Influence of platinum nano-particles on the photocatalytic activity of sol–gel derived TiO$_2$ films

D. Riassetto · C. Holtzinger · M. Langlet

Abstract Different 1-step or 2-step photo-platinization methods have been implemented to load sol–gel TiO$_2$ photocatalytic thin films with platinum nano-particles. These methods enable flexible variations in the amount of loaded particles, and they strongly influence the structure and size of these particles and the morphology of derived platinized films. The photocatalytic activity of platinized films has been studied. It is shown that optimal platinization conditions allow envisaging thin film photocatalysts with enhanced properties. Best performances are reached when the films are loaded with platinum particles for 30 or 60 min using a 1-step platinization method, which yields photocatalytic activities about 4 times greater than that of non-platinized films. Photocatalytic activity differences induced by the 1-step or 2-step photo-platinization methods are discussed in relation to the amount of loaded platinum together with structural and morphological features.

Introduction

Metallic platinum nano-particles loaded at the surface of TiO$_2$ photocatalysts strongly enhance the photocatalytic activity of titania through the formation of a Schottky barrier at the TiO$_2$/Pt interface, which promotes an efficient separation of holes and electrons charge carriers photo-generated under UV-light. Photo-electrons are readily transferred to and trapped in Pt nano-particles, while photo-holes are directed towards the semiconductor surface where they react with molecules to be photocatalytically decomposed. Though this effect has extensively been studied over the three past decades for powder TiO$_2$ photocatalysts, only very recent works report on the platinization of TiO$_2$ photocatalytic thin films [1–5]. Among various platinization methods used to functionalize powder TiO$_2$ photocatalysts, photo-metallization is one of the most employed [6–12]. The photo-platinization of powder TiO$_2$ photocatalysts is usually considered to proceed through the reduction of a Pt^{IV} precursor adsorbed at the TiO$_2$ surface, which is induced by electrons photo-generated in the TiO$_2$ conduction band under UV-light, i.e. a photocatalytic reduction mechanism. In a recent work, we have shown that this photo-metallization method can be applied to platinize TiO$_2$ sol–gel films [13]. Photo-platinization was achieved using a chloro-platinic acid (CPA) precursor diluted in aqueous solution, which was then exposed to UV-light in the presence of a TiO$_2$ sol–gel film. We showed that, using this method, the photocatalytic activity of TiO$_2$ films could be considerably increased. Thus, this work together with other recent studies [1, 2, 4] have demonstrated that, in agreement to what has commonly been reported for powder photocatalysts, surface platinization is a promising way to produce supported film TiO$_2$ photocatalysts with enhanced properties. These supported photocatalysts can in turn be considered for many photocatalytic applications, including self-cleaning surfaces or devices for water purification or air decontamination (see a review in [12]). However, these preliminary works still raise many questions, i.e., how platinization mechanisms influence different features such as the amount, size, and distribution of platinum particles at the surface of TiO$_2$ thin films, and how a suitable control of these morphological

D. Riassetto · C. Holtzinger · M. Langlet (✉)
LMGP, Grenoble Institute of Technology, Minatec, 3 Parvis Louis Neel, BP 257, 38016 Grenoble Cedex 1, France
e-mail: michel.langlet@inpg.fr

and structural features allow optimizing the photocatalytic activity of platinized films. More recently, we have studied photo-platinization mechanisms involved in the formation of platinum nano-particles at the surface of TiO_2 films exposed to UV-light [14]. We showed that metal nano-particles ensued from a straightforward photoreduction of CPA within the irradiated solution, i.e., a photo-chemical reduction directly induced by UV-light, rather than a photocatalytic reduction at the film surface, as commonly admitted in the case of powder TiO_2 photocatalysts. We also showed that a close control of the photoreduction conditions yielded a selective loading of 2 or 20 nm diameter platinum particles at the film surface. Consequently, various photo-platinization protocols could be implemented, which enabled us to flexibly vary the amount, size, and distribution of platinum nano-particles loaded at the surface of sol–gel TiO_2 films. In this article, we present first studies showing how these morphological and structural features influence the photocatalytic activity of platinized TiO_2 films.

Experimental

TiO_2 sol and film preparations

Sol–gel TiO_2 films were deposited from a polymeric sol, which was prepared by mixing tetraisopropyl orthotitanate (TIPT; $Ti(C_3H_7O)_4$ from Fluka) with deionized water, hydrochloric acid, and absolute ethanol as a solvent. TIPT concentration in the solution was fixed at 0.4 M, and the $TIPT/H_2O/HCl$ molar composition was 1/0.82/0.13. The sol was aged at room temperature for 2 days before first depositions, after which it could be used for several months in reproducible deposition conditions. Films were deposited at room temperature on (100) silicon wafers or soda-lime glass substrates (3.3×3.3 cm^2) by spin-coating using a Suss Microtec RC8 apparatus. Prior to deposition, the substrates were cleaned with ethanol, then rinsed with deionised water, and dried with air spray. For each deposition, 300 µL of sol were spread on the substrate rotated at 3,000 rpm. After liquid film deposition, the solvent rapidly evaporated and a solid film formed at ambient atmosphere through the well-known sol–gel polymerization route. A Multi-layer procedure was adopted to fix the final oxide film thickness at around 250 nm. Each as-deposited single-layer film was heat-treated in air for 2 min at 500 °C before deposition of a subsequent single-layer. The final 7-layer film was then heat-treated at 500 °C for 2 h. Our previous works showed that such conditions yielded well crystallized anatase TiO_2 films, which exhibited high optical quality and good photocatalytic activity [15, 16].

