

Light-storing photocatalyst: the possibility of activating titanium dioxide by photoluminescence

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ABSTRACT

Introduction: The aim of the present work was to analyze the possibility of creating a light-storing photocatalyst material, a system that couples a phosphorescent substrate with a titania coating. The substrate could activate the titanium dioxide coating even in condition of darkness thanks to its light emission. This improvement of absorption can be achieved because the titania semiconductor is irradiated both by the direct light and by the luminescent substrate which is activated at the same time.

Methods: TiO₂-based sol-gel solutions were deposited on commercial borosilicate glasses containing 2 different phosphorescent pigments (emission peaks at 470 and 520 nm, respectively). Particular attention was paid to optimize the film-substrate adhesion by using a scratch test to evaluate the optimal temperature of the post-treatment step.

Results and discussion: The main result is that when irradiated the photoluminescent pigments allow an increase in the photocatalytic activity of the coatings. The pigments are able to convert the ultraviolet component of light in order to increase the amount of energy that can be absorbed by titania. Moreover, the hydrophilicity test showed that in the absence of irradiation the phosphorescent samples are characterized by a lower loss of superhydrophilicity.

Keywords: Light storing photocatalyst, Phosphorescent, Photocatalysis, Superhydrophilicity, Titanium oxide

Introduction

The development of functionalized surfaces has recently been a focus of nanotechnology, by investigating self-cleaning surfaces using TiO₂ nanoparticles (1-5). When exposed to radiations of adequate wavelength, titanium dioxide (TiO₂) shows peculiar characteristics like photocatalysis of redox reactions, superhydrophilicity and antibacterial properties. For example, in a recent work, the authors reported the possibility of surface functionalization of industrial ceramic tiles (6) and bricks (7) by sol-gel technique to improve both wear resistance and cleanability of unglazed surfaces (8). TiO₂-SiO₂ binary films were deposited by air-brushing on fired tiles, obtaining photocatalytically active building materials, a self-cleaning and self-sterilizing surface that, moreover, might degrade several organic contaminants in the surrounding environment by UV radiation activation.

Anatase is the most active phase of TiO₂ and it can be activated by radiations with wavelength of 384 nm (9). However, sunlight contains only a small percentage of radiation with enough energy, so new solutions must be sought to improve the photoactivity of TiO₂-based products. Recent literature (10-21) has shown that the photocatalytic activity of TiO₂ can be greatly enhanced by doping it with either metal or non-metal ions or, possibly, both. Another way that has been investigated is the activation of titanium dioxide through the phosphorescence of an appropriate substrate (22-25). The aim of this coupling is one of the theoretical solutions to the problem of increasing the titania absorption of the solar radiation. The whole system, usually called light-storing photocatalyst, seems to have 2 main advantages: the system absorbs a higher percentage of the incident radiation, and the phosphorescent substrate can keep the titanium dioxide active even in conditions of darkness thanks to its light emission. This improvement of absorption is achieved because the semiconductor is irradiated both by the direct light and by the luminescent substrate, which is activated at the same time, and because the absorption spectrum of TiO₂ seems to shift to a higher wavelength when it interacts with a phosphor (22-24).

Zhang et al (25) created a light-storing photocatalyst on a ceramic substrate. A phosphorescent layer (Sr₄Al₁₄O₂₅:Nd,Eu) was screen-printed between 2 layers of glass (the lower with composition SiO₂: Al₂O₃: B₂O₃: Na₂O: ZnO: ZrO₂ = 47: 9:

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13: 12:5: 14 in weight and the upper with composition SiO_2 : Al_2O_3 : K_2O : Na_2O : B_2O_3 = 45: 5: 2.5: 15: 32.5), then the sample was dip-coated in a sol-gel solution containing $\text{Ti}(\text{OCH}_3)_4$ and thermal treated. In this work the analysis of the emission spectrum of the phosphor and the absorption spectrum of the titanium dioxide shows a small overlapping zone, indicating an interaction between the 2 systems: the decomposition of Rhodamine B obtained in conditions of darkness after the activation of the phosphor is the evidence of this interaction.

