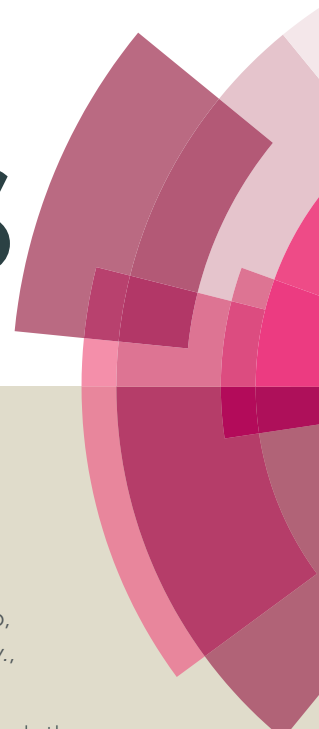


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Charge carrier dynamics and photocatalytic behavior of TiO₂ nanopowders submitted to hydrothermal or conventional heat treatment

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Abstract

The sol-gel technique followed by conventional (TiO₂-1) and hydrothermal (TiO₂-2) thermal treatment was employed to prepare TiO₂-based photocatalysts with distinct particle sizes and crystalline structures. The as prepared metal oxides were evaluated as photocatalysts for gaseous HCHO degradation, methanol, and dye oxidation reactions. Additionally, metallic platinum was deposited on the TiO₂ surfaces and H₂ evolution measurements were performed. The photocatalytic activities were rationalized in terms of morphologic parameters along with the electron/hole dynamics obtained from transient absorption spectroscopy (TAS). TiO₂-2 exhibits smaller particle size, poorer crystallinity, and higher surface area than TiO₂-1. Moreover the hydrothermal treatment leads to formation of the metastable brookite phase, while TiO₂-1 exhibits only the anatase phase. TAS measurements show that the electron/hole recombination of TiO₂-2 is faster than that of the later. Despite of that, TiO₂-2 exhibits higher photonic efficiencies for photocatalytic oxidation reactions, which is attributed to its larger surface area that compensates the decrease of the surface charge carrier concentration. For H₂ evolution, it was found that the surface area has only a minor effect and the photocatalyst performance is controlled by the efficiency of the electron transfer to the platinum islands. This process is facilitated by the higher crystallinity of TiO₂-1, which exhibits higher photonic efficiency for H₂ evolution than that observed for TiO₂-2. The results found here provide new insights into the correlations between thermal treatment conditions and photocatalytic activity and will be useful for the design of high performance photocatalysts.

Introduction

The research in renewable energy sources is intense due to the concerns about the global warming and other environmental issues related to the huge dependence of the global energy matrix on fossil fuels ¹⁻³. Photocatalysis calls particular attention, due the possibility to harvest the abundant solar energy and to convert it into fuels, such as hydrogen ⁴⁻⁶.

TiO₂-based materials are the most intensely investigated photocatalytic system following the breakthrough by Fujishima and Honda ⁷. They exhibit chemical stability, nontoxicity, high reactivity, and can be prepared in different forms and sizes with highly ordered porosity and crystallinity ⁸⁻¹⁰. Typically, the oxide is prepared from a molecular precursor, followed by a thermal treatment to ensure crystallinity. Conventional heating at atmospheric pressure as well as the use of pressurized hydrothermal reactors are the most popular thermal treatments employed ¹¹⁻¹⁵.

Through the use of molecular engineering, the main limitations of TiO₂ have been superposed. For example, visible light activity has been obtained by the introduction of dopants ¹⁶⁻²⁰ or by the formation of nanocomposites ²¹⁻²⁴. Moreover, H₂ evolution without the necessity of an external bias has been observed in the presence of co-catalysts on the oxide surface ²⁵⁻²⁸.

In parallel to the advances of material preparation, large research efforts have been devoted to investigations of well-defined photocatalytic reaction systems and their detailed reaction mechanisms and kinetics using a variety of spectroscopic techniques ²⁹⁻³⁷. Particularly, the use of time-resolved methods, such as transient absorption spectroscopy (TAS) ³⁸⁻⁴¹ and microwave conductivity measurements (TRMC) ^{42, 43} has allowed to enhance the

fundamental understanding of electron/hole trapping and recombination, with the latter being recognized as the limiting step of the photocatalytic process⁴⁴. Despite the remarkable progress, it is not an easy task to establish clear relationships between the photocatalytic properties and the metal oxide morphological and electronic properties. Serpone⁴⁵ and Zhang⁴⁶, among others^{47, 48} have investigated the role of particle size on charge carrier dynamics and photocatalytic activity with the results of these studies being not always similar. More recently, Carneiro and co-workers described the dependence of the methylene blue degradation rate on the concentration of hydroxyl groups and holes at TiO₂ surface among with their correlations with the particle size⁴³. In this work, two different TiO₂-based photocatalysts were prepared by the sol-gel technique, which allows an easy control of the particle size. The as prepared TiO₂ particles were submitted to a conventional thermal treatment at 400 °C in an oven and also to a hydrothermal reactor (200 °C, 12.4 bar), yielding different crystalline phases, surface defects, etc. The samples were fully characterized and evaluated by several photocatalytic oxidation tests and also for H₂ evolution, with the aim to provide new insights into the underlying structure-reactivity relationship. The observed photonic efficiencies were rationalized in terms of the morphological properties of TiO₂-based photocatalysts and the photogenerated charge carrier dynamics studied by nanosecond transient absorption spectroscopy.

