lime glass slides produced by sol-gel technique (22), and also for phenol degradation in high loading TiO₂ aqueous suspensions (44), demonstrating that the assumption made for the calculation of $Y_{HO^{\bullet}}$ in eqn. 9 is plausible. Interestingly, $Y_{HO^{\bullet}_{free}}$ decreases linearly with SR (Fig. 5a), with a similar slope value for both types of TiO₂ but with almost 15% larger intercept value for Hombikat UV100 than for Degussa P25 films, *i.e.* 3.4(±0.2)% and 2.9(±0.3)%, respectively. The intercept of this correlation represents the highest $Y_{HO^{\bullet}_{free}}$ value to obtain with an ideally flat surface of each type of TiO₂. Hence, considering that only the anatase crystalline form is able to release HO[•] from the surface of TiO₂ (15, 38), the largest photocatalytic activity observed for Hombikat UV100 films can be associated with its larger proportion of anatase (≈86-100%) compared with the 75-80% in Degussa P25 (13, 45).

A similar slope value for the inverse correlation of $Y_{HO^{\bullet}_{free}}$ with the SR for both types of TiO₂ films could indicate a topological control on the relative amount of hydroxyl groups at the surface of semiconductor that can be released toward the solution. In that case, the quantum yield of HO[•]_{bound} formation ($\Phi_{HO^{\bullet}_{bound}}$) is proportional to the ratio between the integrated fluorescence intensity of adsorbed HCM (I_F^{HCM}) obtained from the inverted fluorescence images (Table S4) and the intensity of absorbed photons by the film I_a ($\propto F(R)_\lambda I_0$) multiplied by the concentration of dye adsorbed $[CM]_{ad}$ ($= f_{ad}[CM]_0$), eqn. 10.

$$\Phi_{\text{HO}^\bullet_{\text{bound}}} \propto \frac{I_{\text{F}}^{\text{HCM}}}{I_{\text{ab}}[\text{CM}]_{\text{ad}}} = \frac{I_{\text{F}}^{\text{HCM}}}{F(R)_{\lambda} I_{0f_{\text{ad}}}[\text{CM}]_0} \quad (10)$$

Figure 5b shows the plot of the relative quantum efficiency of formation of $\text{HO}^\bullet_{\text{bound}}$, *e.g.*

$Y_{\text{HO}^\bullet_{\text{bound}}}^{\text{rel}} = (\Phi_{\text{HO}^\bullet_{\text{bound}}} / \Phi_{\text{HO}^\bullet_{\text{bound}}}^{\text{max}})$ as a function of SR of the TiO_2 films, confirming that the photocatalytic activity at the film surface decreases with its roughness, probably by the trapping of hydroxyl groups inside of the coarser aggregates formed at the TiO_2 surface.

> FIGURE 5 <

CONCLUSIONS

In this work, we prepared opaque thick ($\sim 15 \mu\text{m}$) TiO_2 films made of commercially available Degussa P25 or Hombikat UV100 powders by the doctor blade method on glass slides followed by annealing treatment at 450°C for 2 h with different content of polyethylene glycol of 20 kDa (PEG20). During the annealing process, the mineralization of the organic complexing agents added in the initial pastes produced the incorporation of small amounts of C atom into the films, inducing a slight reduction of the energy band gap of TiO_2 ($3.02 \leq E_{\text{g}} \text{ (eV)} \leq 3.08$).

The micro-morphological characteristics of the films mainly depend on the amount of PEG20 in the starting paste, producing different landscapes of cracks and aggregates that contribute to a large light scattering and re-transmission phenomena with the result of a three-dimensional excitation of the TiO_2 particles.

The back-face irradiation with UVA of the opaque films produces both surface-bound ($\text{HO}^\bullet_{\text{bound}}$) and free ($\text{HO}^\bullet_{\text{free}}$) hydroxyl radicals with an observed efficiency inversely dependent on the surface roughness of the films. The topological control of the photocatalytic efficiency can be related to the increment of the coarsening of TiO_2 aggregates reducing the number of available $\text{HO}^\bullet$ at the surface of the films.