Photo-platinization conditions

Photo-platinization experiments were performed using CPA hexahydrate ($H_2PtCl_6 \cdot 6H_2O$ from Strem Chemicals) as a platinum precursor. CPA was first diluted in absolute ethanol to give a solution of 1.9 mM platinum concentration. The resulting solution was very stable in the dark and could be used for 1 year or more in reproducible conditions. Before experiments, this solution was further diluted in deionized water and absolute ethanol, with water/ethanol molar ratio of 80/20, and the CPA concentration was fixed at 860 µM. A volume of 100 mL of this solution was then poured into a glass vessel opened to air for further exposure to UV-light. UV-exposures were performed using three UVA lamps (PLS 11 W from Philips). These lamps exhibit a continuous emission spectrum extending between 350 and 400 nm, with an emission maximum centered at around 365 nm, and some additional emission peaks in the short wavelength visible range. They do not emit in the UVB/UVC spectral range. Two generic photo-platinization protocols were studied to form platinum particles and disperse them at TiO_2 film surfaces.

1-Step photo-platinization (1-Pt) method

A titania-coated substrate was settled on a sample holder and immersed in the 860 µM CPA solution, the coated surface being oriented toward bottom of the glass vessel, at a distance of 8 mm. The solution was first stored in dark conditions for 1 h to reach equilibrated adsorption of CPA at the film surface. Sample and solution were then exposed to UV-radiation, the distance between the lamps and glass vessel bottom being fixed at 2 cm. UV-exposure experiments were performed, for various durations ranging up to 15 h, in a climatic cabinet regulated at a 20 °C temperature and 40% relative humidity. Constant agitation of the solution was insured over UV-exposure using a magnetic stirrer rotated at 500 rpm. In such conditions, photoreduction of the solution and adsorption of derived metallic platinum particles at the film surface proceeded simultaneously. After photo-platinization, films were rinsed with deionized water and subsequently heat-treated in air at 110 °C for 2 h.

2-Step photo-platinization (2-Pt) methods

The 860-µM CPA solution was preliminary photoreduced through an exposition to UV-light for 45 min or 15 h, in the absence of any TiO_2 film. After UV-exposure, this solution was further diluted in an 80/20 water/ethanol mixture at various platinum concentrations ranging between 42 and 860 µM. A film was then immersed in 100 mL of these solutions for various durations ranging

from 5 to 120 min, using the same experimental device and conditions as the 1-Pt method, which yielded adsorption at the film surface of platinum particles produced during the preliminary photoreduction step. Adsorption was performed under UV-light exposure or not. However, for reasons discussed in [14], adsorption from a solution preliminary photoreduced for 45 min did not proceed in significant extent in the absence of UV. Thus, derived films will no longer be considered in the present article. After platinum adsorption, the films were rinsed with deionized water and subsequently heat-treated in air at 110 °C for 2 h. In this study, films platinized from the 2-Pt method using a preliminary photoreduction of 45 min or 15 h are labelled 2-Pt-45 m or 2-Pt-15 h, respectively.

Characterization of platinum particles and platinized films

Platinum particles formed in solutions photoreduced for 45 min or 15 h were dispersed on a carbon grid for high-resolution transmission electron microscope (TEM) observations. These observations were performed using a JEOL-2010 LaB$_6$ instrument operated at 200 keV. Transmission UV/visible characterizations were performed on films, platinized or not, deposited on soda-lime glass substrates. Transmission spectra were acquired in a 300–1,100 nm spectral range using a Jasco V-530 spectrophotometer. Other characterizations were performed on films deposited on silicon wafers. A Philips XL 30 Scanning Electron Microscope (SEM) operated at 6 kV was employed for energy dispersive X-ray (EDX) analyses. EDX measurements were systematically performed in five distinct places of the film surface in order to statistically probe areas of approximately 0.5×0.5 mm^2. The amount of platinum was quantified from the averaged Pt (Mα)/Ti (Kα) intensity ratio deduced from EDX analyses. Surface imaging of platinized films was performed using a ZEISS Ultra 55 Field Electron Gun (FEG)-SEM operated at 20 kV.

Photocatalytic properties of platinized films were studied through the oxidative photo-decomposition of Orange G (OG; C$_{16}$H$_{10}$N$_2$Na$_2$O$_7$S$_2$ from Aldrich) in aqueous solution (25 mg/L; 100 mL) using the same device as that used for photo-platinization experiments. Before UV-irradiation, the solution was first stored in the dark for 60 min to reach equilibrated adsorption of OG at the film surface. Then the film was exposed for 3 h to UV-light under magnetic stirring in de-aerated conditions (without air or oxygen bubbling). Small solution aliquots were periodically withdrawn in order to measure the concentration variations of OG as a function of irradiation time. Transmission spectra of liquid samples were collected in the 300–600 nm spectral range using a Jasco V-530 spectrophotometer. OG

concentration variations were deduced from absorbance variations of the main OG absorption band at 480 nm. The photocatalytic activity was determined from the rate of disappearance of OG by plotting Ln(C_0/C) as a function of the irradiation time (t_{UV}), where C_0 and C account for the OG concentration before and after exposition, respectively. Blank UV-irradiations performed for 3 h without titania films did not allow to detect any variation of the OG concentration, which indicated that any additional photochemical (non-photocatalytic) decomposition did not occur over the whole duration of the experiments. Besides, negligible variations of the OG concentration observed after storage of platinized film in the dark for 60 min indicated that any purely catalytic (non-photocatalytic) mechanism, eventually induced by platinum particles, did not significantly participate in the OG decomposition. Both observations allow concluding that photo-decomposition features described in following sections only arise from pure photocatalytic effects. Finally, we also performed preliminary photocatalytic tests using an UV-cut-off filter (GG 400 from Schott; $\lambda > 380$ nm). These tests showed that, in our experimental conditions, the contribution of visible light emitted by our lamps to the photocatalytic decomposition was inexistent. In other words, photocatalytic activities studied in the present study only arise from charge carriers photo-generated under UVA light ($\lambda < 380$ nm).

