



## A simple procedure to quantitatively assess the photoactivity of titanium dioxide films

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### ABSTRACT

A simple and inexpensive procedure based on the bleaching of orange II (acid orange 7) solution has been developed in order to quantitatively assess the photocatalytic activity of titanium dioxide thin films. The influence of experimental parameters including, pH and light flux density on the reaction rate has been investigated. The results of this study suggest that at natural pH (7.2) and low dye concentration, the mechanism responsible for the degradation of orange II is mainly photooxidation via the formation of radicals. The procedure was used to compare the photoefficiency of TiO<sub>2</sub> films poisoned with variable amounts of sodium. The obtained results are in good agreement with the previously reported effect of sodium on the photoactivity of titanium dioxide thin films.

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### 1. Introduction

The remarkable property of titanium dioxide films to degrade a wide range of organic pollutants, when exposed to UV light, offers many applications in several domains such as water and air purification and Self-Cleaning Surfaces (SCS, hereafter). The technology of SCS has greatly improved these last years and commercial self-cleaning glasses are readily produced by several glass companies such as Saint-Gobain (Bioclean<sup>TM</sup>), Pilkington glass (Activ<sup>TM</sup>) and PPG (SunClean<sup>TM</sup>) [1–3]. The self-cleaning property is believed to be due to two phenomena occurring mutually at the titanium dioxide surface: photocatalysis and light-induced hydrophilicity [4,5].

The preparation of TiO<sub>2</sub> films showing photocatalytic activity has attracted great attention from both academic and industrial groups working in varied research fields and not dedicating their activities primarily to photocatalysis. Therefore, there is a need for developing a simple and inexpensive method to evaluate the photocatalytic activity of the TiO<sub>2</sub> films in order to optimize the preparation process and to improve the performance of the films.

Several different methods to evaluate the photocatalytic activity can be found in the literature. Among the different reported tests, those based on the degradation of a thin organic film such as a stearic [6] or palmitic acid [7] are the most widely used. The use of polycyclic aromatic hydrocarbons [8] as probes instead of fat acids has also been reported. However, these tests (i) require the use of heavy equipments such as Fourier Transform infrared spectrometers [6,7] or gaz chromatography [8] and (ii) demands the continuous presence of a trained technician since numerous *ex situ* measurements at periodical time intervals are required [6–8]. Another attractive way to evaluate the photocatalytic activity of TiO<sub>2</sub> films is to use tests based on dye degradation [9–11]. The most popular dye used to quantitatively assess the photoactivity of TiO<sub>2</sub> thin films is Methylene Blue (MB) [9,11]. However, the use of this dye as a reliable probe is subject to debate because it can be reduced to its *leuco* form, which is colourless like the oxidized form of MB [9].

In this paper, we describe a simple procedure to *quantitatively* determine and compare the photoactivity of TiO<sub>2</sub> thin films. The proposed test is based on the bleaching, upon UV–vis light exposition, of an aqueous solution of orange II put in circulation on the TiO<sub>2</sub> surface in closed-loop. The measurements were performed by means of a UV–vis spectrophotometer equipped with a circulating cell. The selection criteria for orange II as a probe are discussed in terms of both adsorption and inherent bleaching mechanisms. The influence of the experimental parameters, including pH and light flux density, on the bleaching kinetic are displayed and discussed. The optimized procedure is used to compare photocatalytic

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activity of sol–gel TiO<sub>2</sub> thin films deposited on glasses containing variable amounts of sodium.

## 2. Experimental details

### 2.1. Materials and reagents

All of the reagents used in this work were of analytical grade and were used without any further purification: titanium tetraisopropoxide (TTIP) Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (Aldrich, 97%); ethanol absolute grade; hydrochloric acid (Aldrich, 37%) and azo dye Orange II (Sigma Chemical Co., 98%).

### 2.2. Preparation of the TiO<sub>2</sub> film

The TiO<sub>2</sub> films were prepared using the sol–gel method and deposited on several types of glass substrates containing variable amounts of sodium, i.e. fused silica (FS), borosilicate glass (BSG, 4 wt% Na) and soda-lime glass (SLG, 14 wt% Na). The presence of Na in the glass substrates allows to obtain TiO<sub>2</sub> films containing Na. This latter diffuses from the glass substrate to the TiO<sub>2</sub> precursor film during the calcination step.