Li and Wang (22) carried on further studies on the basis of the previous article, analyzing the possibility of creating a light-storing photocatalyst with a different phosphor and in powder form. A powder of CaAl_2O_4 : Eu, Nd was added to a sol-gel solution of $\text{Ti}(\text{OBU})_4$, then the coated phosphors were dried and calcined. In this work the analysis of the absorption and emission spectra came to the same conclusion as the previous work, showing the same overlap. The absorption spectrum of titanium dioxide even shows a little shift to higher wavelength when it is applied on the phosphor, and this is a good property for products that need to be activated by the sunlight. The higher decomposition of NO gas obtained by the light-storing photocatalyst compared to pure TiO_2 in absence of a direct illumination is clear evidence of the good functioning of this composite.

In their work, Yoon and Kim (23) used a light-storing photocatalyzer powder similar to the one used by Li and Wang (powder of CaAl_2O_4 : Eu, Nd mixed in a TBOT sol-gel solution and calcined). However, the behavior of the system was analyzed through the photobleaching of methylene blue (MB) aqueous solutions under visible light illumination ($\lambda > 400$ nm). The sensible degradation obtained with the introduction of the phosphor compared with the lower degradation obtained with pure TiO_2 underlines the good interaction between phosphor and titanium dioxide.

Kim and Ham (24) repeated the experiment described in the previous article, reaching the same conclusions, but coating the phosphorescent powder with a low-pressure CVD method instead of the sol-gel method used previously. LPCVD of titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) was used on a powder of CaAl_2O_4 : Eu, Nd in order to obtain a TiO_2 thin film in a columnar structure with a large specific surface.

All the previously mentioned works confirm that the interaction between phosphors and titanium dioxide is possible and that it can bring about a significant increase in TiO_2 activity under visible light irradiation.

The aim of the present work was to analyze the possibility of creating light-storing photocatalyst material using commercial borosilicate glasses containing phosphorescent pigments as long afterglow phosphors. The titania coating was deposited on the glass surface by air-brushing. This deposition technique was chosen on a laboratory scale taking into account its industrial applicability and the possible technological solutions necessary to implement these surface treatments in the traditional industrial process. The films that were obtained were fully characterized to primarily evaluate the effect of the phosphorescent substrate on the hydrophilicity and cleanability of the coatings. Particular attention was paid to optimize the film-substrate adhesion, evaluating the optimal temperature of the post-treatment step by scratch test.

Methods

In order to analyze the real possibility of creating a light-storing photocatalyst, several samples were created through dip-coating, with a TiO_2 -based sol-gel solution (kindly furnished by NextMaterials), on commercial borosilicate glasses (produced by Next Generation) containing 2 different phosphorescent pigments, commercially named Ocean Blue Glass (OBG; Luce Dentro) and Yellow Green Glass (YGG; Luce Dentro). The 2 different glassy substrates containing alkaline earth aluminate phosphors with Eu and Dy had a declared emission peak at 470 nm for the OBG sample (coded as A glass), and at 520 nm for the YGG sample (coded as B glass), respectively.

In order to obtain a perfect film deposition, the sol-gel solution was dip-coated on the samples with immersion and immediately following extraction at 85.7 mm/min for both movements: the coating was then dried in the oven at 120°C, 200°C or 300°C. To evaluate the effect of the substrate-coating interaction on the photoinduced properties, the same coating was also applied on a slice glass (coded as G samples).

In order to investigate the interaction between substrate and coating, the absorption spectra of the TiO_2 coating deposited on a slice glass and the emission spectra of the fluorescent untreated samples were analyzed: the absorption spectra were measured in transmittance through UV-Vis spectroscopy (Lambda 19; Perkin Elmer), while the emission spectra of the phosphors were measured with an optical spectrum analyzer (PMA 11; Hamamatsu) in conditions of complete darkness after 30 minutes of white light irradiation on the sample (Xenon lamp, Oriel 6585).