Results and discussion

Photo-platinization features

Figure 1 illustrates variations of the Pt/Ti ratio deduced from EDX analyses for thin films platinized using the different 1-Pt or 2-Pt methods. This figure shows a certain dispersion of EDX data, which is presumably due to limitations in accuracy of this characterization method, but it can also depict a certain lack of control in the amount of loaded platinum particles. However, it clearly indicates that the amount of loaded particles can flexibly be varied using the different methods through variations of the 1-step or 2-step adsorption duration (Fig. 1) or variations of the platinum concentration within the photoreduced solutions (inset of Fig. 1). Platinization features have also been assessed through UV/visible spectroscopy measurements. Figure 2 illustrates UV/visible transmission spectra of TiO$_2$ films before and after platinization for 1 or 4 h using the 1-Pt method. These spectra depict interference fringes induced by multi-reflexions at film/glass substrate and film/air interfaces, causing transmission minima and maxima located at fixed wavelength values that in turn depend on the film thickness. Very weak variations in the film
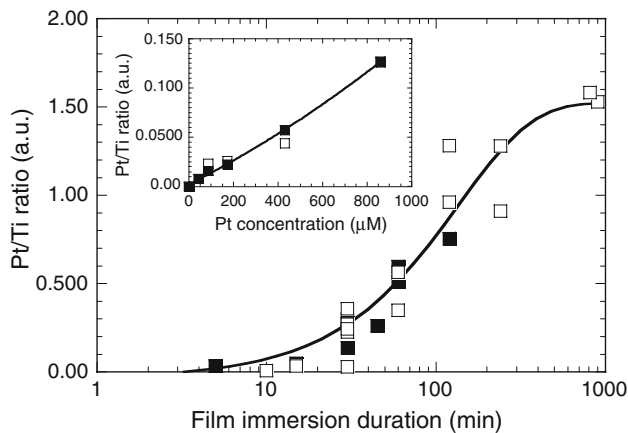
Fig. 1 Variations of the Pt/Ti ratio deduced from EDX analyses for films immersed under UV-light in an 860-μM solution for various durations, using the 1-Pt (□) or 2-Pt-45 m method (■). Inset shows the same variations for films immersed for 5 min, under UV-light (□) or not (■), in solutions of various platinum concentrations using the 2-Pt-15 h method
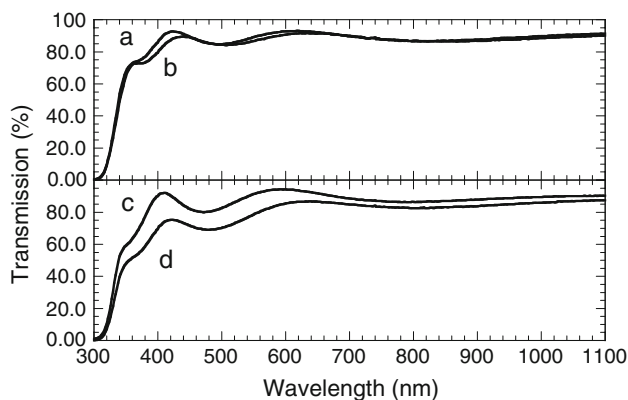

Fig. 2 UV/visible spectra of films before (a, c) and after photo-platinization (b, d) using the 1-Pt method. Platinized films were exposed to UV-light for 1 h (b) and 4 h (d)

thickness, arising from our deposition conditions (maximum variations of 5% in the present study), can induce small modifications in the location of these extrema, which can in turn significantly influence the transmission level near the short wavelength absorption edge of TiO_2 films (absorption onset at around 380 nm). Of course, these modifications only arise from interference effects and do not depict any significant change in the film absorption. Thus, to reliably assess the influence of platinum particles on the transmission spectra, it is necessary to specifically consider the spectrum of each TiO_2 film before (Fig. 2a, c) and after platinization (Fig. 2b, d). According to Fig. 2a and b, a short 1-Pt platinization of 1 h does not appreciably modify the transmission spectrum. Figure 2c and d shows that increasing the platinization duration up to 4 h reduces the transmission level and this reduction is more marked at short wavelengths. These features are attributed to Mie

scattering effects induced by metallic platinum nano-particles loaded in sufficient amount at the film surface [17]. As will be detailed in next sections, previous X-ray photoelectron spectroscopy (XPS) measurement confirmed the metallic character of these particles [14]. Figure 2c and d indicates that, at a 365 nm wavelength, the maximal emission wavelength of the lamp used to perform our photocatalytic characterizations, the transmission decreases from 66 to 53%. It means that, owing to the presence of platinum particles at the film surface, the flux of UV-light actually reaching the TiO_2 film is reduced by about 20%, which can in turn eventually influence the charge carrier photo-generation.