Experimental

Materials. All chemicals were of analytical or HPLC grade and were used as received. TiO₂ photocatalysts were prepared through the hydrolysis of Ti(IV)

isopropoxide (Aldrich, 97%). 5 cm³ of the alkoxide were dissolved in 30 mL of isopropanol under argon atmosphere. The precursor solution was cooled in an ice bath and, under vigorous stirring, 50 cm³ of deionized water were slowly added dropwise to yield a white precipitate. The photocatalyst 1 (TiO₂-1) was obtained by stirring the mixture for thirty minutes at low temperature. The resulting powder was separated by centrifugation (6000 rpm, 20 minutes), washed with deionized water and thermally treated at 400°C for 6 hours in a conventional oven. The photocatalyst 2 (TiO₂-2) was obtained by stirring the hydrolysed precursor solution for 12 hours at room temperature. The white powder was separated by centrifugation (6000 rpm, 20 minutes) and washed with deionized water to eliminate any residual alcohol. The powder was subsequently suspended in 100 mL of water and transferred to a stainless steel reactor, which was heated at 200 °C for 8 hours at 12.4 bar. Afterwards, the photocatalyst was separated by centrifugation and dried at 70°C by 24 h.

Deposition of metallic platinum on the TiO₂ surfaces (0.5 %wt) was carried out as described elsewhere^{49, 50}. Briefly, 50 mg of the photocatalyst were suspended in 50 cm³ of 10% (v/v) methanol aqueous solution in a borosilicate reactor. After purging the suspension with N₂, 130 µL of a 0.1 mol L⁻¹ H₂PtCl₆ aqueous solution was added and the system was exposed to UV-A light (Philips 90 W Hg lamps, 1 mW cm⁻²) by 8 hours. The resulting pale gray powders were separated by centrifugation and dried at 70 °C under reduced pressure.

Characterization. The powders were characterized by X-ray diffraction analysis (XRD) using an XRD600 powder diffractometer (Shimadzu) operating at 40 kV and 30 mA employing Cu K α radiation. The diffractograms were collected between 20 to 90° at 0.5°/min. Scanning transmission electron microscopy

(STEM) images were obtained in a FEI Inspect F50 located at the Brazilian Nanotechnology National Laboratory (LNNano) and operated at 30 kV. N₂ adsorption-desorption isotherms were obtained in an ASAP 2020 analyzer (Micrometrics). The sorption data were analyzed using the Barrett-Joyner-Halenda (BJH) model. Diffuse reflectance measurements were carried out in an UV-1650PC spectrometer (Shimadzu) with the band gap energy being estimated by the Tauc method⁵¹.

Transient absorption spectroscopy (TAS) was carried out employing a LKS80 nanosecond laser flash photolysis spectrometer (Applied Photophysics) equipped with the proper diffuse reflectance accessory. The samples were excited in a quartz cuvette by a LPX 200 excimer laser (XeF; $\lambda_{\text{exc}} = 351$ nm; 14 mJ per pulse) from Lambda Physics. The transient signals were collected by a PMT connected to a computer interfaced to a DSO9064A oscilloscope (Agilent). The data points were converted to absorbance values according to equation (1), where A = absorbance; I₀ = analyzing light level; I_r = light reflected by the absorbing sample; I_a = light absorbed by the absorbing sample. In these experiments, the samples were employed as dry powders.

$$\Delta A = \log\left(\frac{I_0}{I_r}\right) = \log\left(\frac{I_0}{I_0 - I_a}\right) \quad (1)$$

Photocatalytic Studies. The photocatalytic activity of the as prepared TiO₂ powders was evaluated by different methods and compared to the activity of the well-known photocatalyst Evonik Degussa Aeroxide TiO₂ P25 (TiO₂-P25). Acetaldehyde photo-oxidation was carried out accordingly to the ISO 22197-2 standard method⁵² in an experimental setup described previously^{21, 53}. The

active area of the samples was 15 cm^2 . All samples were cleaned under UV-irradiation (10 W/m^2 , 365 nm) prior the experiments. The gaseous reaction mixture was prepared by mixing streams of dry air (500 mL/min), wet air (500 mL/min , relative humidity of 50%), and 10% of a $\text{CH}_3\text{CHO}/\text{N}_2$ mixture (approximately 50 mL/min) to obtain a final CH_3CHO concentration of 1 ppm at 297 K . Prior to the photocatalytic tests, the photoreactor was purged with the CH_3CHO /water vapor/air mixture without illumination until a steady CH_3CHO concentration was achieved at the reactor outlet. Afterwards, the sample was irradiated for approximately 120 min.

For methanol photo-oxidation, 50 mg of TiO_2 were suspended in $3.0 \times 10^{-2} \text{ mol L}^{-1}$ aqueous methanol solution placed in a round borosilicate reactor. The system was irradiated using UV-A light ($3.04 \times 10^{-7} \text{ Einstein s}^{-1}$). The amount of formaldehyde produced at different time intervals was determined by the Nash method^{49, 54, 55}. The photonic efficiency values (ξ), which is defined as the ratio of CH_3CHO degradation or HCHO formation and the incident photon flux, were calculated as previously described^{53, 56}.

The activity of the TiO_2 samples was also evaluated through UV-A degradation of the azo-dye Ponceau-4R (P4R) or trisodium (8Z)-7-oxo-8-[(4-sulphonatonaphthalen-1-yl)hydrazinylidene]naphthalene-1,3-disulphonate.

Detailed description of the experimental setup can be found elsewhere⁵⁷. The photon flux in the range between 300 and 815 nm was $(3 \pm 1) \times 10^{-6} \text{ Einstein s}^{-1}$ as determined by a radiometric/ photometric setup described previously⁵⁸. The degradation rate was evaluated by Total Organic Carbon measurements (TOC) carried out in a Shimadzu TOC-VCPH Analyzer. Control experiments were

taken in the absence of any photocatalyst to evidence the role of the TiO_2 on the photochemical reaction.