Therefore, we have demonstrated the capability of the doctor blade technique combined with the morphological control of the film surface by the addition of complexing agents such as PEG20 for

the tuning of the photocatalytic efficiency of immobilized TiO₂ on glass supports. These results can open the development of simple technologies for air and water decontamination and disinfection by using glass vessels covered at the interior by TiO₂ films that can be back-face irradiated.

ACKNOWLEDGEMENTS:

We thank the following funding agencies of Argentina: Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PUE-2018-0035), Universidad Nacional del Santiago del Estero (UNSE, CICyT-23A215), Fondo para la Investigación Científica y Tecnológica (FONCyT, PICT-2015-0828). We thank also to Juan Manuel Fernández (INBIONATEC) for technical assistance.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article:

Table S1. Mass (g), weight percentage [% wt] (between brackets) of the components of the pastes prepared by doctor blade method, the final TiO₂ mass loading persquare centimeter after annealing at 450 °C. Paste preparations were made by triplicate and the average values with the corresponding standard deviation (SD) are reported.

Figure S1. Photographs of the home-built Stirred Tank Reactor (STR), composed by a Spectroline ENF-260C/FE illuminator equipped with UVA lamp (Phillips, 6 W, $\lambda_{\text{max}} = 360 \pm 42$ nm) adapted with an attached holder for a black-painted Petri dish with a rectangular transparent window at the bottom. The plot shows the light transmittance (%) for the Petri-dish with the clean glass slide attached (orange line), together with the UVA beam intensity spectra across the STR and the clean glass slide without (solid blue line) and with Degussa P25 TiO₂ film (dashed-dot blue line) placed on the center of the transparent window (as indicated in left-side photos). The average value of total transmittance $\%T = (I_{\text{TiO}_2}/I_0) \times 100 = 2.0 \pm 0.5$ was estimated for the set of prepared

films, comparing the intensities at the emission maximum of the transmitted UVA spectrum through the STR and the glass slide without (I_0) and with (I_{TiO_2}) TiO₂ films. These spectra were registered with an Ocean Insight USB2000 spectrometer coupled with a cosine corrector attached to the surface of the samples. The transmittance spectrum of the Petri dish with the glass slide attached was obtained with Agilent 8453 spectrophotometer.

Figure S2. Diffuse reflectance spectra, plotted as $(1 - R)$, of Hombikat UV100 and Degussa P25 TiO₂ films with different % wt PEG20/ TiO₂ obtained by the doctor blade method on glass slides and 2 h of annealing at 450 °C.

Table S2. Parameters of the Tauc's equation obtained by linear fitting of data in the insets of Figure 2 (see main text).

Figure S3. EDS patterns of Hombikat UV100 TiO₂ films with PEG/TiO₂ = 78.8 % wt after annealing treatment at 450 °C. The red circle indicates the region analyzed.

Table S3. Elemental composition determined by EDS of the annealed films of TiO₂ into glass slides with the PhenomWorld Pro-X apparatus and excitation energy of 15 kV.

Figure S4. Mechanical stability (adherence) of the TiO₂ films on glass slides prepared with different PEG20/TiO₂ mass ratios by doctor blade method followed by annealing at 450 °C. The films were placed in contact with distilled water during 135 min under continuous orbital shaking. Error bars represent the corresponding standard deviation of a set of three measurements.

Figure S5: Fluorescence emission intensity changes monitored at 455 nm ($\lambda_{\text{ex}} = 335$ nm) during UVA irradiation of a supernatant aliquot of 9 μ M coumarin (CM) solution in the absence (■) and presence (●) of the TiO₂ film prepared with Degussa P25 with 79.5% wt PEG20/TiO₂ in the STR.

Figure S6. Inverted fluorescence microscopy images of 7-OH-coumarin (HCM) formed at the surface of the TiO₂ films obtained with the Carl Zeiss Axio-Observer Z1 fluorescence inverted microscope with a 40 $\times$ objective and excitation/beam splitter/emission filter set of 365/395/450 nm.

Table S4. Gray-scale integrated fluorescence intensity (a.u.) of adsorbed HCM obtained from inverted fluorescence images of Figure S6.

REFERENCES

1. Teoh, W. Y., Scott, J. A. and Amal, R. (2012) Progress in heterogeneous photocatalysis: From classical radical chemistry to engineering nanomaterials and solar reactors. *J. Phys. Chem. Lett.* **3**,

629–639.