Figure 3 shows FEG-SEM images of films loaded with platinum particles from an 860-μM solution using the 1-Pt or 2-Pt-15 h method. No platinum particle could be detected when the film was immersed for less than 15 min using the 1-Pt method. A 1-Pt platinization of longer duration initially yielded the dispersion of 20-nm diameter spherical particles at the film surface. The amount of such particles gradually decreased with increasing the 1-Pt platinization duration and these particles were progressively replaced by 2-nm diameter particles homogeneously distributed at the film surface. These features are illustrated in Fig. 3a and b for a 1-Pt platinization of 1 and 4 h, respectively. Further increase of the immersion duration, for around 15 h, yielded films exclusively coated with 2-nm particles [14]. Films platinized under UV-light using a 2-Pt-45 m method exhibited morphologies similar to those illustrated in Fig. 3a and b (not illustrated here), i.e., a first dispersion of essentially 20-nm platinum particles over the first post-photoreduction adsorption stages (adsorption of 1 hr or less), followed by a progressive replacement of these particles by 2-nm ones over a prolonged film immersion under UV-light. Films platinized using a 2-Pt-15 h method were exclusively coated of 2-nm platinum particles homogeneously distributed at the film surface, whose amount depended on the film immersion duration (under UV-light or not) or platinum concentration in the photoreduced solution. Figure 3c shows a typical FEG-SEM image of such a film immersed for 5 min within an 860-μM photoreduced solution. It is observed that the size and surface distribution of 2-nm platinum particles are similar to that observed after a 4-h platinization using the 1-Pt method (Fig. 3b), but preliminary photoreduction of the CPA solution for 15 h yielded a complete disappearance of 20-nm particles. A TEM image of a 20-nm particle formed in the solution during the preliminary 45 min photoreduction step is presented in Fig. 4a. It is observed that such a particle consists of aggregated 2-nm single particles, which are identified by circles in the figure. The TEM image of Fig. 4b illustrates platinum particles formed in the CPA solution preliminary photoreduced for 15 h,
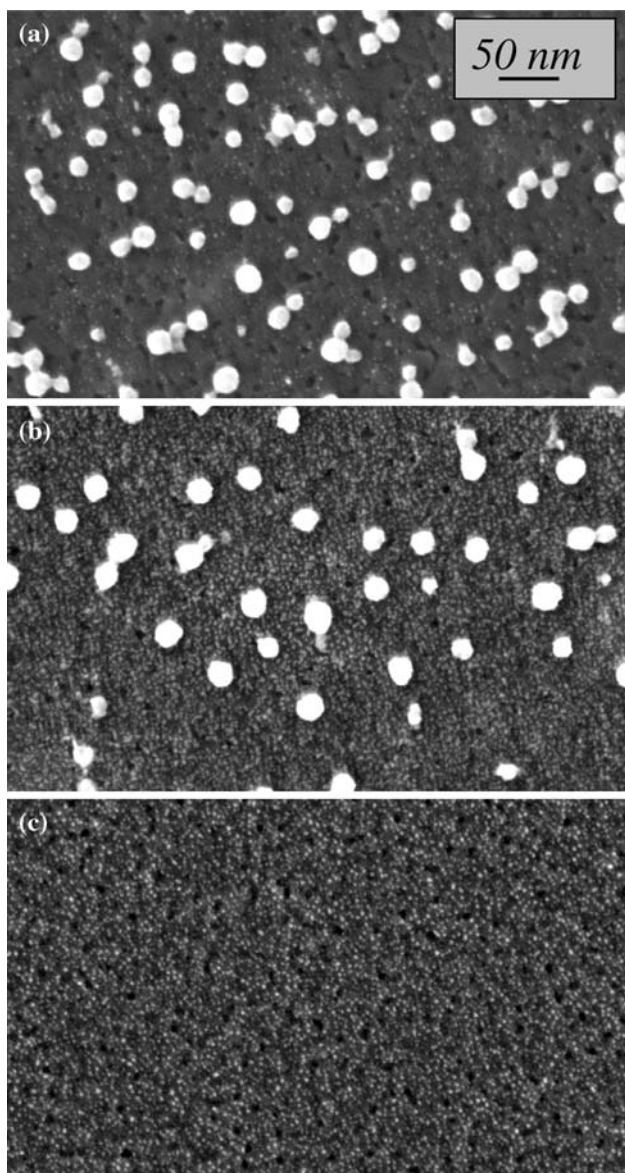
Fig. 3 FEG-SEM images of films immersed under UV-light in an 860-μM solution using the 1-Pt method with an immersion duration of 1 h (**a**) or 4 h (**b**), and a film immersed under UV-light in an 860-μM solution using the 2-Pt-15 h method with an immersion duration of 5 min (**c**). Different images are presented at a same scale

Fig. 4 TEM images of 20 nm (**a**) and 2 nm particles (**b**) formed in 860-μM solutions, which were exposed to UV-light for 45 min and 15 h, respectively. *Circles* indicate individual platinum single particles. Different images are presented at a same scale

and confirms the 2-nm diameter of these particles, as already illustrated in Fig. 3c. TEM images of Fig. 4a and b also show crystallographic planes (see circles), which indicate the crystalline nature of 2-nm metallic platinum single particles.

As discussed in our previous study, data presented in Figs. 3 and 4 depict a two-step photo-chemical reductive process, which would be governed by photo-induced fragmentation mechanisms occurring within the solution exposed to UV-light (Figs. 4a, b and 3c) and at the film surfac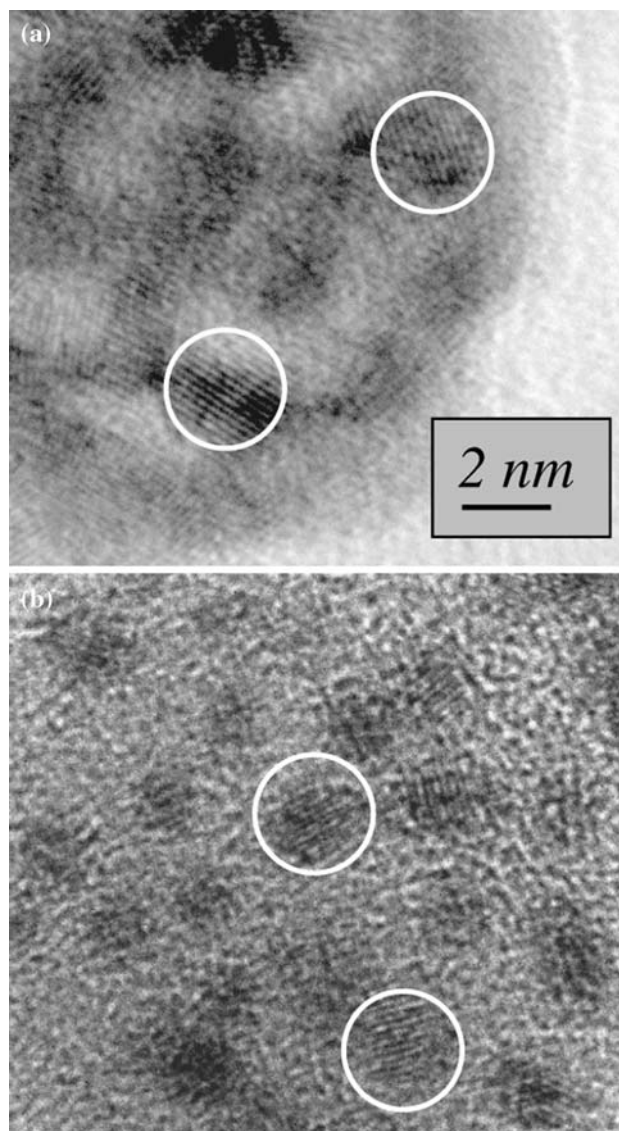e exposed to UV-light (Fig. 3a, b); [14]. In other words, aggregates initially formed within a solution exposed to UV-light for a short duration can dissociate under prolonged UV-exposure and generate 2-nm single-particles within the solution or at the film surface. This photo-induced fragmentation is probably promoted by the strong photo-chemical activity of noble metal nano-particles, and has already been described by other authors for silver particles exposed to UV-light [18, 19]. In the present case, further studies will be necessary to understand mechanisms inducing such a fragmentation of platinum particles within the solution or at the film surface. However, a main consequence of these fragmentation mechanisms is that we can selectively disperse 20-nm