#### 2.2.1. Preparation of the TiO<sub>2</sub> sol

Titanium tetraisopropoxide (Ti(OiOC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) was used as a precursor to synthesize the titania sol via an acid catalysed sol–gel process at room temperature and under argon atmosphere. 10 ml of TTIP were dissolved in 50 ml of ethanol absolute grade under magnetic stirring and 1.3 ml of HCl (37%) was added to catalyze the hydrolysis. After 30 min stirring, the obtained solution was hydrolyzed by drop-wise addition of water (18 ml)/EtOH (50 ml) mixture under stirring during 2 h. The obtained TiO<sub>2</sub> sol was transparent, very fluid and stable for several weeks and its pH ranged from 0.6 to 1.

#### 2.2.2. Coating

Prior to use, each glass substrate (76 mm × 26 mm × 1.1 mm) was cleaned with detergent, acetone and ethanol in an ultrasound bath for 30 min, rinsed with distilled water and finally dried at 100 °C. It was coated with the sol by dip coating at a withdrawal speed of 11.5 cm/min. under a relative humidity in the range 50–55% and then dried at 70 °C during 5 min. This operation was repeated several times in order to obtain a thickness of several tens of nm. The obtained coatings were dried in an oven at 80 °C for 12 h and then calcinated at 450 °C in air during 2 h. In order to limit cracks of the film, the temperature rise was 5 °C/min and the sample was gradually cooled down to room temperature.

### 2.3. Determination of the photocatalytic activity

Fig. 1 shows a detailed view of the photoreactor (a) and a scheme of the whole experimental setup (b).

The photoreactor consisted of two glass microscope slides of 76 mm × 26 mm × 1.1 mm size (A) facing each other and maintained by three rectangular frames (B) made of polyetheretherketone (PEEK), and sealed by a rectangular Viton seals (C). The distance between the two glass slides inside the photoreactor was 0.7 cm and the resulting inner volume was of about 12 ml. The photocatalyst was immobilized on the internal surface of the upper glass slide (A) so that it was illuminated from the backside as sketched by the arrow in Fig. 1(a). We did not use the front side approach because a significant part of the UV flux would be absorbed by the dye before reaching the TiO<sub>2</sub> surface. As a result, the flux reaching the TiO<sub>2</sub> surface would become dependent on dye concentration. The average absorbance in the UVA region of a 10 mg L<sup>-1</sup> OII solution is 0.1 for 7 mm path length. For such a concentration, the UVA flux reaching the TiO<sub>2</sub> surface would be

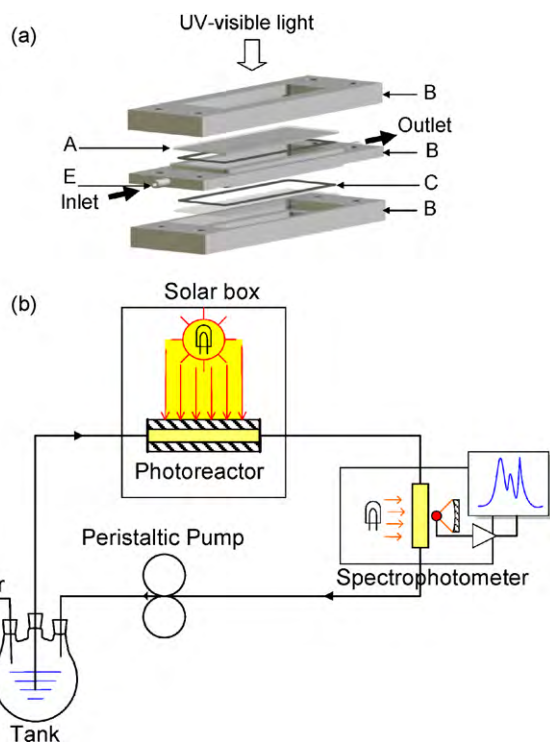


Fig. 1. Detailed view of the photoreactor (a) and a scheme of the global experimental setup (b).

attenuated by a factor 1.25 and a factor 1.6 for an initial concentration of 20 mg L<sup>-1</sup>. We will show that the glass absorption in the UV region is much weaker.