2. Jafari, T., Moharreri, E., Amin, A., Miao, R., Song, W. and Suib, S. (2016) Photocatalytic Water Splitting—The Untamed Dream: A Review of Recent Advances. *Molecules* **21**, 900.
3. Banerjee, S., Dionysiou, D. D. and Pillai, S. C. (2015) Self-cleaning photocatalytic activity: Materials and applications. *Appl. Catal. B Environ.* **176**, 396–428.
4. Chong, M. N., Jin, B., Chow, C. W. K. and Saint, C. (2010) Recent developments in photocatalytic water treatment technology: A review. *Water Res.* **44**, 2997–3027.
5. Elhage, A., Lanterna, A. E. and Scaiano, J. C. (2017) Tunable Photocatalytic Activity of Palladium-Decorated TiO₂: Non-Hydrogen-Mediated Hydrogenation or Isomerization of Benzyl-Substituted Alkenes. *ACS Catal.* **7**, 250–255.
6. Dunlop, P. S. M., Sheeran, C. P., Byrne, J. A., McMahon, M. A. S., Boyle, M. A. and McGuigan, K. G. (2010) Inactivation of clinically relevant pathogens by photocatalytic coatings. *J. Photochem. Photobiol. A Chem.* **216**, 303–310.
7. Nosaka, Y. and Nosaka, A. Y. (2017) Generation and Detection of Reactive Oxygen Species in Photocatalysis. *Chem. Rev.* **117**, 11302–11336.
8. Nasr, M., Eid, C., Habchi, R., Miele, P. and Bechelany, M. (2018) Recent Progress on Titanium Dioxide Nanomaterials for Photocatalytic Applications. *ChemSusChem* **11**, 3023–3047.
9. Dunlop, P. S. M., Galdi, A., McMurray, T. A., Hamilton, J. W. J., Rizzo, L. and Byrne, J. A. (2010) Comparison of photocatalytic activities of commercial titanium dioxide powders immobilised on glass substrates. *J. Adv. Oxid. Technol.* **13**, 99–106.
10. Hinkova, A., Henke, S., Bubnik, Z., Pour, V., Salova, A., Slukova, M. and Sarka, E. (2015) Degradation of Food industrial pollutants by photocatalysis with immobilized titanium dioxide. *Innov. Food Sci. Emerg. Technol.* **27**, 129–135.
11. Lopez, L., Daoud, W. A. and Dutta, D. (2010) Preparation of large scale photocatalytic TiO₂ films by the sol-gel process. *Surf. Coatings Technol.* **205**, 251–257.
12. Hajkova, P., Spatenka, P., Horsky, J., Horska, I. and Kolouch, A. (2007) Photocatalytic effect of TiO₂ films on viruses and bacteria. *Plasma Process. Polym.* **4**, 397–401.
13. Simonsen, M. E., Jensen, H., Li, Z. and Søgaard, E. G. (2008) Surface properties and

photocatalytic activity of nanocrystalline titania films. *J. Photochem. Photobiol. A Chem.* **200**, 192–200.

14. Buxton, G. V., Greenstock, C. L., Helman, W. P. and Ross, A. B. (1988) Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in Aqueous Solution. *J. Phys. Chem. Ref. Data* **17**, 513–886.

15. Nosaka, Y. and Nosaka, A. (2016) Understanding Hydroxyl Radical ($\cdot\text{OH}$) Generation Processes in Photocatalysis. *ACS Energy Lett.* **1**, 356–359.

16. Geiger, S. M. and Salvático, N. (2012) Unjust Water: An Investigation of the Drinking Water Situation in Argentina. In *Climate Change and the Sustainable Use of Water Resources* (Edited by Leal Filho, W.), pp. 499–513. Springer Berlin Heidelberg.

17. Dinh, N. N., Quyen, N. M., Chung, D. N., Zikova, M. and Truong, V. Van (2011) Highly-efficient electrochromic performance of nanostructured TiO_2 films made by doctor blade technique. *Sol. Energy Mater. Sol. Cells* **95**, 618–623.

