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The role of nanoparticulate agglomerates in TiO$_2$ photocatalysis: degradation of oxalic acid

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Abstract The simultaneous bimodal study of the photocatalytic oxalic acid degradation by aqueous TiO$_2$ suspensions revealed that particular systems possess the capacity to protect a certain amount of oxalic acid from oxidation, thus hindering, to some extent, the photocatalytic reaction. While measurements of the oxalic acid concentration in the bulk liquid phase indicated full photocatalytic degradation; in situ pH-stat measurements allowed the quantification of the amount of oxalic acid remaining in the part of the nanoparticulate agglomerates where light could apparently not access. An explanation for this phenomenon takes into account the possibility of the formation of TiO$_2$ agglomerates in which these molecules are hidden from the effect of the light, thus being protected from photocatalytic degradation. Studies of different TiO$_2$ materials with different particle sizes allowed a deeper exploration of this phenomenon. In addition, because this property of encapsulating pollutant molecules by photocatalytic systems is found to be a reversible phenomenon, P25 appears to be more convenient and advantageous as compared to the use of large surface area photocatalysts.

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Introduction

Heterogeneous photocatalysis employing semiconductor nanoparticles continuously gains increasing interest as it finds multiple applications for solving a wide variety of environmental problems concerning the purification of water and air, disinfection, or the energy to fuel conversion (Wang et al. 2013).

TiO$_2$ is an inexpensive semiconductor which is most of the times the preferential choice as the photocatalyst material. Nanoparticulate TiO$_2$ can be used in a wide pH range of, aqueous or organic, solutions, and due to its band structure and the redox potential of the photogenerated electron–hole pairs, it appears to be photocatalytically active for the degradation of a wide variety of pollutants (Chen and Wang

2012; Fujishima et al. 2008; Kudo and Miseki 2009). This is the reason why different kinds of TiO$_2$, either self-prepared or commercially produced, are permanently under thorough investigation to unravel unknown features and to solve unanswered questions regarding the mechanism(s) responsible for the obvious photocatalytic activity, or simply for the sake of finding a highly active material for technological applications. Among the commercial TiO$_2$ products, Evonik Degussa Aeroxide TiO$_2$ P25 (P25) is still one of the most widely spread semiconductor materials (Brunelli et al. 2013) which are frequently employed for both research and applications. Despite this, a truly comprehensive explanation of its high photocatalytic activity still remains an open question to be solved.

Fundamental studies usually target the understanding of the respective TiO$_2$ properties: bulk and surface properties (Diebold 2003; Henderson 2011), i.e., band structure, atomic positions, defects in the crystals, thermal and electrical conductivity parameters, etc. However, a photocatalytic reaction is a complex system further affected by additional parameters beyond the specific properties of the semiconductor itself. In this regard, the collective behaviour of a group of particles conveniently arranged is one of the system's properties of interest.

For instance, the antenna mechanism originally suggested by Wang et al. (Wang et al. 2006) operates on a chain of topotactically attached particles in which light can be absorbed by one of them while the electron–hole pairs thus generated may be transported along these chains, thus reacting with the pollutant adsorbed at a different particle of the agglomerate.

Another mechanism within this collective category is the deaggregation mechanism initially proposed by Pagel and Dohrmann (2007) and later used to explain experimental observations in TiO$_2$ layer systems (Mendive et al. 2011). This mechanism accounts for thermal processes beyond the light absorption and the charge separation for the generation of electron–hole pairs. Thus, the thermal energy liberated upon recombination can be absorbed by the system and subsequently used to, e.g., break weak bonds between particles promoting the deaggregation of part of the agglomerate.

Both the antenna and the deaggregation mechanism lead to an enhancement of the photocatalytic efficiency of the semiconductor, because in both of them the availability of essentials is increased, i.e., light and

surface area, in the first and in the second case, respectively.

In this study, we have chosen a model compound with good sticking properties, i.e., oxalic acid, to thoroughly study the mechanism of the photocatalytic action of TiO$_2$ P25, comparing its performance to that of other commercial TiO$_2$ products, thus challenging the still unanswered question concerning its extraordinary photocatalytic activity.

The results obtained herein are explained suggesting a collective behaviour of particles as a crucial property of photocatalytic systems, in which stable agglomerates act by encapsulating the adsorbate, thus protecting it from its photocatalytic degradation. We discuss these findings in terms of specific properties of the photocatalytic material, e.g., particle size, exposed surface area for adsorption, as well as mechanical stability with respect to the deaggregation mechanism (Mendive et al. 2011).