The photoreactor was placed in a Solar box (Atlas Suntest CPS+) simulating natural UV–vis radiation (light source: xenon lamp, 300 nm < λ < 800 nm). In spite of its air cooling system, we found difficult to maintain a room temperature inside the box whatever the irradiation power. That is why the experiments were conducted at a temperature of 35 °C i.e., the minimum temperature we could maintain at a constant value whatever the irradiation power. The dye solution was introduced tangentially between the two glass slides via a 4 mm diameter glass tube (E) and evacuated at the opposite side. It was put in circulation in closed loops by means of a peristaltic pump and tubing from a tank (a flat bottom three neck flask of 100 mL capacity), initially filled up with 60 ml dye solution, to a monobeam UV–vis spectrophotometer (Shimadzu PC-1200) equipped with a 1 cm-length quartz flow cell.

The dye solution was vigorously agitated in the flask by a magnetic stirrer in order to aerate it. The bleaching of the OII solution was monitored by recording its maximum absorbance at 484 nm. Before each test, the tank was filled with distilled water in order to rinse the photoreactor and the tubing. This operation was repeated twice before performing the baseline correction with renewed distilled water. Before the light was turned on, the dye was put in circulation during 30 min in the dark in order to reach the equilibrium adsorption when it occurred.

The photocatalytic activity of the films was quantitatively evaluated by comparing the bleaching reaction rates. We assumed that the reaction rate follows a Langmuir–Hinshelwood kinetic and can be described by a pseudo-one order model when the dye concentration is low.

$$r = -\frac{dc}{dt} = k_a c \quad (1)$$

where  $r$  is the bleaching rate,  $t$  the irradiation time,  $c$  the dye concentration and  $k_a$  the apparent reaction rate. The integration of Eq.

(1) gives:

$$\ln \frac{c_0}{c} = k_a t \quad (2)$$

where  $c_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ ).

The light power density at the sample location was measured by means of a photoradiometer (Deltaohm 2101) equipped with visible, UVA and UVB heads. In a typical experiment, the power density of visible, UVA and UVB were  $100 \text{ W m}^{-2}$ ,  $25 \text{ W m}^{-2}$  and  $1.6 \text{ W m}^{-2}$  respectively. The flow rate of the dye solution was set at the maximum allowed by our pump i.e.,  $33 \text{ ml min}^{-1}$ . The initial concentration of the dye was  $10 \text{ mg L}^{-1}$  and the measured pH was 7.2 (natural pH). The evolution of the absorbance was recorded during 2 h.

We also performed dye degradation experiments using only visible light. In that case, all the experimental parameters were the same except for the fact that UV part of the light which was cut by means of a 12-mm-thick GG400 filter (Schott) placed on the photoreactor. To discuss the effect of the pH on the degradation kinetic, the dye solution was acidified to pH 4.5 by an appropriate amount of HCl.

#### 2.4. Characterization of $\text{TiO}_2$ films

The morphology of  $\text{TiO}_2$  films were examined by a scanning electron microscope (Philips XL30 SFEG) equipped with a field effect gun and their microstructure by X-ray diffractometry using  $\text{Co-K}\alpha$  ( $\lambda = 0.17889 \text{ nm}$ ) radiation at grazing incidence ( $0.05^\circ$ ). The thickness of the films were determined by using spectroscopic ellipsometry (Horiba Jobin-Yvon S.A.S). The measurements were carried out at the incident angle of  $70^\circ$  in a spectral range of 300–800 nm.

### 3. Results and discussion

#### 3.1. Characterization of $\text{TiO}_2$ thin film

Whatever the nature of the glass, the obtained films were transparent, homogeneous and highly adherent. Typical SEM micrographs of the films deposited on SLG ( $\text{TiO}_2/\text{SLG}$ ) and FS ( $\text{TiO}_2/\text{FS}$ ) are presented in Fig. 2(a) and (b), respectively. No significant difference was observed between the morphology of  $\text{TiO}_2/\text{FS}$  and that of  $\text{TiO}_2/\text{BSG}$ . The films presented a granular structure with grains size of  $\approx 30\text{--}50 \text{ nm}$  for  $\text{TiO}_2/\text{SLG}$  and finer  $\approx 10\text{--}30 \text{ nm}$  for  $\text{TiO}_2/\text{FS}$ . The difference in particle size is in good agreement with the reported effect of  $\text{Na}^+$  on the particle size [12]. Small cracks, probably due to the difference of thermal expansion between the glass substrate and the film during the heat treatment, were observed on  $\text{TiO}_2/\text{SLG}$  (Fig. 2(a)). This feature allowed to roughly estimate the film thickness at 50–60 nm.