particles (1-Pt or 2-Pt-45 m method with a short film immersion under-UV light) or 2-nm particles (2-Pt-15 h method) at the TiO_2 film surface.

Photocatalytic kinetics of platinized films

Figure 5a and b shows typical variations of the decomposed OG molar fraction versus UV-exposition duration for a non-platinized film and for a film platinized for 60 min using the 1-Pt method, respectively. For the non-platinized film, the term Ln (C_0/C) exhibits a nearly linear increase with t_{UV} over the three-first hours of UV-exposition. Thus, photocatalytic mechanisms follow an apparent first-order reaction [20]. Previous studies have shown that, in the presence of a TiO_2 photocatalyst, OG not only undergoes a photo-decolorization but is also efficiently photocatalytically decomposed [21]. The slope derived from Ln (C_0/C) = f (t_{UV}) variations of Fig. 5a, has been considered to assess the apparent rate constant of the photocatalytic reaction, yielding a 0.052 h^{-1} value. Statistical studies, performed on different non-platinized TiO_2 films, revealed an experimental error of ±0.002 h^{-1}, which accounted both for experimental variations in the film elaboration and photocatalytic characterization conditions. Contrary to a non-platinized film, variations illustrated in Fig. 5b indicate that the photocatalytic decomposition induced by platinized films does not rigorously follow a first-order. In a first transitory regime, the molar fraction of decomposed OG is observed to increase rapidly. Then, the photocatalytic reaction decelerates and, in a subsequent steady state regime, the Ln (C_0/C) term starts to linearly increase with further increase of the UV-exposition time, i.e., the reaction starts to follow apparent first-order kinetics.

In this study, photocatalytic decomposition of OG in aqueous solution has been studied in de-aerated conditions. These conditions allow a simple implementation of photocatalytic experiments, and then are compatible with a fast routine and comparative study of numerous samples. It is known that in presence of water, in de-aerated conditions or not, the oxidative photocatalytic decomposition efficiently proceeds through the formation of strongly oxidant $OH^{\bullet}$ radicals originating from water [20]. However, de-aerated conditions in water medium are not incompatible with an efficient oxidative photo-decomposition, they can influence the photocatalytic decomposition rates. Some authors reported on a long-term deceleration of photo-reactions induced by powder Pt-TiO_2 photocatalysts [10, 22], which was attributed to an insufficiently efficient evacuation of photo-electrons from platinum particles to molecular oxygen present in the surrounding medium and adsorbed at the photocatalyst surface. In a de-aerated liquid system like the one used in the present study, oxygen is probably not present in large amount within the liquid medium and at the film surface, which may cause a progressive deceleration of the photocatalytic reaction induced by our platinized films. Further experiments under oxygen bubbling will be necessary to better assess this aspect.

To preliminary study the photocatalytic activity of platinized films, an apparent rate constant $k1$ has been defined as the slope deduced from an arbitrary linearization of Ln (C_0/C) values measured over the overall 180 min of UV-exposure, and a rate constant $k2$ accounting for the second steady-state regime has been deduced from a linearization over the final 90 min of UV-exposure (see Fig. 5b). Variations of these rate constants are illustrated in Fig. 6 in the case of films platinized for various durations using a 1-Pt method. This figure clearly indicates that both rate constants follow very similar trends and, for films
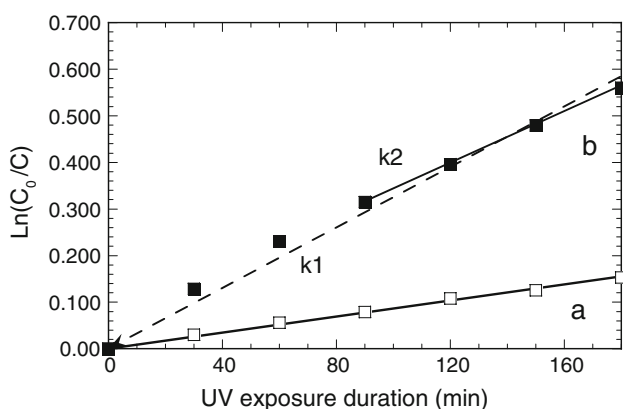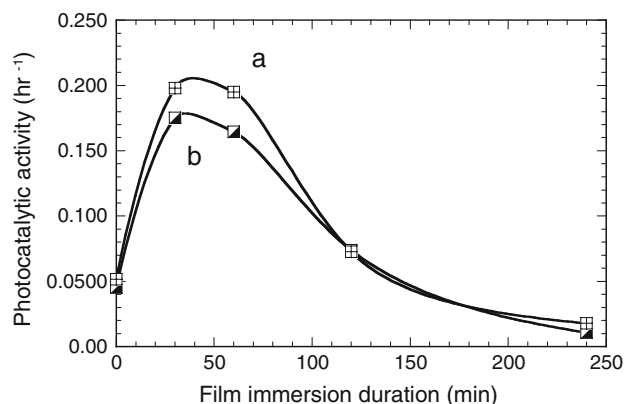

Fig. 5 Variations of the decomposed OG molar fraction versus UV-exposition duration for a non-platinized film (a) and for a film platinized for 60 min using the 1-Pt method (b). (b) *Lines* illustrate the two rate constant definitions used to plot data of Fig. 6

Fig. 6 Variations of the photocatalytic activity, as deduced from the $k1$ (a) and $k2$ (b) definitions of the rate constant, for films immersed in an 860-µM solution for various durations using the 1-Pt method

illustrated here, differences between both constants do not exceed 15%. Thus, in following parts of this study, we have arbitrarily chosen to use the $k1$ definition of the rate constant to study influences of the platinization protocols on the photocatalytic activity of platinized TiO_2 films.