Experimental procedures

Materials

All chemicals were of analytical grade and used as received without further purification. All solutions were prepared with deionized water from a Sartorius Arium 611 apparatus (resistance $= 18.2$ MΩ cm^{-1}). The following commercial TiO$_2$ powders were employed in this work[1]: P25 (manufactured by Evonik, 80 % anatase and 20 % rutile, 30 nm primary particle size), PC50 (manufactured by Cristal Global, 100 % anatase, 40 nm primary particle size), PC500 (manufactured by Cristal Global, 100 % anatase, 7 nm primary particle size) and S230 (manufactured by Kemira, 100 % anatase, 7 nm primary particle size). The aqueous suspensions of all TiO$_2$ powders were measured by dynamic light scattering in a Malvern Zetasizer Nano S, equipped with a laser of 632.8 nm.

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[1] The four TiO$_2$ materials were characterized by Rietveld refined powder X-ray diffraction (XRD) for the identification of the constituting polymorph and the calculation of the mean crystalline domain which is usually used as the particle size. The measurements were carried out on a Bruker D4 Endeavour diffractometer (Cu Kα radiation, Ni filtered) at the Institute of Mineralogy of the Leibniz Universitaet Hannover.

Procedures

Photocatalytic tests

The photocatalytic degradation experiments of the selected model compound, oxalic acid (OA), were carried out under vigorous stirring in a glass reactor equipped with a cooling jacket. The system was irradiated using a Xe arc lamp, CSX 450 W (Phillips), in a lamp housing (LAX 1450) and connected with the power supply SVX 1450 (Müller Elektronik-Optik). A 10-cm IR-blocking filter was placed between the reactor glass window and the lamp to protect the reaction solution from overheating. The temperature of the reaction mixture was maintained constant at 25 °C during the entire experiment using a thermostatic bath (Julabo Company). During the photocatalytic reactions, the suspensions were always purged with molecular oxygen to guarantee O_2 saturation, thus avoiding kinetic limitations resulting from the electron uptake reaction. Further details of the employed set-up can be found in ref. (Ivanova et al. 2013).

For each experiment, the reactor was filled with 230 ml of a suspension of 2.5 g TiO_2/l in 10×10^{-3} mol/l KNO_3 and 2×10^{-3} mol/l OA, except for S230, where the initial OA concentration was 3.2×10^{-3} mol/l. First, the suspension was allowed to equilibrate in the dark for 24 h. Then, the pH was adjusted to 3.70 and after an additional equilibration time of 40 min, the system was irradiated for 100–200 min.

The photocatalytic degradation measurements on each system were performed by two independent analytical methods, i.e., potentiostatically by means of a pH-stat technique and by high-performance ion chromatography (HPIC).

The pH-stat set-up consisted of an automatic dosing unit (Basic Titrino 794 from Metrohm) with a high-performance titrimetric pipette which is able to add drops of 0.5 μl, a highly sensitive semi-micro pH electrode combined with an Ag/AgCl reference electrode (Thermo-Orion Ross 8115) with pH accuracy up to the third decimal and a computer to control and record the results. The ionic strength provided by the nitrate solution had a double function ensuring, e.g., on the one hand, constant electro-ionic surface and Zeta potentials for the adsorption of OA over the entire duration of the photocatalytic reaction and on the other
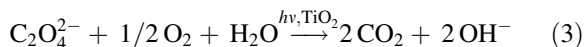
hand, accurate pH measurements by stable potentials at both sides of the highly sensitive membrane of the electrode. The calibration of the electrode was performed at the same ionic strength.

For the chromatographic measurements, an aliquot of 1 ml of the suspension was withdrawn from the system at regular time intervals, i.e., every 30 min, to monitor the OA concentration in the bulk solution free of photocatalyst particles. For every withdrawal, a new, clean—not used—set of syringe, filter and syringe–filter holder was employed. The filters were from Macherey–Nagel (Germany) with 0.45 μm pore diameter. It should be noted here that the type of filters was carefully chosen to properly separate the particles and to yield a clear solution for injection in the chromatograph. At the same time, it was ensured that this procedure was not affecting the measurement of OA by causing any undesired particle agglomeration reaction that may alter the OA concentration present in the suspension prior to the filtration. Thus, the samples did not go through any change in ionic strength that could affect aggregation. A DIONEX ICS-1000 chromatograph with a conductivity detector and an electro-regenerator–suppressor was employed. The column was an Ion Pac AS9-HC 2×250 mm and the guard column was an Ion Pac AG9-HC 2×50 mm from DIONEX. The eluent was an alkaline solution of 8×10^{-3} mol/l Na_2CO_3 and 1.5×10^{-3} mol/l $NaHCO_3$. The temperature of the conductivity detector cell was kept constant at 35 °C. The detection limit for OA (oxalate) is 0.1 μmol/l at the characteristic retention time of 35 min. The column allows very good resolution among small carboxylic acids, with large retention time differences with respect to inorganic anions.