The XRD patterns of the obtained films are exhibited in Fig. 3. All the samples show XRD peaks attributed to the  $\text{TiO}_2$  anatase phase (JCPDS File No. 21-1272) with trace of brookite (JCPDS File No. 76-1934). This result proves that the heat treatment performed at  $450^\circ \text{C}$  in air allows to obtain anatase as the dominant phase whatever the nature of the substrate. At low diffraction angle, a broad diffraction peak from the glass substrate was observed for  $\text{TiO}_2/\text{BSG}$  and  $\text{TiO}_2/\text{FS}$ . The fact that this feature was not observed for  $\text{TiO}_2/\text{SLG}$  suggests that the  $\text{TiO}_2$  film is thicker than those deposited on BSG and FS. This difference can be related to a distinct film growth in connection with the presence of sodium.

The ellipsometric parameters as a function of wavelength in the spectral range of 300–800 nm and the modelled curves performed on  $\text{TiO}_2/\text{BSG}$  and  $\text{TiO}_2/\text{FS}$  samples are presented in Fig. 4(a) and (b), respectively. The structure of the film was modelled along its normal direction as an upwards decreasing density. This latter was

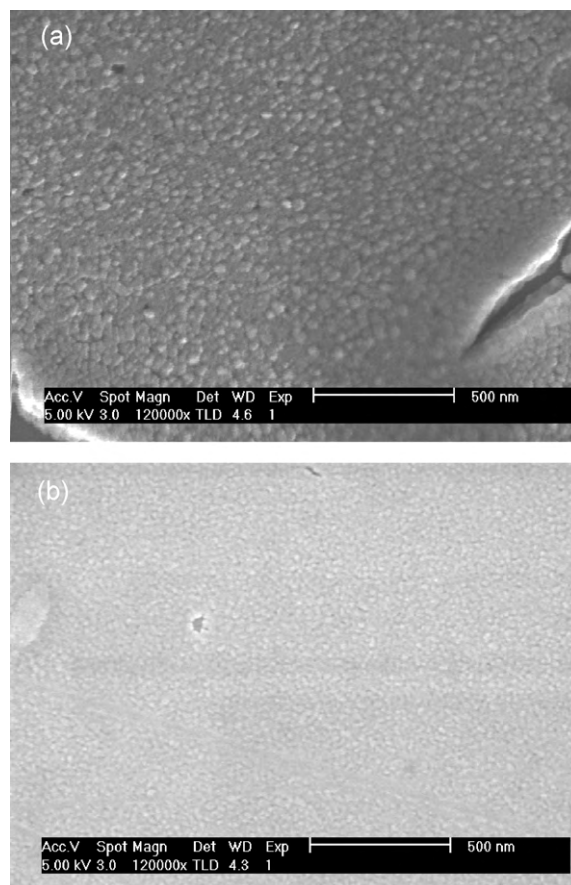


Fig. 2. Scanning electron micrographs showing the microstructure of the  $\text{TiO}_2$  film deposited on soda-lime glass (SLG) (a) and fused silica (FS) (b).

performed by mixing a linearly decreasing fraction of  $\text{TiO}_2$  with void. The  $\text{TiO}_2$  was described by a Cauchy dispersion law [13]. The results obtained for  $\text{TiO}_2/\text{SLG}$  are not presented because we failed to fit the ellipsometric parameters because of the cracks.

Fig. 4(a) and (b) reveals the rather good agreement reached between the measured and the modelled values of the ellipsometric parameters for both  $\text{TiO}_2/\text{BSG}$  and  $\text{TiO}_2/\text{FS}$  samples. These results are coherent with the granular structure of the film observed by SEM (Fig. 2(b)). Thickness values of 41 nm and 42 nm were obtained for  $\text{TiO}_2/\text{BSG}$  and  $\text{TiO}_2/\text{FS}$ , respectively. Both values are very close and comparable to those of commercial self-cleaning glasses. An optical index of 2.17 at 630 nm was found for both samples. This

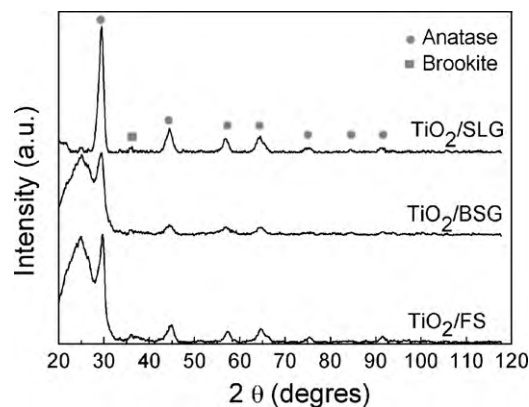


Fig. 3. Grazing incidence X-ray diffraction pattern of the  $\text{TiO}_2$  films deposited on the different glasses.