The photoinduced hydrophilicity was afterwards examined for each sample through the measurement of the static contact angle of a 4- μL water droplet (OCA 20; Data-physics Contact Angle System). To avoid any surface contamination, all specimens were rinsed in tetrahydrofuran, THF, and carefully air-dried just before measurement. In this test the samples were placed under a UV light with wavelength range 325-390 nm and light intensity 8.0 mW/cm² (400 W flood; Dymax 5000) for 60 minutes and then left in total darkness. The contact angle was measured every 30 minutes from the beginning of the irradiation to the complete recovery of the initial contact angle. At the end of this test only the 4 most active samples were chosen for the following analysis, in addition to the untreated phosphorescent samples.

Photo-degradation of methylene blue solution (500 ppm) was used to assess the photocatalytic activity of the coating. The samples were placed in a beaker with a $3 \cdot 10^{-5}$ M methylene blue (MB) solution under a UV irradiation of 7.0 mW/cm² for 300 minutes and then left in total darkness. The ratio between the photocatalytic surface of the sample and the solution volume was kept constant for all the samples to assure comparability between the measurements, and each beaker was isolated in order to avoid any evaporation. The concentration of MB solutions as a function of time was measured through UV-spectroscopy at 664 nm (the absorption peak of MB solutions) and the measurements continued even in conditions of darkness after turning off the irradiation. To evaluate the dye degradation due only to the effect of UV light,



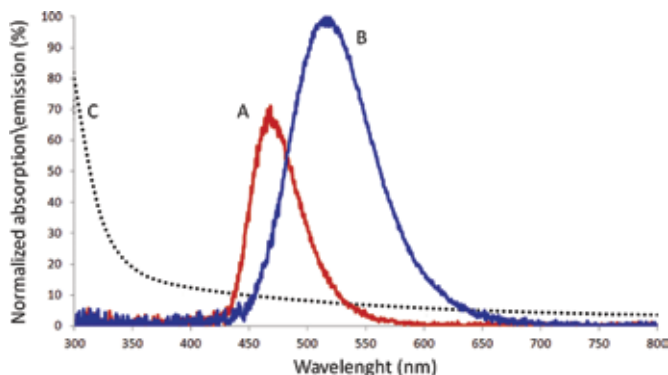


Fig. 1 - Normalized emission spectra of TiO₂-coated OBG (A) and YGG (B) glasses; normalized absorption spectra of TiO₂-coated slice glass dried at 300°C (C sample).

the same test was also repeated on the MB pure solution (S sample).

Finally, the surface microstructure of the 4 most active phosphorescent samples was evaluated through AFM analysis in noncontact mode (Autoprobe CP; Veeco) and scanning electron microscopy (SEM; Philips XL-40 after Au-Pd metalization with Emitech K550) while the adhesion of the titania film to the vitreous substrate were measured with a scratch tester (Micro-Combi Tester; Anton Paar). The analysis was conducted with a Rockwell tip (100 μm radius) with an incision speed of 1 mm/min and an increasing load from 50 mN to 30 N. At least 3 scratches were performed on each coating, with the minimum distance between 2 scratches set at 4 mm to achieve results representative of the average response over larger surfaces. The critical load Lc2 (edge spallation) was determined by optical microscopy.

Results and discussion

The emission spectra of the phosphorescent samples are reported in Figure 1 with the absorption spectra of the TiO₂ layers dried at 300°C (chosen as representative, Fig. 1). To provide easy comparison, the spectra were normalized by the average spectrum of the A and B glasses, respectively. The normalized amplitudes relative to the peak-wavelength, the wavelength corresponding to the emission peak of the spectra, is characterized by a very low variation. Such variations could depend on both: (i) the measurement uncertainty due to the used measurement system and measurement method and (ii) variations in the investigated glasses. As a result, the little variations obtained during the experimental activities suggested that the coating thickness and the temperature of the thermal treatment had little effect on the emission of the phosphorescent glasses, whose peak-wavelengths (after 60 seconds from turning off the irradiation) remained at 468 nm for the Ocean Blue Glasses (A glass) and 514 nm for the Yellow Green Glasses (B glass). With respect to the titania-coated sample (C sample), a small overlapping zone between the tails of the curves is shown. This result is in agreement with that reported by Li-Wang (21) and Zhang et al (25) but, as in the mentioned articles, the graphs show that the overlapping zone is small and characterized by low intensity.