In some cases, two consecutive photocatalytic cycles were carried out. The initial OA concentration in the second cycle was such resulting from the sum of the OA remaining in the system and the new addition of 2×10^{-3} mol/l.

Calculation of the OA concentration by the pH-stat method

The photocatalytic degradation of OA was deconvoluted in terms of all three species of oxalic acid in equilibrium in aqueous solutions, i.e., $H_2C_2O_4$ (species A), $HC_2O_4^{-}$ (species B) and $C_2O_4^{2-}$ (species C), at pH 3.7 and 25 °C according to Eqs. 1–3.

$$H_2C_2O_4 + 1/2\,O_2 \xrightarrow{hv,\,TiO_2} 2\,CO_2 + H_2O \qquad (1)$$

$$HC_2O_4^- + 1/2\,O_2 \xrightarrow{hv,\,TiO_2} 2\,CO_2 + OH^- \qquad (2)$$

$$C_2O_4^{2-} + 1/2\,O_2 + H_2O \xrightarrow{hv,\,TiO_2} 2\,CO_2 + 2\,OH^- \qquad (3)$$

The pH-stat set-up was therefore programmed to keep the pH constant at 3.7 by addition of HNO_3. Thus, the number of moles of H^+ necessary to neutralize all OH^- produced is computed and stoichiometrically assigned to the number of moles of species B or C that were photocatalytically degraded. The concentration of all species present in the system at any time is therefore calculated as the difference between their corresponding initial and the degraded concentrations. Since the oxidation of OA leads to carbon dioxide directly and as the latter exists in aqueous solution in equilibrium with carbonic acid, the pH 3.7 of the entire experiment was strategically chosen in order to minimize to negligible values additional titrations which could arise from the dissociation of the H_2CO_3. The negligibility is therefore ensured by three parameters: (1) the carbon dioxide hydration equilibrium constant, $[H_2CO_3]/[CO_2] = 1.7 \times 10^{-3}$ in pure water, (Housecroft and Sharpe 2005) and 1.2×10^{-3} in seawater (Soli and Byrne 2002) by which the majority of the carbon dioxide is not converted into carbonic acid, thus remaining as CO_2 molecules, (2) the first dissociation constant of carbonic acid, e.g., pK_a 3.6 at 25 °C or pK_a' 6.3 at 25 °C and low ionic strength, where ' denotes that both species, which is carbonic acid and dissolved carbon dioxide, are included (Greenwood and Earnshaw 1997) and (3) the very low dissociation constant of bicarbonate, e.g., pKa 10.33 at 25 °C and low ionic strength (Smith and Martell 1979).

All volume changes, e.g., added and withdrawn amounts, were taken into account for the calculation of the concentrations of all species at any time step.

Species A ($H_2C_2O_4$) cannot be detected by this method because it does not produce any OH^-. It must be noted that its concentration is negligible at pH 3.7;[2]

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[2] The pK_a constants at 25 °C and low ionic strength are 1.25 and 4.27 Smith and Martell (1979). Critical stability constants. New York, Plenum Press.

Fig. 1 Photocatalytic degradation of OA on different TiO_2▶ particles, from top to bottom: P25, PC50, PC500, S230. The initial oxalic acid concentration was 2 mM in 10 mM KNO_3 at pH 3.7. **a** Oxalic acid concentration measured using a pH-stat technique: (*open square*) species (B + C), (*open circle*) species B and (*open triangle*) species C. **b** (*filled circle*) Oxalic acid concentration in the solution measured by HPIC

thus, it will not affect the calculated concentration of both ionic species B and C.

The analysis of the data required as well assuming that the degree of protonation of adsorbed and dissolved OA is the same. This assumption is based on the results of theoretical calculations (Mendive et al. 2009) since assessing experimentally the degree of protonation of adsorbed species is till nowadays technically impossible. In that work, it was found that three of the four most stable adsorbed OA species on anatase are protonated while only one is non-protonated. Such abundances are in good agreement with those of dissolved species at pH 3.7 (Smith and Martell 1979). Furthermore, the amounts (concentration) of adsorbed species in equilibrium are less than 5 % (see adsorption curves) of the dissolved concentrations, contributing scarcely to the total computed amounts.

All concentrations, including those of the suspensions, were carefully chosen to fit into a range in which they do not approach the instrumental detection limits.