18. Alonso-Tellez, A., Masson, R., Robert, D., Keller, N. and Keller, V. (2012) Comparison of Hombikat UV100 and P25 TiO_2 performance in gas-phase photocatalytic oxidation reactions. *J. Photochem. Photobiol. A Chem.* **250**, 58–65.

19. Roșu, M. C., Suciu, R. C., Dreve, S. V., Silipaș, T. D., Bratu, I. and Indrea, E. (2012) The influence of PEG/PPG and of the annealing temperature on TiO_2 -based layers properties. *Rev. Roum. Chim.* **57**, 15–21.

20. Anastasescu, M., Teodorescu, V. S., Buiu, O., Osiceanu, P., Calderon-Moreno, J. M., Predoana, L., Preda, S., Nicolescu, M., Marin, A., Serban, B., Mihaila, M., Stoica, M., Zaharescu, M. and Gartner, M. (2014) Substrate impact on optical and microstructural properties of TiO_2 -PEG sol-gel films. *Ceram. Int.* **40**, 11803–11811.

21. Leandri, V., Gardner, J. M. and Jonsson, M. (2019) Coumarin as a Quantitative Probe for Hydroxyl Radical Formation in Heterogeneous Photocatalysis. *J. Phys. Chem. C* **123**, 6667–6674.

22. Černigoj, U., Štangar, U. L., Trebše, P. and Sarakha, M. (2009) Determination of catalytic properties of TiO_2 coatings using aqueous solution of coumarin: Standardization efforts. *J. Photochem. Photobiol. A Chem.* **201**, 142–150.

23. Bowman, W. D. and Demas, J. N. (1976) Ferrioxalate actinometry. A warning on its correct

use. *J. Phys. Chem.* **80**, 2434–2435.

24. Ishibashi, K., Fujishima, A., Watanabe, T. and Hashimoto, K. (2000) Quantum yields of active oxidative species formed on TiO₂ photocatalyst. *J. Photochem. Photobiol. A Chem.* **134**, 139–142.

25. León, A., Reuquen, P., Garín, C., Segura, R., Vargas, P., Zapata, P. and Orihuela, P. A. (2017) FTIR and raman characterization of TiO₂ nanoparticles coated with polyethylene glycol as carrier for 2-methoxyestradiol. *Appl. Sci.* **7**, 1–9.

26. Howard, D. L., Kjaergaard, H. G., Huang, J. and Meuwly, M. (2015) Infrared and Near-Infrared Spectroscopy of Acetylacetone and Hexafluoroacetylacetone. *J. Phys. Chem. A* **119**, 7980–7990.

27. Amalvy, J. I. and Soria, D. B. (1996) Vibrational spectroscopic study of distribution of sodium dodecyl sulfate in latex films. *Prog. Org. Coatings* **28**, 279–283.

28. Yoon, K. H., Noh, J. S., Kwon, C. H. and Muhammed, M. (2006) Photocatalytic behavior of TiO₂ thin films prepared by sol-gel process. *Mater. Chem. Phys.* **95**, 79–83.

29. Kelly, S., Pollak, F. H. and Tomkiewicz, M. (1997) Raman spectroscopy as a morphological probe for TiO₂ aerogels. *J. Phys. Chem. B* **101**, 2730–2734.

30. Hanaor, D. A. H. and Sorrell, C. C. (2011) Review of the anatase to rutile phase transformation. *J. Mater. Sci.* **46**, 855–874.

31. Myrick, M. L., Simcock, M. N., Baranowski, M., Brooke, H., Morgan, S. L. and McCutcheon, J. N. (2011) The Kubelka-Munk diffuse reflectance formula revisited. *Appl. Spectrosc. Rev.* **46**, 140–165.

32. Tauc, J., Grigorovici, R. and Vancu, A. (1966) Optical Properties and Electronic Structure of Amorphous Germanium. *Phys. Stat. Sol.* **15**, 627–637.

33. López, R. and Gómez, R. (2012) Band-gap energy estimation from diffuse reflectance measurements on sol-gel and commercial TiO₂: A comparative study. *J. Sol-Gel Sci. Technol.* **61**, 1–7.