Platinized samples were employed for hydrogen evolution measurements using the experimental setup described previously²⁵. Briefly, the TiO_2 photocatalysts were suspended in 50 mL of 10% (v/v) methanol aqueous solution placed in a double jacket quartz reactor. The system was connected to a quadrupole mass spectrometer (QMS) for gas analysis (Hiden HPR-20) and purged with argon until no traces of O_2 and N_2 could be observed. UV-A irradiation was performed using a 150 W Xe lamp. The photon flux was 1.90×10^{-6} Einstein s^{-1} .

Results

Electronic and morphological characterization. The two TiO_2 -based photocatalysts are constituted of agglomerates of spherical nanoparticles, as visualized in the respective STEM images (Figure 1). The particle sizes estimated from these images are (25 ± 2) nm and (12 ± 3) nm, respectively for TiO_2 -1 and TiO_2 -2.

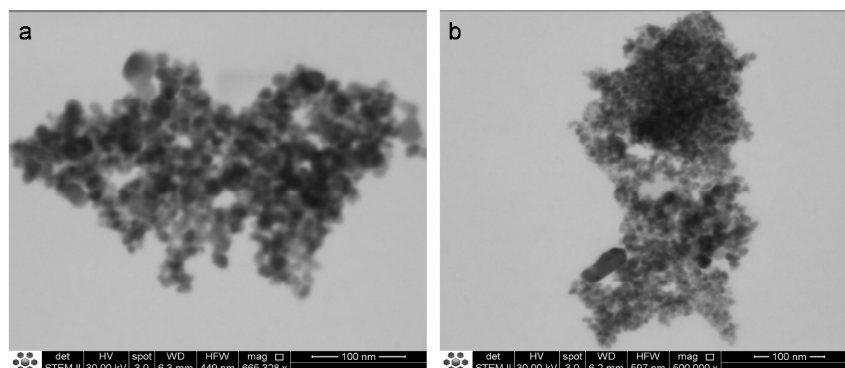


Figure 1. STEM images of TiO_2 -1 (a) and TiO_2 -2 (b) photocatalysts.

XRD analyses of the powders, Figure 2, show that TiO₂-1 is constituted only by the anatase polymorph, while TiO₂-2 exhibits peaks characteristic of anatase and brookite. Rietveld refinement of the XRD data (see Table S1 and Figures S1, S2, and S3 in the Supplementary Information) reveals that the brookite content is approximately 45%. The appearance of the brookite phase in the TiO₂ samples prepared by the hydrothermal method agrees with previous studies carried out by Isley and Penn⁵⁹, as well as by other authors^{60, 61}. This photocatalyst also exhibits broader diffraction peaks as compared with TiO₂-1 and the commercial sample (P25), which is in agreement to the smaller particle size observed in the STEM images. Crystallite sizes calculated by the Scherrer equation were 18 nm and 10 nm, respectively for TiO₂-1 and TiO₂-2, similar to the values found by electron microscopy. Moreover, the lattice parameters obtained for TiO₂-2 (Table S1) indicate a more distorted structure in relation to TiO₂-1 or TiO₂-P25, especially in the *c* axis.

As expected, both photocatalysts exhibit absorption only in the UV region with an optical bandgap of 3.2 eV, similar to the values reported for TiO₂ anatase⁶². Diffuse reflectance spectra of the as prepared powders can be found in the Supplementary Information (Figure S4).

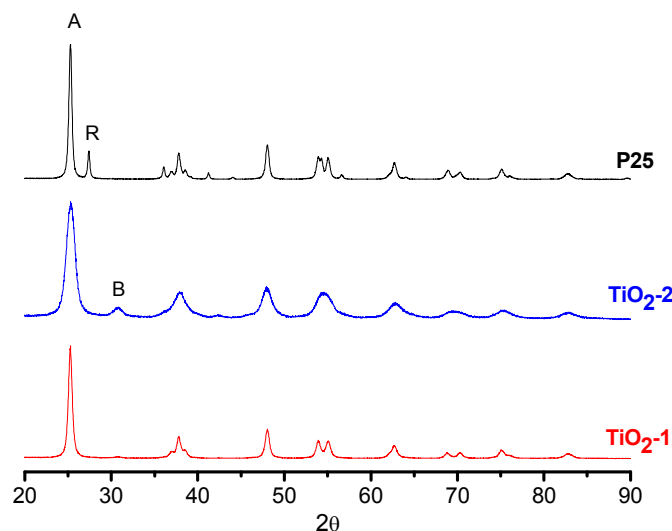


Figure 2. XRD patterns of TiO₂ photocatalysts. The peaks marked as A, R, and B, refer to the main diffraction peaks of anatase, rutile and brookite, respectively.

The samples were also characterized by N₂-adsorption/desorption isotherms using the B.E.T. method (Figure S5). Type IV sorption curves were observed, according to the IUPAC classification⁶³, which are characteristic of mesoporous materials. The surface areas calculated for the samples were 66 and 164 m² g⁻¹, respectively for TiO₂-1 and TiO₂-2. In addition to the higher surface area, the photocatalyst prepared via hydrothermal treatment also exhibits greater porosity, 27%, as compared with 15%, for TiO₂-1.

The morphological characterization of the as synthesized photocatalysts confirmed the expected differences between samples thermally treated in a hydrothermal reactor at relatively low temperature and those treated in a conventional oven. TiO₂-2 exhibits smaller particle size and higher surface area, since it was treated at low temperatures thus avoiding grain boundaries. Another consequence of the hydrothermal treatment at 200 °C is the smaller

crystallinity of TiO_2 -2 in relation to TiO_2 -1, which was sintered at 400 °C and exhibited only anatase XRD patterns, with no signal from the metastable brookite phase.