Adsorption isotherms

Suspensions of 2.5 g l^{-1} TiO_2 in 0.01 mol/l KNO_3 and an appropriate amount of OA were brought to pH 3.70 followed by vigorous shaking for 24 h to reach the adsorption equilibrium. Thereafter, the pH was adjusted to 3.70 at time intervals of 1 for 5 h by addition of KOH or HNO_3, as required. This procedure was repeated for several and different OA concentrations ranging from 0.3 to 1.2×10^{-3} mol/l.

The adsorption equilibrium was assumed when the pH remained constant. Then an aliquot of the suspension was withdrawn, and the OA concentration in the solution free of particles was measured by HPIC (c_{eq}). Identical OA solutions were prepared in the absence of TiO_2 (c_{total}) in order to calculate the adsorbed amount of OA in every TiO_2 system (c_{ad}) as the difference $c_{total} - c_{eq}$. The results were plotted in graphs with c_{ads} as a function of c_{eq}.

The nature of the adsorption behaviour of OA at the surface of nanoparticulate anatase and rutile is
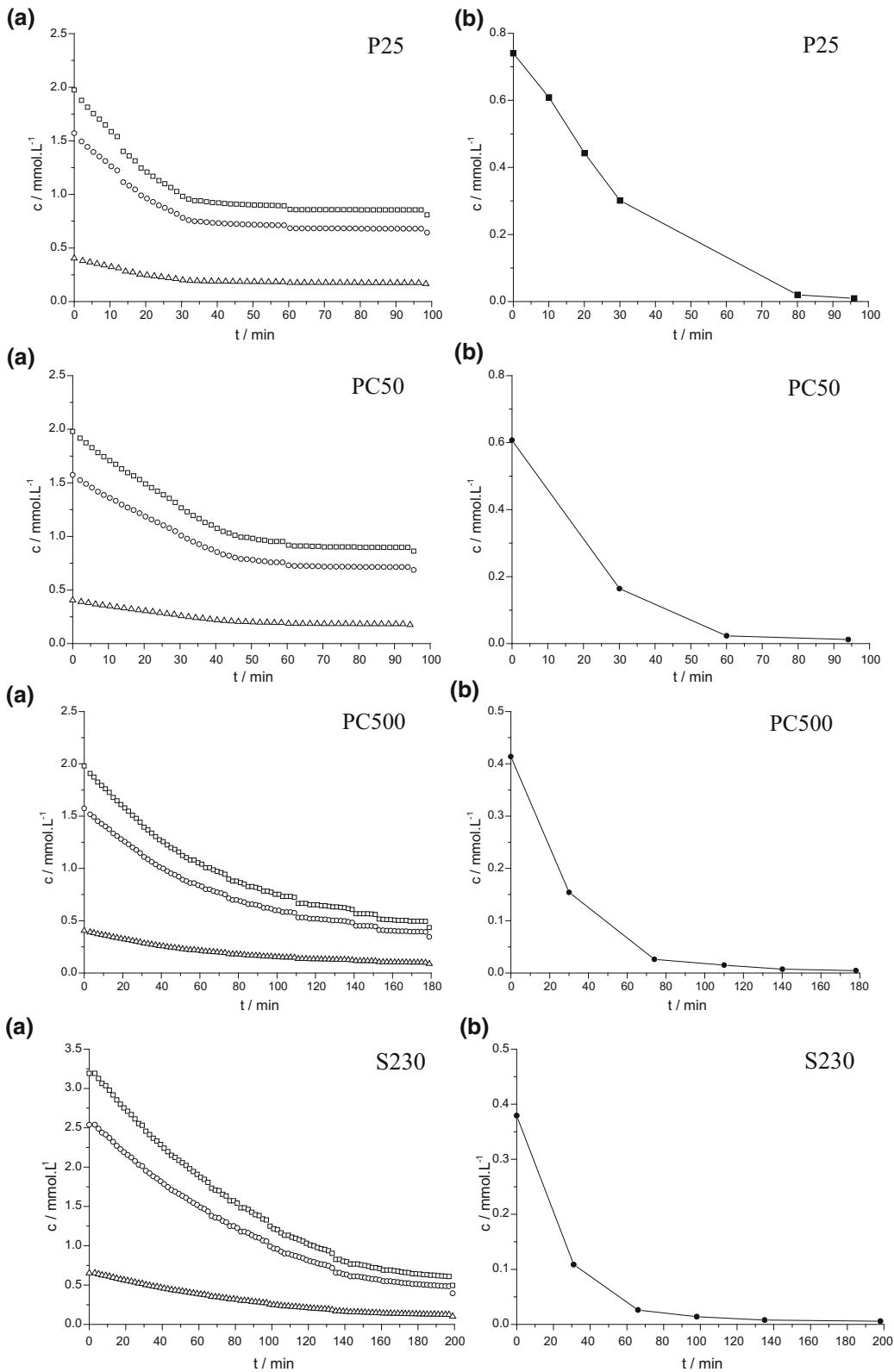
consistent with a strong chemisorption by covalent bond formation at surface Ti and O atoms of the exposed facets (Mendive et al. 2008, 2009). Therefore, the experimental points of the graphs were interpreted as adsorption isotherms at constant ionic strength and fitted to two models, i.e., Langmuir (Eq. 4) and Brunauer–Emmet–Teller, BET, (Eq. 5).