Photocatalytic activity of films platinized using the 1-Pt method

Figure 6a shows that a short 1-Pt platinization of 30 min yields a $k1$ rate constant of about 0.20 h^{-1}, i.e., a photocatalytic activity enhancement by a factor around four compared to a non-platinized film. Increasing the film immersion duration up to 60 min does not yield any improvement of the photocatalytic activity, leading to a rate constant similar to that measured after a 30-min immersion. Further increase of the immersion duration yields a drop of the photocatalytic activity, and a film photo-platinized for 4 h even exhibits a photocatalytic activity three times weaker than that of a non-platinized film. To summarize, Fig. 6 illustrates the beneficial effect of platinum particles dispersed at the film surface upon a platinization of short duration (30–60 min), which is in turn attributed to enhanced effects of Schottky barrier, but it also suggests that, after a prolonged photo-platinization, platinum particles have a detrimental effect on the film photo-activity.

Several features can account for large differences in the photocatalytic activity of photo-platinized films. In our previous study, we showed that ethanol photo-oxidation by-products adsorbed at the film surface during a 1-Pt photo-platinization (carbon monoxide, as well as aldehyde, carboxylate, or carbonate species) could strongly alter the photo-activity of platinized films, but this effect became secondary when platinization was performed in a 80/20 water/ethanol liquid medium and platinized films were post-treated at 110 °C or more [13]. Since films studied in the present study fulfil such criteria, it is inferred that ethanol by-products do not predominantly affect the photocatalytic activity. In previous study, we indicated that a poor metallization degree of loaded platinum particles could also alter the extent of Schottky barrier effects and the related efficiency of charge carrier separation [13]. However, in a more recent study we showed that, according to XPS measurements, the different 1-Pt or 2-Pt methods discussed in the present study led to platinum particles with a similarly strong metallization degree, showing the good reduction yield of the photoreduction mechanisms [14]. In any conditions, XPS measurements indicated a Pt° to Pt4f intensity ratio of around 70–80%. A secondary XPS component was attributed to Pt° with adsorbed oxygen, which resulted from the known tendency of oxygen to rapidly chemisorb on a clean platinum surface

during storage under ambient conditions [23, 24]. Finally, XPS measurements revealed a very minor contribution of Pt^{II} species and the absence of any Pt^{IV} ones. Thus, the similarly strong metallization degree of platinum particles studied in the present study cannot explain large differences of photocatalytic activities illustrated in Fig. 6. As explained before, the visible light emitted by our lamps does not contribute to the photocatalytic decomposition and thus cannot either explain data of Fig. 6. Some authors have reported on the photo-activity of platinized powder photocatalysts exposed to visible light, which was attributed to sensitization mechanisms induced by adsorbed Pt^{II} or Pt^{IV} salts or complexes [25, 26]. In our case, XPS showed the negligible extent of Pt^{II} and Pt^{IV} species, i.e., of Pt^{II} or Pt^{IV} salts or complexes, adsorbed at the film surface. It indicates that any sensitization mechanism, which would eventually induce a photo-activity under visible light, cannot occur at the surface of our films.

According to Fig. 6, it seems that there exists an optimal platinum loading threshold above which loaded particles alter the film photo-activity. This threshold seems to be reached after a 60 min platinization using the 1-Pt method. According to Fig. 1, a Pt/Ti ratio of around 0.45 ± 0.10 has been deduced from EDX analyses in the case of films platinized for 60 min using this method. It may thus be considered that a Pt/Ti EDX ratio of 0.45 depicts an order of magnitude of this optimal loading threshold. Increasing the amount of loaded particles above this threshold can, for instance, reduce the interactions of UV-light with the TiO_2 film and induce a weaker amount of photo-generated charge carriers in the film. Accordingly, spectra of Fig. 2c and d indicate some transmission reductions induced by platinum particles after a 1-Pt platinization of 4 h. However, these weak reductions cannot explain that a film platinized for 4 h using the 1-Pt method exhibits a photocatalytic activity about 12 times weaker than that of films platinized for 30 or 60 min. Finally, Fig. 3a, and b shows that, beside differences in the amount of loaded platinum particles, films photo-platinized for 1 and 4 h using the 1-Pt method also exhibit large differences in platinum particle sizes. Thus, in order to better assess how the platinum particle size may influence the photocatalytic activity of platinized films, we have taken advantage of our 2-Pt methods that allow a selective control in the amount of 2- and 20-nm particles dispersed at the film surface.

Photocatalytic activity of films platinized using the 2-Pt methods

Figure 7 compares $k1$ rate constant values measured on films platinized using both 2-Pt methods. The $k1$ values are plotted as a function of the Pt/Ti ratio deduced from EDX measurements, as illustrated in Fig. 1. As shown in Fig. 7a
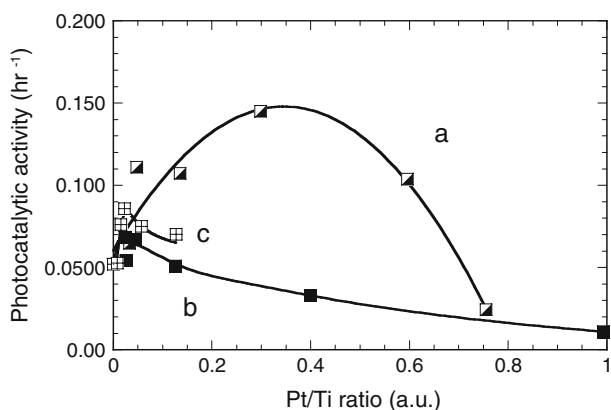
Fig. 7 Photocatalytic activity (*k*1 definition) of films immersed for various durations under UV-light in an 860-µM solution using the 2-Pt-45 m method (a) and films immersed for 5 or 120 min, under UV-light (b) or not (c), in solutions of various platinum concentrations using the 2-Pt-15 h method. The photocatalytic activity has been plotted as a function of the Pt/Ti ratio deduced from EDX analyses, as illustrated in Fig. 1