34. Mahé, M., Heintz, J. M., Rödel, J. and Reynders, P. (2008) Cracking of titania nanocrystalline coatings. *J. Eur. Ceram. Soc.* **28**, 2003–2010.

35. Wang, X., Han, F., Wang, X. and Li, Y. (2014) Effect of aluminum foam support and

polyethylene glycol on surface morphology and photocatalytic behavior of TiO₂ films. *Mater. Chem. Phys.* **145**, 68–74.

36. Liu, Z., Jin, Z., Li, W. and Qiu, J. (2005) Preparation of ZnO porous thin films by sol-gel method using PEG template. *Mater. Lett.* **59**, 3620–3625.

37. Syrokostas, G., Leftheriotis, G. and Yianoulis, P. (2014) Effect of acidic additives on the structure and performance of TiO₂ films prepared by a commercial nanopowder for dye-sensitized solar cells. *Renew. Energy* **72**, 164–173.

38. Zhang, J. and Nosaka, Y. (2014) Mechanism of the OH radical generation in photocatalysis with TiO₂ of different crystalline types. *J. Phys. Chem. C* **118**, 10824–10832.

39. Ishibashi, K. I., Fujishima, A., Watanabe, T. and Hashimoto, K. (2000) Detection of active oxidative species in TiO₂ photocatalysis using the fluorescence technique. *Electrochem. Commun.* **2**, 207–210.

40. Zhang, J. and Nosaka, Y. (2015) Photocatalytic oxidation mechanism of methanol and the other reactants in irradiated TiO₂ aqueous suspension investigated by OH radical detection. *Appl. Catal. B Environ.* **166–167**, 32–36.

41. Kim, W., Tachikawa, T., Moon, G. H., Majima, T. and Choi, W. (2014) Molecular-level understanding of the photocatalytic activity difference between anatase and rutile nanoparticles. *Angew. Chemie - Int. Ed.* **53**, 14036–14041.

42. Murakami, Y., Endo, K., Ohta, I., Nosaka, A. Y. and Nosaka, Y. (2007) Can OH Radicals Diffuse from the UV-Irradiated Photocatalytic TiO₂ Surfaces? Laser-Induced-Fluorescence Study. *J. Phys. Chem. C* **111**, 11339–11346.

43. Odling, G. and Robertson, N. (2015) Why is anatase a better photocatalyst than rutile? the importance of free hydroxyl radicals. *ChemSusChem* **8**, 1838–1840.

44. Serpone, N. (1997) Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. *J. Photochem. Photobiol. A Chem.* **104**, 1–12.

45. Mehrvar, M., Anderson, W. A. and Moo-Young, M. (2002) Comparison of the photoactivities of two commercial titanium dioxide powders in the degradation of 1,4-dioxane. *Int. J. Photoenergy* **4**, 141–146.

FIGURE CAPTIONS

Figure 1. (a) Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of the paste prepared with 77.0 % wt TiO₂ Degussa P25, and the complexing agents (CA): 15.7 % wt PEG20, 0.04 %wt SDS, and 7.3 %wt AcAs before and after annealing treatment at 450 °C, compared with that of the neat TiO₂ powder; (b) Normalized Raman spectra of neat Degussa P25 powder before and after annealing at 450 °C and 750 °C.

Figure 2. (a) Diffuse reflectance spectra, plotted as $(1 - R)$, of glass slides without and with a Degussa P25 TiO₂ film containing PEG20 at the relative weight ratio of 79.5%, obtained by the doctor blade method on glass slides and annealing at 450 °C. Inset: photograph of the analyzed film. (b) Spectra of the modified Kubelka-Munk (K-M) remission function $F(R)$, eq. 7, for TiO₂ films prepared with Degussa P25 with different amounts of PEG20. The normalized emission intensity spectrum of the UVA illuminator is plotted in filled light gray. Inset: Tauc's plots for the calculation of energy band gap of the semiconductor (32).

Figure 3. (a) SEM images with magnification of 350× of TiO₂ films deposited on glass slides as a function of the PEG20/ TiO₂ (%wt) as indicated in Table 1. The bottom panel shows examples of SEM images with different magnification for Degussa TiO₂ films: (b) 13000× for surface roughness and (c) 1200× for film thickness calculations, respectively. In all cases electron acceleration was 5 kV.