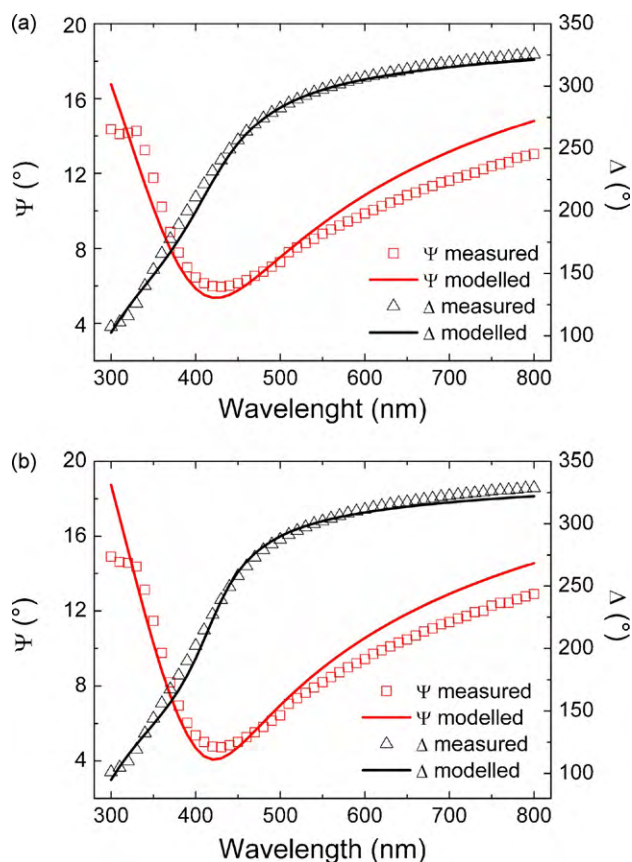


Fig. 4. Measured (symbols) and modelled (lines) ellipsometric parameters for  $\text{TiO}_2/\text{BSG}$  (a) and  $\text{TiO}_2/\text{FS}$  (b).

value is in good agreement with the values reported in other works [14].

### 3.2. Degradation mechanism of orange II

Fig. 5 shows a typical time evolution of the absorbance at 484 nm in the presence of  $\text{TiO}_2/\text{BSG}$  and uncoated BSG under UV–vis illumination.

First, we evaluated the dark adsorption of the dye onto the film and/or on any other internal surface of the system (tubing, tank, UV cell). The dye solution at natural pH (7.2) was put in circulation during two hours in the dark on the surface of a representative

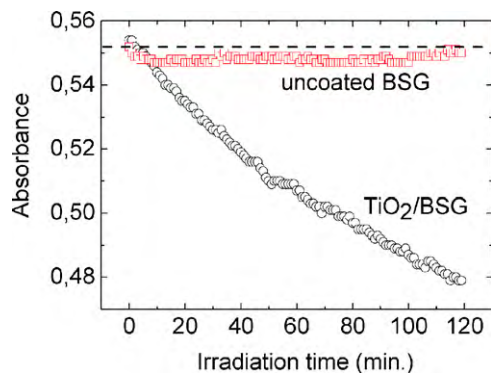


Fig. 5. Typical time evolution of the absorbance of OII solution in presence of a  $\text{TiO}_2/\text{BSG}$  sample (○) and an uncoated BSG substrate (□) under UV–vis light illumination. The horizontal dashed line indicates the initial absorbance value. The UVA power density was  $25 \text{ W m}^{-2}$ , the initial OII concentration  $10 \text{ mg L}^{-1}$ , the flow rate  $33 \text{ ml min}^{-1}$  and the pH of the dye solution 7.2 (natural pH).