for 2-Pt-45 m films, *k*1 variations globally confirm trends illustrated in Fig. 6 for the 1-Pt method. Let us recall that, for short film immersion durations, the 2-Pt-45 m essentially yield the surface dispersion of 20-nm platinum particles, similarly to what occurs with the 1-Pt method (see Fig. 3a). Figure 7a shows that the photocatalytic activity first increases with the amount of platinum, i.e., the duration of the post-photoreduction adsorption. This result, here again, illustrates beneficial effects of the Schottky barrier induced by platinum nano-particles. A longer post-photoreduction immersion promotes a drop of the photo-activity. Figure 7a shows that, compared to a non-platinized film, the photocatalytic activity is enhanced by a factor around 3 for a Pt/Ti EDX ratio of 0.3, while this enhancement no longer exceeds a factor 2 for a Pt/Ti EDX ratio of 0.6. Within the accuracy of EDX characterization, this range of Pt/Ti ratios is in fairly good agreement with the threshold previously discussed for the 1-Pt method, which confirms a rather good correlation in results obtained from the 1-Pt and 2-Pt-45 m methods. However, for reasons that are not yet clear, Figs. 6a and 7a also indicate that maximal photo-activity enhancements arising from a 2-Pt-45 m method are somewhat weaker (around ×3) than best enhancements arising from the 1-Pt method (around ×4). Figure 7b and c illustrates fundamentally different trends in the case of 2-Pt-15 h films. For these films, the amount of Pt particles has been varied through a post-photoreduction film immersion, for 5 or 120 min under UV-light or not, in solutions of various platinum concentrations. Figure 7b and c shows that increasing the amount of platinum particles, up to a very weak Pt/Ti EDX ratio of around 0.05, yields some limited enhancements of the photocatalytic activity. Then, this activity gradually

decreases with further increase of the platinum amount. Very small differences observed when the post-photoreduction immersion occurs with or without UV-light are considered to be insignificant and will not be further discussed in this study.

Main differences arising from the different platinization methods can be summarized as follows. While, in the range of the platinum amount threshold (Pt/Ti EDX ratio around 0.45), platinization promotes a photocatalytic activity enhancement by factors around 3 and 4 for the 2-Pt-45 m and 1-Pt methods, respectively, a 2-Pt-15 h method leads to a photo-activity reduction by a factor around 2. Let us recall that a 2-Pt-15 h method exclusively yields the distribution of 2-nm platinum particles at the film surface, as illustrated in Fig. 3c. Thus, beside previously discussed effects of a platinum amount threshold, we might attribute the poor activity of films platinized through a 2-Pt-15 h method to the small 2-nm diameter of platinum particles loaded at the film surface. However, several papers have reported on the good activity of powder TiO₂ photocatalysts loaded with platinum particles of ca. 2 nm diameter [6, 27]. It can hardly be thought that such a particle size intrinsically promotes drastic differences in the photo-activity of powder and thin film TiO₂ photocatalysts. Furthermore, our TEM studies show that 20-nm particles arising from a 1-Pt or 2-Pt-45 m method with sufficient short film adsorption duration actually consist of aggregates of 2 nm primary particles. It is likely that electronic properties of platinum aggregates, and thus their influence on the film photo-activity, are more probably governed by the primary particle size rather than the aggregate size, which would reinforce assumption that platinum size effects do not intrinsically cause differences between trends illustrated in Figs. 6 and 7a–c. It is thus believed that an additional factor predominantly influences the photocatalytic activity of our platinized films, which is discussed in the next section.

Influence of the surface distribution of platinum nano-particles: discussion

It is commonly accepted that an efficient prevention of the charge carrier recombination in powder Pt-TiO₂ photocatalysts necessitates a sufficiently large charge carrier separation distance (CCSD) in the photocatalyst and, for comparable sizes of platinum particles, this CCSD is governed by the number density of particles loaded at the photocatalyst surface [6]. As schematically illustrated in Fig. 8, we believe that such arguments can be applied to the case of thin film TiO₂ photocatalysts. For a sufficiently small number of platinum particles distributed at the film surface (Fig. 8b), there exists a large TiO₂ free surface where photo-holes can photocatalytically react, while being
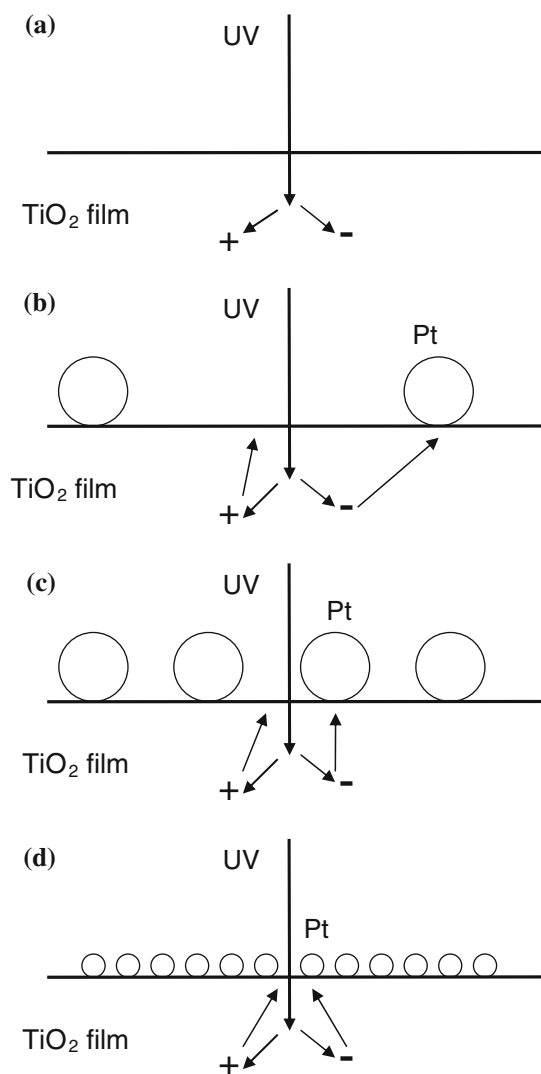
Fig. 8 Schematic representation of the CCSD in a non-platinized TiO$_2$ film (**a**), in films platinized with platinum particles of comparable sizes distributed at the film surface in weak quantity (**b**) and strong quantity (**c**), and in films platinized with platinum particles of smaller size than in (**b**) but with a same overall amount of platinum (**d**). (Adapted from [6] to the case of a thin film photocatalyst)