Photocatalytic activity. The effectiveness of the TiO_2 samples as photocatalysts was evaluated comparing the efficiency of the oxidation of a dye (Ponceau 4R), gaseous acetaldehyde, and methanol, and also the photocatalytic hydrogen evolution, using platinum as co-catalyst. A summary of the observed rates and the respective photonic efficiencies is presented in Table 1 along with the main morphological data.

Table 1. Main morphological parameters and photocatalytic performances of bare and platinized TiO₂-based photocatalysts.

Sample	S _{BET} (m ² g ⁻¹)	Particle diameter (nm)	Dye Degradation	Gaseous CH ₃ CHO degradation		MeOH oxidation		H ₂ evolution	
			C/C ₀ (%)	rate ^{&} x10 ⁻⁴	ξ (%)	rate [*]	ξ (%)	rate [*]	ξ (%)
P25	42	30 ± 2	82	3.3	5.5	5.0	8.3		
TiO ₂ -1	66	25 ± 2	33	2.0	3.4	4.8	7.9		
TiO ₂ -2	164	12 ± 3	75	2.4	4.0	6.4	10.6		
P25-Pt						5.2	8.5	0.15	7.7
TiO ₂ -1-Pt						5.2	8.5	0.11	5.6
TiO ₂ -2-Pt						3.5	5.8	0.10	5.0

[&] in μmol s⁻¹; ^{*} in μmol L⁻¹ s⁻¹ g⁻¹

In Figure 3, the time profile of the gaseous CH₃CHO photodegradation is shown using the two photocatalysts prepared here in comparison to the commercial titanium dioxide P25. Apparently, the commercial photocatalyst exhibits a higher efficiency as compared with both samples prepared by the sol-gel method. Among the synthesized powders, TiO₂-2 exhibits the best performance. The same trend is observed for the degradation of the Ponceau 4R dye (time profile TOC curves for the different photocatalysts can be found in the Supplementary Information, Figure S6).

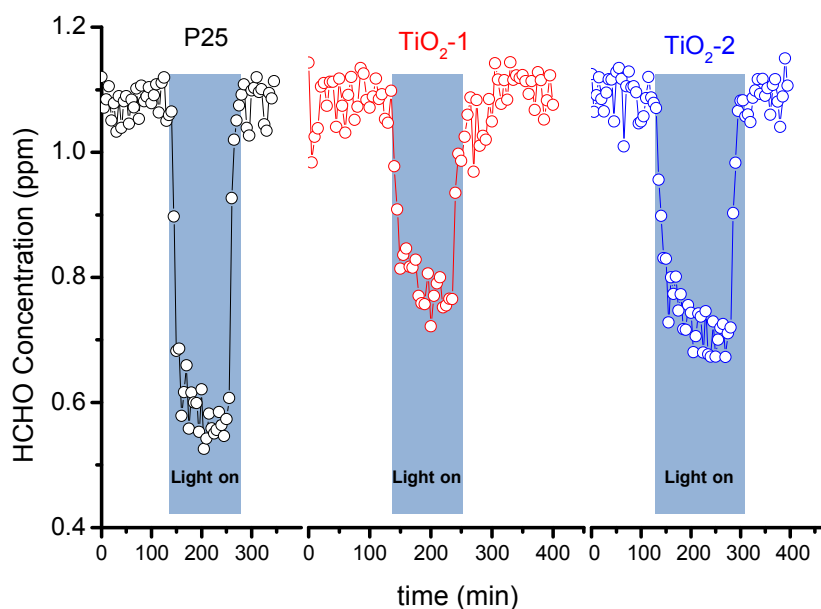


Figure 3. Time profiles of the CH_3CHO photodegradation upon UV(A) irradiation (1 mW cm^{-2}) in the presence of different TiO_2 -based photocatalysts.

For the photocatalytic methanol oxidation, the performance of bare TiO_2 -2 is higher than that observed for the commercial oxide and approx. 35% better than that observed when using TiO_2 -1, Figure 4. Interestingly, after platinization, the photocatalytic activity of TiO_2 -2 decays by 50%, while for TiO_2 -1 and P25, the photonic efficiencies increase by 7.5% and 2.4%, respectively.

The time profiles of the photocatalytic hydrogen evolution obtained by mass spectrometry are shown in Figure 5. For both samples, one can observe a fast increase of the H_2 production after the light is turned on. Then, the H_2 evolution rate reaches a plateau and remains almost constant until the irradiation is turned off. The slight decrease on H_2 evolution rate over time is likely related to the decrease of the sacrificial agent concentration. The photocatalytic production of hydrogen follows the same trend as that observed for the methanol oxidation, with TiO_2 -1-Pt exhibiting a higher performance than TiO_2 -2-

Pt. It is worthwhile to note that the efficiency of TiO₂-2 decreases after Pt deposition.

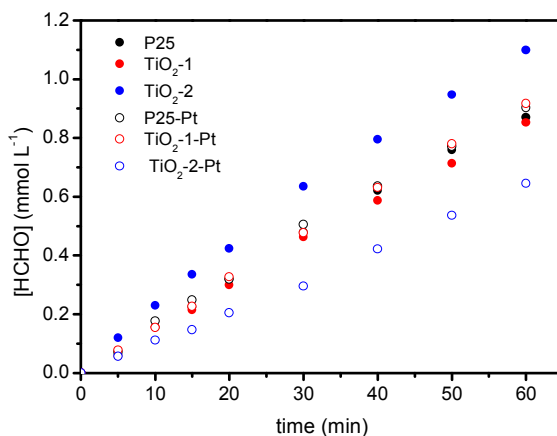


Figure 4. Time evolution of the HCHO concentration as a result of the photocatalytic methanol oxidation under UV(A) irradiation (1 mW cm^{-2}) in the presence of bare and platinized TiO₂ photocatalysts.