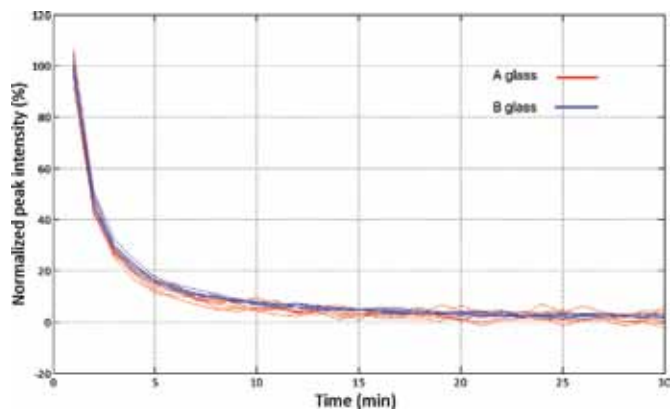


Fig. 2 - Time evolution of the normalized peak-wavelength amplitude of the TiO₂-coated OBG (A) and YGG (B) glasses plotted in logarithmic axis scale.

Figure 2 reports the time evolution of the amplitudes relative to peak-wavelength for A and B glasses, respectively. As before, the data were normalized by the peak-amplitude of the respective average spectrum recorded after 60 seconds from the end of the optical pumping. The graph shows that after some minutes both types of phosphorescent glasses almost completely lost their activation. The data are clearly overlapped, underlining that independently of the pigment, the 2 glasses have the same behavior.

SEM and AFM analysis showed that the samples dried at 300°C presented a similar coating microstructure. In Figure 3, the SEM images of sample surfaces are reported. The images of the coated Yellow Green Glass treated at 300°C, chosen as representative, show a very planar and homogeneous TiO₂ coating on the whole surface. By producing a fracture in the coating (Fig. 3B) it is possible to measure the film thickness, which is about 100 nm. The sample roughness was calculated with AFM analysis on the basis of 10 profiles 25 μm long for each sample (Fig. 4): the results show an average roughness of 3 to 6 nm.

To verify the adhesion of the coatings to the glasses, scratch tests with a linearly increasing load were performed on the samples. The scratch test showed that the critical load at which the TiO₂ coatings detached from the glass (Lc2) increases as the temperature of the thermal treatment is increased (Tab. I). In particular, for the coating obtained at 300°C, Lc2 is in the range 23 to 25 N, underlining the perfect adhesion of the titanium dioxide coating on the vitreous substrate. The results obtained on the uncoated glass show that the glass starts to be heavily scratched at loads around 8 to 10 N. Therefore, the damaging of the coating with the load increase begins because of the substrate fracture while the coating of TiO₂ is still adherent to the glass itself. This achievement is the proof that these samples could be used in everyday life application. Indeed, the loss of the photoactive coating follows the complete breaking of the glassy surface under heavy loads: this means that the object produced in this way would be physically unusable before it becomes inactive. The results demonstrated that 200°C to 300°C is the optimal temperature to obtain a transparent titania coating with good adhesion and good scratch resistance. For this reason, the photocatalytic activity of the coatings was determined only on these samples.