Figure 4. (a) Variation of a coumarin (CM) concentration during the adsorption-desorption equilibrium in the darkness (blue circles) and by the photocatalytic generation of hydroxyl radical (orange squares) after UVA irradiation of a 79.5 %wt PEG20/TiO₂ Degussa P25 film. (b) UV-absorbance spectral changes produced in the initial CM solution (blue spectrum) after achievement of the adsorption-desorption equilibrium process (orange spectrum) and UVA photolysis (gray spectrum) of the same TiO₂ film as in (a). (c, d) Excitation-emission matrix (EEM) spectra of an aliquot of the supernatant CM aqueous solution equilibrated with same TiO₂ film than in (a),

before (left panel) and after (right panel) 60 min of UVA photolysis. (e) Optical transmission and inverted fluorescence images of 98.8 %wt PEG20/TiO₂ Hombikat UV100 and 79.5 %wt PEG20/TiO₂ Degussa P25 films, before and after 60 min of UVA irradiation.

Figure 5. Effect of the surface roughness (SR) of the TiO₂ films prepared with different mass ratio PEG20/ TiO₂ on: (a) operational quantum efficiency of formation of free hydroxyl radicals ($Y_{\text{HO}^\bullet_{\text{free}}}$), eq. 9, and (b) relative quantum efficiency of formation of surface bound hydroxyl radicals,

$$Y_{\text{HO}^\bullet_{\text{bound}}}^{\text{rel}} = (\Phi_{\text{HO}^\bullet_{\text{bound}}} / \Phi_{\text{HO}^\bullet_{\text{bound}}}^{\text{max}}).$$

Table 1. Optical, morphological, and photocatalytic properties of Degussa P25 and Hombikat TiO₂ films on glass slides as the solid support, prepared using the doctor blade method followed by annealing at 450 °c with different amounts of polyethylene glycol of 20 kDa (PEG20). Average values with their standard deviation of a set of triplicate experiments are reported.

PEG20/TiO ₂ (%wt)	$F(R)_\lambda$ (a.u.)	Surface roughness (nm)	Thickness (μm)	f_{ad}	ν_0 (nM.s^{-1})	$Y_{\text{HO}^{\cdot}\text{free}}$ (%)
Degussa P25						
0	0.349 ± 0.004	152 ± 25	15 ± 3	5 ± 1	1.45 ± 0.21	2.00 ± 0.29
20.4 ± 0.1	0.461 ± 0.005	135 ± 24	17 ± 2	9 ± 2	2.03 ± 0.18	2.11 ± 0.19
59.2 ± 0.2	0.503 ± 0.007	302 ± 59	16 ± 3	25 ± 6	1.03 ± 0.12	0.98 ± 0.11
79.5 ± 0.2	0.399 ± 0.005	314 ± 19	14 ± 2	17 ± 4	0.88 ± 0.09	1.06 ± 0.10
100.0 ± 0.4	0.333 ± 0.005	343 ± 75	13 ± 2	36 ± 9	0.70 ± 0.09	1.01 ± 0.12
Hombikat UV100						
0	0.276 ± 0.003	175 ± 26	16 ± 2	5 ± 3	1.68 ± 0.20	2.92 ± 0.41
20.7 ± 0.1	0.325 ± 0.004	439 ± 60	13 ± 3	15 ± 8	0.65 ± 0.16	0.96 ± 0.27
60.4 ± 0.3	0.387 ± 0.005	406 ± 45	14 ± 4	35 ± 10	1.00 ± 0.14	1.24 ± 0.14
78.8 ± 0.4	0.351 ± 0.004	243 ± 16	14 ± 3	20 ± 7	1.48 ± 0.15	2.02 ± 0.12
98.8 ± 0.3	0.387 ± 0.004	208 ± 30	18 ± 2	10 ± 4	1.83 ± 0.15	2.27 ± 0.11

php_13320_f1.jpg

php_13320_f2.jpg

php_13320_f3.jpg

php_13320_f4.jpg

php_13320_f5.jpg

multi-step
reaction

other
non-fluorescent
products

Coumarin
(CM)

7-HO-Coumarin
(HCM)