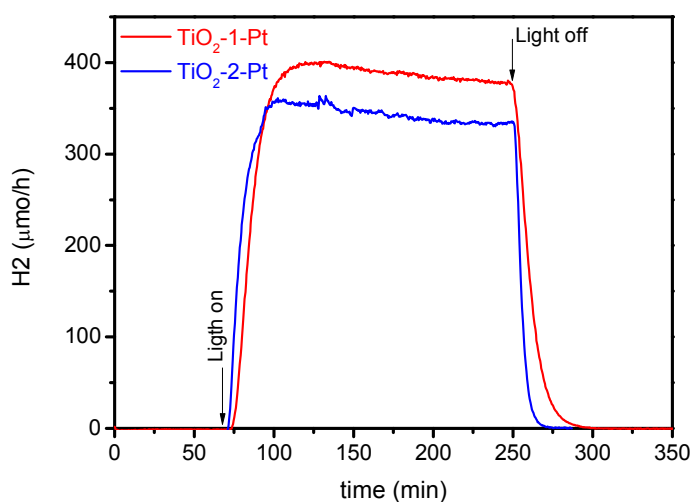


Figure 5. Time profile for the H₂ evolution from 10% (v/v) aqueous methanol solution upon UV irradiation in the presence of platinized TiO₂-1 (—) and TiO₂-2 (—) photocatalysts.

Time-resolved absorption spectroscopy (TAS). In order to better understand the role of morphological parameters and thermal treatment conditions on the photocatalytic performance of TiO₂ photocatalysts, the reaction dynamics of the

photogenerated charge carriers were investigated by means of nanosecond TAS, employing bare and platinized samples. In TAS measurements carried out at the nanosecond time domain, the absorption signatures originate from trapped electrons and holes, since free charge carriers tend to recombine (or be trapped) at the picosecond time scale ⁴. Typical transient absorption spectra obtained under N₂ atmosphere for the TiO₂ photocatalysts prepared here are shown in Figure 6.

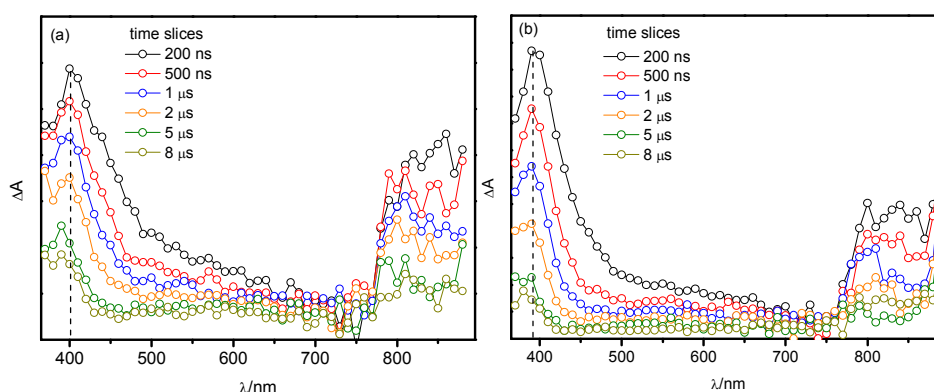


Figure 6. Transient absorption spectra measured for TiO₂-1 (a) and TiO₂-2 (b) under N₂ atmosphere at different time scales following the laser pulse.

One can observe a peak at 380-500 nm, a broad band between 500-700 nm and a further peak at 760-890 nm. For TiO₂-1, the high energy absorption maximum exhibits a hypsochromic shift at longer times after the laser excitation, which is not observed for TiO₂-2. The introduction of metallic platinum at the photocatalyst surface induces some changes on the transient absorption spectra, as exemplified for TiO₂-1 in Figure 7.

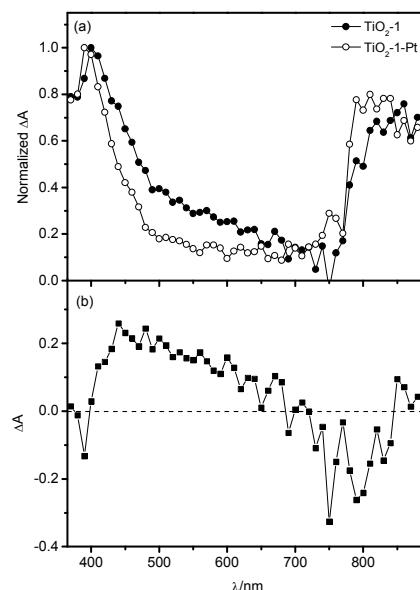


Figure 7. (a) Transient absorption spectra of TiO₂-1 and TiO₂-1-Pt measured 200 ns after the laser excitation under N₂ atmosphere. (b) Difference spectrum between the bare and the platinized photocatalyst.

It is well known that metallic platinum acts as electron acceptor on the TiO₂ surface, with electrons being transferred within 10 ps⁴. Thus, in ns- transient absorption spectra of the TiO₂-Pt photocatalysts, the signals from trapped electrons should be greatly reduced in comparison to the bare photocatalysts. The difference spectrum shown in Figure 7(b) thus evidences a strong contribution of the trapped electron absorption between 400 and 650 nm. Below 400 nm and above 700 nm, the transient absorption spectra seem to be dominated by trapped holes. Such interpretations are corroborated by previous studies carried out by Serpone et. al.⁴⁵ attributing the transient absorption in the range of 490-650 nm to electrons trapped as Ti³⁺ centers and also in different energy midgap levels. However, absorption features of trapped holes have also been reported in the 400-700 nm region¹¹, overlapping with the contribution of photogenerated electrons and hence making it difficult to identify the individual absorption signatures of the trapped carriers in the investigated spectral range.