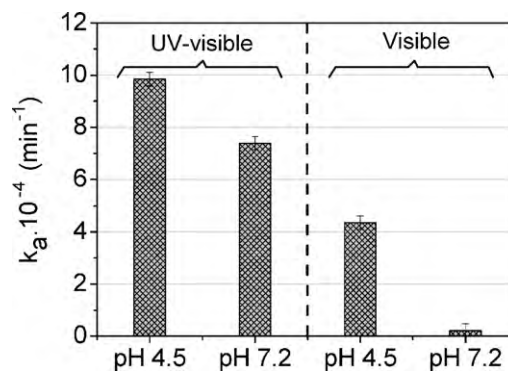


Fig. 6. Bleaching rate (apparent kinetic constants) of OII solution at natural pH (7.2) and acidic pH (4.5) in presence of a  $\text{TiO}_2/\text{SLG}$  sample under UV–vis and visible light illumination. The UVA power density was  $25 \text{ W m}^{-2}$ , the initial OII concentration  $10 \text{ mg L}^{-1}$  and the flow rate  $33 \text{ ml min}^{-1}$ .

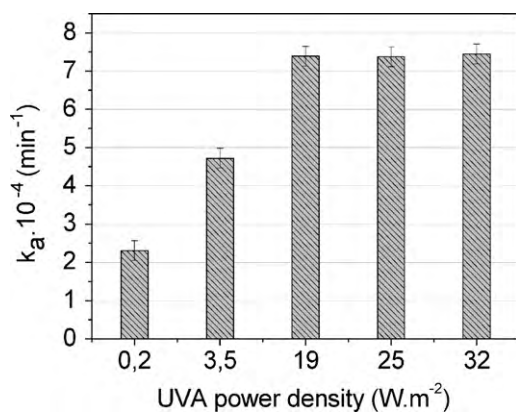
$\text{TiO}_2/\text{BSG}$  sample. No measurable decrease of the initial absorbance (concentration) was observed. The dependence of OII dark adsorption in a  $\text{TiO}_2$  colloidal solution on the solution pH was investigated by Bourikas et al. [15]. These authors showed that the amount of adsorbed dye on the surface of  $\text{TiO}_2$  particles (i) decreases with increasing pH and becomes even negligible for pH values above 7. Therefore, it was not surprising that the amount of OII adsorbed on the surface of the  $\text{TiO}_2$  films was not significant. Furthermore, in our case, the initial dye concentration was one order magnitude smaller than the one reported by these authors.

The absorbance change observed in the presence of an uncoated BSG under UV–vis illumination (Fig. 5) was not significant, showing that orange II was not bleached by photolysis. In contrast, a significant absorbance decrease was observed when the same experiment was conducted with a  $\text{TiO}_2$  layer (Fig. 5). After two hours, the initial concentration decreased by 13%, showing that the  $\text{TiO}_2$  thin film was responsible for the dye bleaching.

Stylidi et al. [16] have studied the pathways of OII degradation in aqueous  $\text{TiO}_2$  suspension as a function of UV/visible irradiation time. According to these authors, the bleaching process is the result of an oxidative cleavage of the molecule in the vicinity its chromophore (an azo bond) leading to numerous degradation products before mineralisation. Several mechanisms can be proposed to explain this cleavage. It can be the result of several competing reactions including (i) direct oxidation of the adsorbed dye (ii) photocatalyzed oxidation via radicals ( $\text{OH}^\bullet$ ) formation and (iii) degradation via dye photosensitisation. In cases (i) and (iii), the adsorption of the dye on the catalyst surface is a *sine qua non* condition for the charge transfer, and thus the reaction to occur. In order to elucidate the role of the pH in the possible degradation mechanisms, we studied the effect of pH (and adsorption) on the bleaching rate of OII.

The degradation rates of an OII solution in presence of  $\text{TiO}_2/\text{SLG}$  at pH 4.5 and 7.2 (natural pH) under visible and UV–vis illumination were compared. Fig. 6 gathers the apparent kinetic constants resulting from these four experiments. Under UV–vis illumination and pH 7.2, the apparent kinetic constant was about  $7.5 \times 10^{-4} \text{ min}^{-1}$ .

At pH 4.5 before turning on the light, the absorbance of the flowing dye decreased by about 5% after 30 min, showing that a significant amount of dye adsorbed on the  $\text{TiO}_2$  surface. Taking into account the volume of the flowing solution that was 60 mL, the weight of the adsorbed dye on the surface of  $\text{TiO}_2$  is estimated to be  $30 \mu\text{g}$  i.e., about  $0.1 \mu\text{mol}$ . A rough estimation of the  $\text{TiO}_2$  weight, assuming that its density is similar to that of the bulk material, leads to an amount of adsorbed OII of about  $300 \mu\text{mol g}^{-1}$ . This latter value is of the same order magnitude than the typical values measured for  $\text{TiO}_2$  colloidal solutions in acidic conditions [15].