sufficiently distant from photo-electron trapped by the closest platinum particles. Such a configuration promotes a much larger CCSD compared to a non-platinized film (Fig. 8a), which efficiently reduces the charge carrier recombination probability. Increasing the number of platinum particles reduces the TiO$_2$ free surface and the distance between platinum particles, and thus the CCSD (Fig. 8c), yielding an increased recombination probability. CCSD can even become weaker than in a non-platinized film and, in that case, platinum particles cause a reduction of the photocatalytic activity compared to a non platinized TiO$_2$ photocatalyst, as already reported by others [6]. From such a description, it is believed that trends illustrated in

Figs. 6 and 7 traduce, at least partially, a competitive mechanism between Schottky barrier and CCSD effects. A first increase of the platinum amount, by increasing the film immersion duration and/or concentration of platinum in the photoreduced solution, yields enhanced Schottky barrier effects leading to an initial improvement in the photocatalytic activity of platinized films. The subsequent decrease of photocatalytic activity observed with further increase of the platinum amount would ensue from a reduction of the CCSD. There should exist, therefore, an optimal platinum loading allowing a compromise between enhanced Schottky barrier and large enough CCSD, which in turn depends on the photo-platinization method as discussed below.

For simple geometry considerations, provided that platinum particles are uniformly distributed at the film surface and platinum amounts do not differ excessively, a reduction of the platinum particle size should induce a narrower distance between these particles. This feature is illustrated in FEG-SEM images of Fig. 3a and c. Despite a greater amount of loaded particles (Pt/Ti EDX ratio of around 0.45), the film illustrated in Fig. 3a, which is essentially loaded with 20-nm particles, exhibits a mean inter-particle distance of several tens of nanometers, while the film illustrated in Fig. 3c (Pt/Ti EDX ratio of only 0.13), which is exclusively loaded with 2-nm particles, exhibits a mean inter-particle distance of only few nanometers. Thus, weaker CCSD's induced by much shorter platinum inter-particles distances should logically favor a greater charge carrier recombination probability for this latter film compared to the former (as illustrated in Fig. 8b, d). Accordingly, Fig. 7c shows that, for the latter film, platinization yields insignificant enhancement of the photocatalytic activity, while a photocatalytic activity enhancement by a factor around 4 is illustrated in Fig. 6a for the former. It is therefore believed that poor photocatalytic performances, globally illustrated in Fig. 7b and c when using a 2-Pt-15 h platinization method, at least partially express that increasing the amount of 2-nm particles rapidly decreases the CCSD below a certain critical value, which cancels beneficial effects of a Schottky barrier. Conversely, since for sufficiently short film immersion durations 1-Pt and 2-Pt-45 m films are essentially loaded with more distant platinum particles of 20 nm diameter, yielding larger CCSD's, it allows greater amounts of platinum to be loaded at the film surface, thus producing enhanced Schottky barrier effects that induce important improvements of the photocatalytic activity. From that point of view, in the case of 1-Pt and 2-Pt-45 m methods, it is inferred that subsequent decreases of photocatalytic activity observed for prolonged film immersions under UV-light arise (i) from an increased amount of loaded platinum yielding a CCSD decrease, and (ii) from the fact that, over a prolonged film immersion under UV-light,

20-nm particles are progressively replaced by 2-nm ones, which reinforces again the CCSD decrease in platinized films. Photo-electrochemical measurements are often employed to study the extent of charge carrier recombination and/or their separation efficiency within photocatalysts exposed to UV-light [6, 22]. In further studies, such methods will be implemented to better assess how platinum particles loaded from our 1-Pt and 2-Pt methods influence the photocatalytic activity of derived platinized films.

Conclusions

Different 1-step or 2-step photo-platinization methods have been implemented to load sol–gel TiO_2 photocatalytic thin films with platinum nano-particles. These platinization methods allow flexible variations in the amount of loaded particles through the adjustment of the film immersion duration in the platinum solution and/or the platinum concentration in the solution. They yield the distribution at the film surface of combinations of 20-nm aggregates and/or 2-nm single particles, the relative amount of which being selectively adjusted from the experimental conditions. It is shown that the photocatalytic activity of platinized films is strongly influenced by the platinization method, which has been discussed on the basis of several arguments: (i) photocatalytic activity improvements arising from our photo-platinization methods would rely on a competitive mechanism between Schottky barrier and CCSD effects, (ii) this competitive mechanism would in turn be governed by the amount, size, and surface distribution of loaded particles, and (iii) best results are obtained from a 1-Pt method, and in lesser extent a 2-Pt-45 m method, that allow minimizing the amount of 2-nm loaded particles and maximizing platinum inter-particle distance, which would in turn favor greater amounts of platinum to be loaded while preventing excessive decrease of CCSD. Accordingly, best platinized films exhibit a photocatalytic activity enhancement by a factor around 4 compared to pure TiO_2 films, which expresses an efficient separation of charge carriers photo-generated under UV-light, and allows envisaging thin film photocatalysts with enhanced properties.

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