Zawadzki⁶⁴ performed calculations based on the Density Functional Theory and assigned the transient hole absorption in the 400-700 nm range to interpolaron transitions from O^- centers located in the bulk to neighboring oxygen lattice sites. This author showed that holes trapped in the bulk are responsible for the lower energy transient absorption signals and that this feature is blue-shifted as the holes migrate to the surface. Hence, these calculations can explain the hypsochromic shift observed for the high energy band in the TiO_2 -1 transient absorption.

The TAS decay traces observed at three selected wavelengths (400, 500, and 780 nm) are presented in Figure 8 for the bare as well as for the platinized photocatalysts. As shown in Figure 8c, in the presence of platinum (as electron scavenger), the transient absorption signal at 780 nm does not even decay in the microsecond time-range. This behavior is different to that observed at 400 nm and evidences that the broad band observed in the range between 750 and 890 nm contains a strong contribution of holes located in a different trap state as compared with those responsible for the peak at higher photon energies (Figure 8a). The lifetime of the photogenerated holes increases considerably once the electrons are transferred to the Pt islands on the oxide surface. This result is qualitatively similar to that reported by Yoshirara et al.³³ for TiO_2 nanoparticles with diameters of 10-15 nm. These authors observed two transient absorption peaks at 520 nm and 1200 nm, both of which were attributed to holes. The high energy feature was ascribed to holes trapped more deeply than the ones responsible for the transient absorption at 1200 nm. This conclusion is corroborated by the observations made here. The decay at 400 nm is less affected by the presence of metallic platinum than the signal at 780

nm, which is an indicative that the holes responsible for the lower energy absorption signature are also the main responsible for the photocatalytic activity.

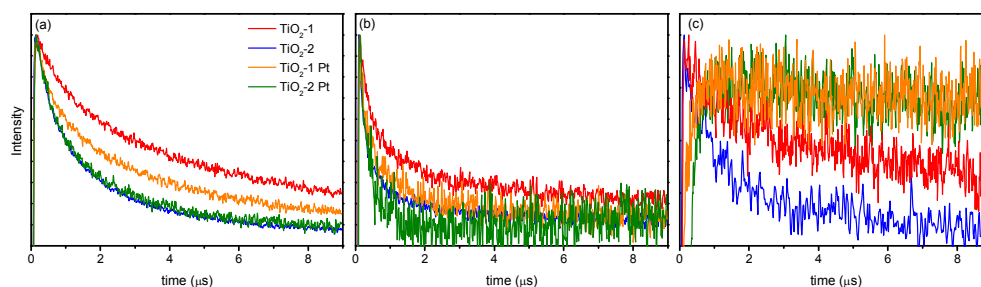


Figure 8. Absorption time profile of bare and platinized photocatalysts at (a) 400 nm, (b) 500 nm, and (c) 780 nm.

Other interesting features can be taken from the decay profiles at 400 nm and 500 nm (Figure 8a and b, respectively). Both decay curves do not exhibit single exponential behavior, with some residual absorption still being observed after 10 μ s. Results for the biexponential fits of the transient absorption data are shown in Table 2.

Table 2. Biexponential fits for the transient absorption decay of bare and platinized TiO_2 -based photocatalysts under N_2 atmosphere.

Sample	λ_{probe}	τ_1 (μ s)	τ_2 (μ s)
TiO_2 -1	400	1.0 (38%)	9.0 (65%)
TiO_2 -1-Pt		0.78 (50%)	7.1 (50%)
TiO_2 -2		0.73 (67%)	5.0 (33%)
TiO_2 -2-Pt		0.80 (69%)	6.0 (31%)
TiO_2 -1	500	0.51 (65%)	15 (35%)
TiO_2 -1-Pt		0.46 (77%)	13 (23%)
TiO_2 -2		0.29 (80%)	12 (20%)
TiO_2 -2-Pt		0.30 (95%)	>10 (5%)
TiO_2 -1	780	2.2 (46%)	29 (54%)
TiO_2 -2		0.88 (58%)	6.6 (42%)

At all investigated wavelengths the decay kinetics of the TiO₂-2 photocatalyst are approx. 30% faster than those observed for TiO₂-1. For TiO₂-2, the decay at 400 nm does not change after platinum deposition, thus the signal can possibly be related to strongly trapped holes that do not contribute to any photocatalytic reaction. For TiO₂-1, the presence of platinum increases the rate of these decay processes in relation to the bare powder. This can be explained by the migration of holes between different trapping sites, once the electrons have been transferred to the platinum islands.

At 500 nm, where the contribution of trapped electrons is higher, one can observe that the initial decay is faster than that at 400 nm, particularly for the TiO₂-2 photocatalyst. Such faster decay rate can be clearly seen in the normalized time-resolved absorption spectra (see Supplementary Information, Figures S7 and S8) and can be related to a faster charge carrier recombination rate in this photocatalyst. As can be seen in Figure 8b and also in the transient spectra (Figure 6), the relative intensity of the TiO₂-1 transient absorption between 500 and 600 nm is higher than that in TiO₂-2. Apparently, more electron/hole pairs are recombining in TiO₂-2 than in TiO₂-1.

The charge carrier dynamics observed for TiO₂-2 can be correlated to the hydrothermal treatment applied during its preparation. The low temperature employed (200 °C) should lead to the formation of more defects in the crystalline structure. These defects may act as recombination centers, decreasing the electron/hole lifetime. Another key aspect influencing the efficiency of the charge separation in TiO₂ is the particle size. Serpone et al. studied the influence of the particle size on the charge carrier dynamics and

found that the fastest recombination rate is observed for the smallest TiO₂ nanoparticles⁴⁵. Herein TiO₂-2 exhibits the smallest particle size.