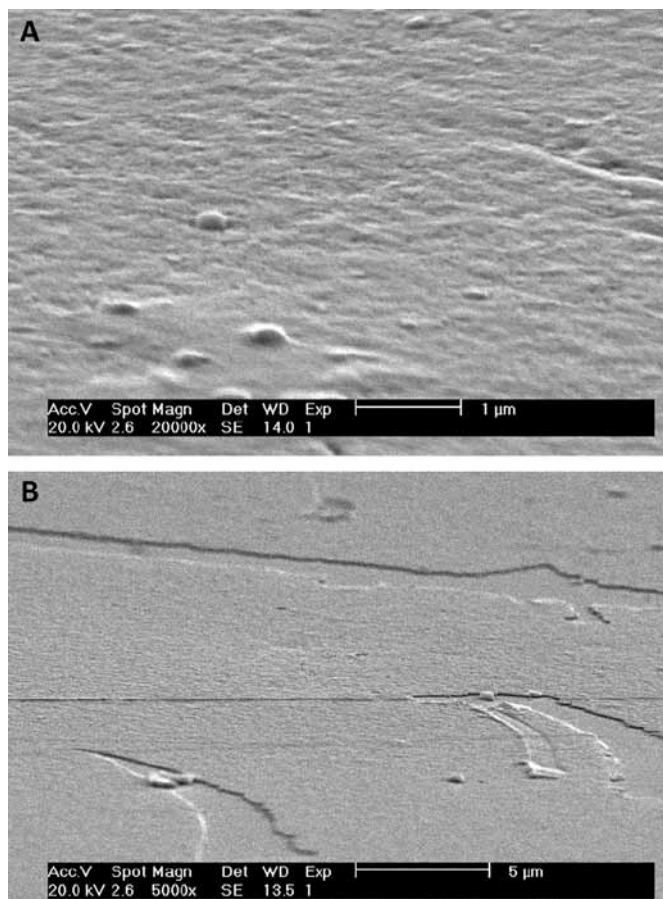


Fig. 3 - SEM micrographs of a TiO₂-coated phosphorescent samples (sample A_300 chosen as representative).

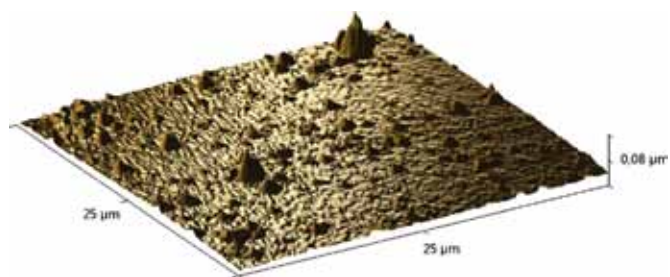


Fig. 4 - AFM micrograph of a TiO₂-coated phosphorescent sample on a 25 × 25-µm area (sample A_300 chosen as representative).

To evaluate the photocatalytic activity of the coated samples, contact angle (CA) measurements were performed. The data showed that, initially, the CAs of coated samples are generally higher than that of uncoated glass (dashed line in Fig. 5). However, in illuminated conditions, all the coated glasses were characterized by a decrease in CAs as the irradiation time is increased; that is, the glass surfaces become more hydrophilic by UV-light irradiation (26). The CA of the uncoated photoluminescent glasses, instead, do not change during UV illumination. The coating deposited on the photoluminescent glasses (A and B samples) were characterized by faster kinetics with respect to the coating deposited on a slice glass (G samples), underlining a synergic effect of titania and photoluminescent pigments. In any case, each sample achieved superhydrophilicity conditions within the first 40 minutes of UV irradiation. In darkness conditions, however, the recovery of the initial contact angle needed 4 to 5 hours for the most active phosphorescent samples compared to the 30 minutes that characterized the titania-coated slice glass (G samples). From these results it seems that a light-storing photocatalyst could increase the photoactivity of titania coating and could extend the titania activation for a non-negligible period of time even under conditions of darkness. Independently of the glass substrate, the most active samples were the samples obtained with a thermal treatment at 300°C. This treatment was evidently the ones that allowed a more active surface to be obtained in terms of the thickness and quality of the titanium dioxide layer. These samples were further tested together with the nonphosphorescent titania-coated glasses.

Photo-degradation of methylene blue solution was used to assess the photocatalytic activity of the samples. In Figure 6

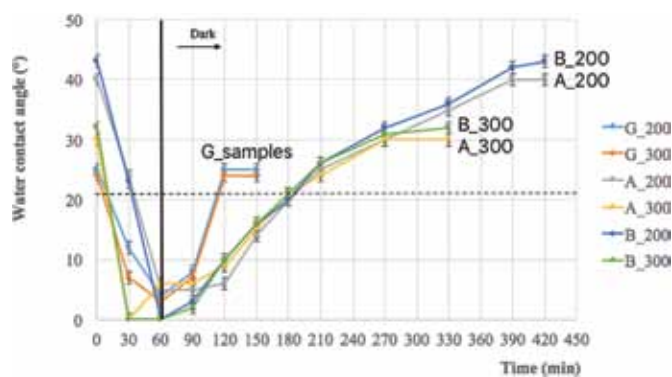


Fig. 5 - Water contact angle under UV irradiation and in complete darkness for TiO₂-coated samples.