**Fig. 7.** Bleaching rate of OII solution at natural pH in presence of TiO<sub>2</sub>/SLG sample for several values of UVA power densities. The initial OII concentration 10 mg L<sup>-1</sup> and the flow rate 33 ml min<sup>-1</sup>.

The same experiment performed on a naked glass did not reveal any absorbance change, proving that the adsorption occurred on the catalyst and not on another internal surface of the system (tubing or glass).

The bleaching rate observed after two hours of UV–vis illumination was found to increase by about 30% compared to that measured at pH 7.2. By contrast under visible illumination and pH 4.5, the bleaching rate decreased by about 40% ( $k_a = 4.3 \times 10^{-4} \text{ min}^{-1}$ ) compared to the one observed under UV–vis illumination and pH 7.2. Under visible illumination and pH 7.2, the photoactivity of the TiO<sub>2</sub> thin film vanished.

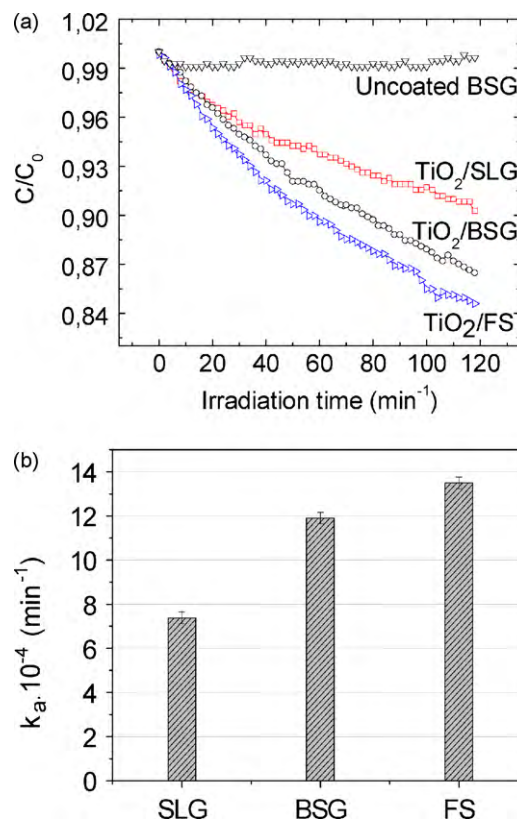
The fact that the dark adsorption of dye was negligible at pH 7.2 suggests that the mechanism of dye bleaching under UV–vis illumination is mainly photooxidation via radicals formation. The possibility of a degradation path involving free radicals living the TiO<sub>2</sub> surface and reacting in the bulk solution has even been suggested by several authors [17,18].

In acidic medium, the increase of the bleaching rate may be interpreted as a contribution of photosensitized degradation of the dye. This hypothesis is supported by the observed dark adsorption of the dye at pH 4.5 and the photoactivity despite the visible light illumination. However, a possible UV-induced modification of the surface of TiO<sub>2</sub>, leading to adsorption of the dye, cannot be excluded. Indeed, several experiments carried out in TiO<sub>2</sub> colloidal solution revealed a discrepancy between the dark adsorption constant in the L-H model and the apparent adsorption constant obtained under UV illumination. Ollis [19] interpreted this inconsistency as the formation of active sites such as Ti III under UV illumination.

To sum up, our results suggest that at pH 7.2 and an initial concentration of 10 mg L<sup>-1</sup>, the bleaching of OII was caused by photooxidation via formation of radicals and/or a UV-induced modification of the surface leading to adsorption/bleaching of the probe molecule [19].

### 3.3. Effect of UV power density

Experiments were carried out on TiO<sub>2</sub>/SLG to assess the bleaching rate of OII as a function of UV power densities. Fig. 7 gathers the apparent kinetic constants for several (UVA+UVB) flux ranging from (0.20±0.01) to (32±2) W m<sup>-2</sup>. These results show that for low UVA power density (0.2 and 3.5 W m<sup>-2</sup>), the bleaching rate increases with increasing photon flux whereas for high values i.e., in the range 18–32 W m<sup>-2</sup>, the bleaching rate becomes independent of the UV flux. These results suggest that below a given threshold, the photon flux is not sufficient to excite the entire catalyst. When the UV power density is sufficiently high, the entire layer is