Discussion

One of the objectives of this work is to establish relationships between the photocatalyst preparation, its morphological and electronic properties, and, finally, its photocatalytic activity. Given the large number of variables and factors that have to be taken into account, such task can be puzzling and it is usually not easy to establish a direct correlation valid for all photocatalysts. However, the data collected herein allow us to determine some interesting features that can be helpful for the development of highly efficient materials for photocatalysis.

The photocatalytic tests performed showed that in comparison to TiO₂-1 the TiO₂-2 photocatalyst exhibits better efficiencies for dye degradation, gaseous acetaldehyde oxidation, and methanol oxidation. The performance of the photocatalyst prepared via hydrothermal treatment was even better than that observed for the commercial photocatalyst P25 for methanol oxidation. In these experiments the higher surface area of TiO₂-2 seems to play the major role determining the photocatalytic effectiveness. All these processes involve the transfer of photogenerated holes to adsorbed species or the indirect transfer to an adsorbed water molecule yielding [•]OH radicals at the surface, which will further oxidize the substrate molecules⁶⁵. In both mechanisms, higher surface areas should lead to higher photonic efficiencies and, additionally, faster hole transfer processes should result in increased degradation rates. In the case of the photocatalytic methanol oxidation, the interfacial charge transfer occurs

within 300 ps⁴ and partially compensates the faster recombination rate observed for TiO₂-2 in relation to TiO₂-1.

If we normalize the degradation rates by the surface areas of the respective photocatalysts, the role of the electron/hole dynamics turns more evident. Taking the methanol oxidation, the normalized rates are 12×10^{-2} , 7×10^{-2} and 4×10^{-2} $\mu\text{mol L}^{-1} \text{s}^{-1} \text{m}^{-2}$, respectively for TiO₂-P25, TiO₂-1, and TiO₂-2. These values follow the same trend observed for the electron/hole lifetimes obtained by TAS. Thus, in a given time after excitation, more charge carriers are available on the TiO₂-1 than in TiO₂-2, but as the surface area of the former is lower, fewer molecules are oxidized.

Another interesting relationship that can be established between the TAS data and the photocatalytic activity arise from the comparison of the degradation rates (corrected by surface area) and the relative intensity of the peaks at low and high energy. The $\Delta A(800 \text{ nm})/\Delta A(400 \text{ nm})$ ratio immediately after the laser pulse is around 0.7 in TiO₂-1 and 0.45 in TiO₂-2. This decrease is in the same order than that observed for the corrected degradation rates for methanol oxidation and confirms that the holes responsible for the absorption signature at lower energy are the photoactive ones.

The crystal structure as well as the crystallinity also plays an important role on the observed photocatalytic behaviour. Initially, TiO₂-2 was expected to exhibit a more efficient charge separation as compared with TiO₂-1, as the former exhibits both, brookite and anatase crystallites in its structure. As reported earlier^{66, 67}, the conduction band edge of brookite TiO₂ is *approx.* 0.14 eV more negative than that of anatase, which should impose an energy barrier for the

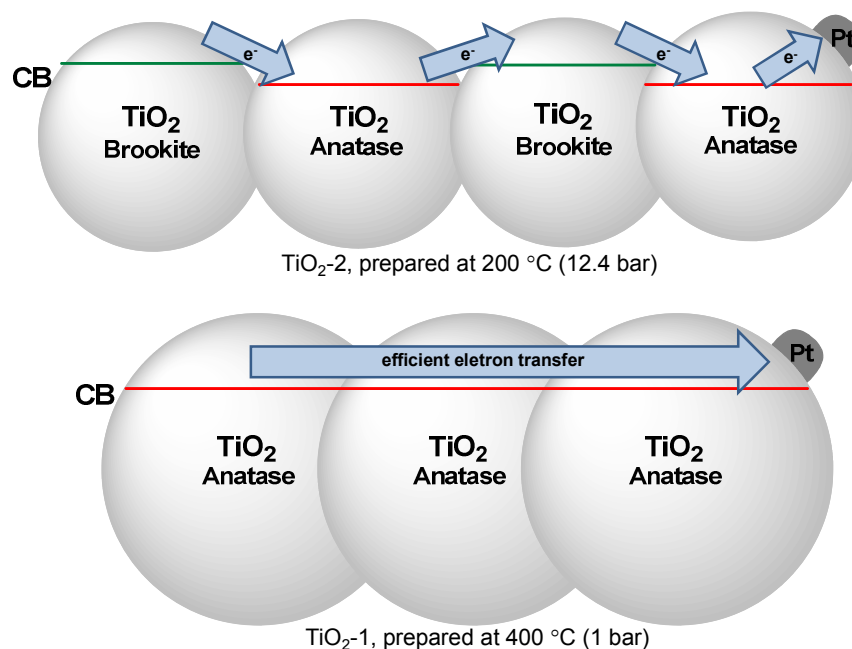
back electron transfer. However, in the case of TiO₂-2 the larger amount of defects within its crystalline structure along with its smaller particle size seem to facilitate the charge recombination, reducing the charge carriers available for photocatalytic processes.

Charge carrier recombination can obviously be expected to be dependent on the light intensity employed in the laser experiments and further studies are necessary to understand more deeply the reason of the faster recombination rates observed for TiO₂-2. As stated previously⁶⁸, the electron/hole recombination kinetics depend on the number of charge carriers generated per particle, being much faster at very high concentrations of electron/hole pairs in each TiO₂ particle. Therefore, it can be expected that light intensity effects will be more evident in TiO₂-2 due to its smaller primary particle size. The results found here for the bare photocatalysts are in good agreement with those reported by Carneiro et al.⁴³ These authors concluded that, for powders consisting of primary particles with 7-15 nm diameter, the surface area and the available adsorption sites play a major role for the photocatalytic performance, while for 15-35 nm particles, the higher hole concentration and the greater crystallinity decreases the dependency on the surface area.