TABLE I - Sample codes and Lc2 values obtained by scratch test

Glass substrate	Temperature (°C)	Code	Lc2 (N)	Glass Substrate	Temperature (°C)	Code	Lc2 (N)
A	Uncoated	A	10	B	Uncoated	B	8
A	120	A_120	14	B	120	B_120	12
A	200	A_200	18	B	200	B_200	22
A	300	A_300	23	B	300	B_300	25



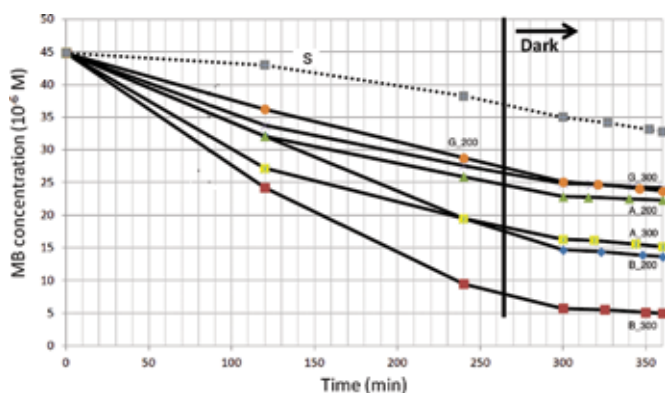


Fig. 6 - Photodegradation of MB aqueous solution under UV irradiation in beakers without sample (A) and with TiO₂-coated sample (B).

the MB concentration in both illumination and darkness conditions are reported. It is important to notice that each TiO₂-coated sample (even the nonphosphorescent ones, G samples) showed a dye degradation greater than the one caused by the UV radiation itself (S curve), underlining the effective catalyst effect of titanium dioxide under UV irradiation. The sample behavior is very similar both for the phosphorescent and for the nonphosphorescent ones, although the kinetic of MB decomposition strongly depends on the type of substrate used. This means that when irradiated the photoluminescent pigments bring about an increase in the photocatalytic activity of the coatings. In fact the pigments are able to convert the ultra violet component of light in order to increase the amount of energy that can be absorbed by titania. This hypothesis is in agreement with the absorption curve of the titania coating and the emission curves of the photoluminescent glasses reported in Figure 1. Moreover, the figure shows an overlap area among the curves that is greater for the B glass. Indeed, according to the MB decomposition measures (shown in Fig. 6), this glass is the substrate that most increases the kinetics of MB decomposition.

Finally, when the UV irradiation was turned off, this test showed that the MB degradation was stopped independently of the type of sample: this result demonstrates that the presence of a phosphor does not increase titania activity in the darkness.

Conclusions

The initial analysis of the emission spectra of the 2 phosphorescent glasses and the absorption spectra of the TiO₂ layers showed that an overlap between the curves exists and that the interaction between phosphors and titanium dioxide is possible. In agreement with other works, however, this overlap is very small in the system studied here as well.

Nonetheless, when irradiated the photoluminescent pigments allow an increase in the photocatalytic activity of the coatings against MB. The pigments are able to convert the UV component of light in order to increase the amount of energy that can be absorbed by titania. Instead in darkness, the dye decomposition is undetectable even in the presence of phosphors. The hydrophilicity test also showed good behavior of

the phosphorescent samples, which allow a slower loss of superhydrophilicity in the absence of irradiation. Once activated by UV irradiation, this property of TiO₂ is likely to be positively affected by the presence of the phosphor, although further investigations on the chemical interaction between the 2 layers must be done.

SEM, AFM and scratch analysis showed that TiO₂-based nanostructured coating with high quality and strong adhesion can be obtained on vitreous substrate with simple methods like dip-coating: the deliberately simple procedures used in this work confirm that the large-scale production of photocatalyst products for everyday applications is possible.

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Disclosures

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