**Fig. 8.** Evolution of the normalized concentration of OII solution at natural pH for an uncoated BSG substrate, TiO<sub>2</sub>/SLG, TiO<sub>2</sub>/BSG and TiO<sub>2</sub>/FS as a function of illumination time (UV–vis) (a) and the corresponding bleaching rates (apparent kinetic constant  $k_a$ ) (b). The UVA power density was 25 W m<sup>-2</sup>, the initial OII concentration 10 mg L<sup>-1</sup> and the flow rate 33 ml min<sup>-1</sup>.

excited but the rate of electron–hole creation is limited by the rate of electron–hole charge recombination. Therefore, in high power density range, the rate of formation of active species/sites becomes independent of the power density.

### 3.4. Comparison of the photocatalytic efficiencies of TiO<sub>2</sub>/SLG, TiO<sub>2</sub>/BSG and TiO<sub>2</sub>/FS

The photoactivity of TiO<sub>2</sub>/SLG, TiO<sub>2</sub>/BSG and TiO<sub>2</sub>/FS was assessed under typical experimental conditions. The bleaching curves and the resulting bleaching rates are shown in Fig. 8(a) and (b), respectively. The bleaching rate observed for TiO<sub>2</sub>/FS was twice as high as that of TiO<sub>2</sub>/SLG and about 20% superior to that of TiO<sub>2</sub>/BSG. These results show that the lower the amount of sodium in the substrate, the greater the bleaching rate. The effect of sodium contamination due to its diffusion from the glass to the TiO<sub>2</sub> precursor film during the calcination step is a well-documented fact [12,20,21]. H. Tada and M. Tanaka [20] observed a clear difference of photocatalytic activity between sol–gel TiO<sub>2</sub> films deposited on quartz and soda–lime glass. They attributed this difference to the presence Na<sup>+</sup> ions in the TiO<sub>2</sub> film that act as recombination centers for the photocarriers. Nam et al. [12] reported that Na<sup>+</sup> diffusion in the films affects its photocatalytic activity through an increase of the particles size. Moreover, these authors clearly revealed a correlation between the amount of Na in the glass substrate and the photocatalytic activity of the TiO<sub>2</sub> film.

Since the catalyst was illuminated through the back side of the glass substrate, it was crucial to verify whether the attenuation of the UV light by the glass substrates was not responsible for the observed differences between the photocatalytic activities of the three samples.

On the one hand, for SLG, the average transmittance is of 93% and 33% in the UVA and UVB, respectively. Taking into account these values, the interval of (UVA+UVB) flux really reaching the TiO<sub>2</sub> film and for which the bleaching rate remain constant ranges from (17+0.35) to (30+0.66) W m<sup>-2</sup>. On the other hand, the FS substrate is transparent in both UVA and UVB regions while BSG is slightly less transparent in the UVB region (75%). Since in a typical experiment, the (UVA+UVB) incident flux was (25+1.6) W m<sup>-2</sup>, the (UVA+UVB) flux reaching the TiO<sub>2</sub> film is close to (25+1.6) W m<sup>-2</sup> for the FS substrate, about (25+1.2) W m<sup>-2</sup> for the BSG substrate and (23.3+0.53) W m<sup>-2</sup> for the SLG substrate. These values are clearly above the lowest UV flux limit i.e., (17+0.35) W m<sup>-2</sup> for which the bleaching rate becomes constant. As a conclusion, the differences between the photocatalytic activities of sample can be ascribed to the marked poisoning effect of sodium and probably through the Na-induced change of particle size of the TiO<sub>2</sub> film.

#### 4. Conclusion

On the one hand, we shown that orange II as a probe is a good candidate to quantitatively assess the photocatalytic activity of TiO<sub>2</sub> thin films. On the other hand, our results strongly suggest that the bleaching is due to free radicals though the UV-induced formation of active site leading to adsorption/bleaching of the dye cannot be excluded. One of the major advantages of this procedure is the fact that it needs neither the use of sophisticated and expensive analytical equipment nor a trained technician. The main investment is a visible monobeam spectrophotometer equipped with a flow cell. The light source used in this study was a solar simulator but a simpler UVA source can be used instead. We believe that this

procedure may be useful for research groups whose activity is not primarily dedicated to photocatalysis but who need to compare in a quantitative, simple and costless manner the photoactivities of thin films showing potential applications in photocatalysis or solar cells.

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