After platinum deposition on the TiO₂ surface, the photocatalytic activities for methanol oxidation and H₂ evolution increase for TiO₂-1 and TiO₂-P25, as a result of the improved charge separation efficiency. However, the photonic efficiency of TiO₂-2 for methanol oxidation decreases by 50% in relation to the bare photocatalysts with its performance for H₂ evolution being the worst among the investigated powders. Metal deposition leads to a decrease of the available adsorption sites on the TiO₂ surface, as previously observed for other TiO₂-

based photocatalysts⁶⁹. In fact, the surface areas of the as synthesized TiO₂ powders decrease c.a. 10% after Pt deposition. Although, as the surface area reduction is observed for all catalysts, the decrease in the TiO₂-2 photocatalytic activity should be related to the concentration of charge carriers on each catalyst surface.

For all samples, the presence of platinum leads to a decrease in the charge carrier recombination rates in relation to those of the bare photocatalysts, since the metal islands act as efficient electron acceptors. Therefore, the results indicate that the lower crystallinity and the reduced particle size of TiO₂-2 lead to a smaller concentration of electrons effectively transferred to the Pt islands. It has previously been shown that the so-called antenna mechanism provides an important pathway for H₂ evolution on Pt-TiO₂ photocatalysts⁶⁹. This mechanism is based on the interparticle charge carrier transport within TiO₂ agglomerates until the electrons reach the Pt islands (or the holes reach oxidizable adsorbed substrate molecules, respectively). Hence, the difference in the conduction band energies of anatase and brookite present in TiO₂-2 impedes the electron mobility, further decreasing the amount of H₂ evolved, scheme 1. For the bare TiO₂-2 photocatalyst, the larger surface area compensates the decrease of the charge carrier concentration resulting in an overall efficiency higher than that observed for the other oxides. However, this parameter only has a minor effect for the H₂ evolution in the presence of a co-catalyst.



Scheme 1. Diagram illustrating the effect of the as prepared TiO₂ crystal structures on the electron transfer process to Pt islands.

Conclusions

In this work two different TiO₂ powders were prepared by the sol-gel method followed by thermal treatment in a conventional oven at 400 °C (TiO₂-1) or in a hydrothermal reactor at 200 °C and 12.4 bar (TiO₂-2). The later material exhibited higher surface area than the former, and its XRD pattern evidences the presence of approx. 45% of brookite along with the anatase polymorph. Rietveld refinement indicates a higher distortion on the TiO₂-2 crystalline structure. The photocatalytic activities of the as prepared powders were evaluated using different reactions and were compared to those of the commercial photocatalyst TiO₂-P25. The bare TiO₂-2 exhibited better performance in photocatalytic processes involving an adsorption step, which can be directly related to its higher surface area. When metallic platinum is deposited on the TiO₂ surfaces and the samples are tested for H₂ evolution

using methanol as the hole scavenger, the photonic efficiency of TiO₂-1 is approx. 10% higher than that of TiO₂-2. These results were rationalized using nanosecond transient absorption spectroscopy (TAS). It was found that:

1. The electron/hole recombination rates in TiO₂-2 are faster than in TiO₂-1 due to the more distorted crystalline structure and smaller particle size of the former. This negative aspect is overcompensated by the higher surface area of TiO₂-2 in the absence of any co-photocatalyst.
2. In the presence of platinum as co-catalyst, the photocatalytic efficiency is dominated by the availability of charge carriers at the metaloxide surface.

Thus, the thermal treatment conditions determine two main factors, which influence very strongly the photocatalytic activity of the samples studied here, namely, the crystallinity and the surface area. The high crystallinity, obtained under higher temperatures, is particularly important for the transport of the charge carriers and this seems to be crucial for the production of molecular hydrogen, in which the electrons are transported to the Pt islands, through the oxide particles.

On the other side, the defects (lower crystallinity) are important for the harvesting of the charge carriers after they reach the particle surface, where a higher surface area yields an increase of the reaction rate constants. This behaviour is clearly observed for the TiO₂ particles prepared by the hydrothermal treatment. An important conclusion of this work is that the best photocatalyst for a given photoreaction will not necessarily be the best choice for all photocatalytic processes! This will become particularly critical in the case

of the photocatalytic H₂ evolution where the presence of co-catalysts is necessary.

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Electronic Supplementary Information: Rietveld analysis of XRD diffraction patterns, UV-Vis reflectance spectra and N₂ adsorption/desorption isotherms of the TiO₂ samples, time-profile curves for dye degradation in the presence of different photocatalysts and additional time-resolved absorption data.

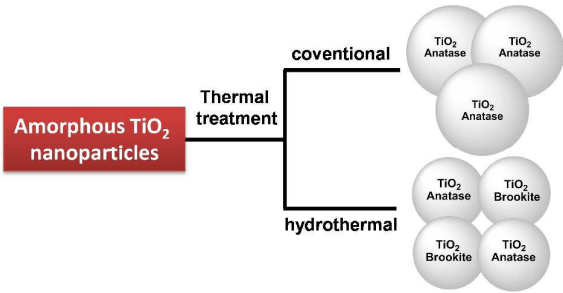
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Table of Contents (TOC) Image



The role of thermal treatment on the electron/hole dynamics and on the photocatalytic activity of TiO_2 is investigated by transient absorption spectroscopy.