$$y = \frac{N \times K \times x}{1 + K \times x} \qquad (4)$$

$$y = \frac{N \times K' \times \left(\frac{x}{P}\right)}{1 - \left(\frac{x}{P}\right)}$$
$$\times \frac{1 - (l+1) \times \left(\frac{x}{P}\right)^{l} + l \times \left(\frac{x}{P}\right)^{l+1}}{1 + (K'-1) \times \left(\frac{x}{P}\right) - K \times \left(\frac{x}{P}\right)^{l+1}} \qquad (5)$$

where y is the adsorbed amount (c_{ads}), x is the bulk concentration at equilibrium (c_{eq}), K is the adsorption (sticking) constant for the case of the Langmuir model and K' is a constant which includes the information related to the adsorption equilibrium of the first monolayer and that on upper layers (Ebadi et al. 2009), N is the maximal number of adsorption sites (first monolayer), P is an equilibrium concentration (which could be interpreted as the solubility in water, at least within the close vicinity of the surface) and l is the number of adsorbed multilayers.

Being aware that both equations arise from models originally applied to the gas phase physisorption on perfect metallic surfaces, in an analogous manner to the use of the Langmuir isotherm which is often found in the literature to describe the adsorption of aqueous species at different oxides surfaces, the BET equation employed here is regarded as a useful attempt to estimate the number of multilayers formed upon chemisorption modelling the uptake of additional oxalic acid after saturation.

Results and discussion

The photocatalytic degradation of oxalic acid (OA) on different TiO$_2$ polymorphs, which also differ in particle size, surface area and the employed synthesis procedure, has been studied employing both the pH-stat method and the HPIC analysis of the bulk aqueous phase. The results are presented in Fig. 1a, b, respectively. The pH-stat data (Fig. 1a) show that after different periods of illumination time, depending on the employed photocatalyst, the concentration of OA stops

decreasing, indicating an incomplete degradation. On the other hand, the photocatalytic reaction was monitored simultaneously by an independent method (ion chromatography), in which the dissolved amount of OA was quantified from a withdrawal of a given amount of suspension followed by the filtering of the particles. Interestingly, these results indicate that the complete photocatalytic degradation of the dissolved oxalate is achieved (Fig. 1b), contradicting, at a first glance, the pH-stat data.

Time 0 min corresponds to the moment when the irradiation starts. Hence, the initial OA concentration at this moment is clearly different as depicted by both measuring techniques. By HPIC only the concentration remaining in equilibrium (adsorption equilibrium) in the bulk solution is registered. Since the pH-stat method accounts for no addition of nitric acid, since no OH$^-$ is produced at time 0 min, the initial OA concentration is that one given to the system. And the amounts of species B and C shown in Fig. 1a are given by the mass balance upon equilibrium in the dark.

Figure 1a, b shows that the rate of the photocatalytic degradation of either each individual species or both species together decreases during the course of the reaction. It must be noted that the species must reach the TiO$_2$ surface for the photocatalytic reaction. A characteristic diffusion control profile (despite the strong mechanical stirring) at longer irradiation times with a continuous change in slope differing from the quasi-linear decay at time 0 min is also evinced. This is supported by the HPIC measurements which show small amounts of OA remaining in the bulk liquid phase at longer irradiation times. But such small amounts of OA do not mean that almost all the initial OA has been photocatalytically degraded, because the mass balance calculated by titrimetry shows that there is still a non-negligible amount of OA present in the system. For instance, after one or 2 h, for large or small particle TiO$_2$, respectively, the pH-stat technique accounts for the presence of approximately a quarter or the half of the initial concentration of OA (Fig. 1a). Interestingly, it is not detected by HPIC, at all.

It may be suggested that this amount of OA remaining in the system must be quite strongly adsorbed at the TiO$_2$ particles since no desorption occurs during the filtration process prior to injection in the chromatograph. Moreover, it can be also concluded that the light accessibility to this strongly adsorbed fraction of molecules must be poor, because
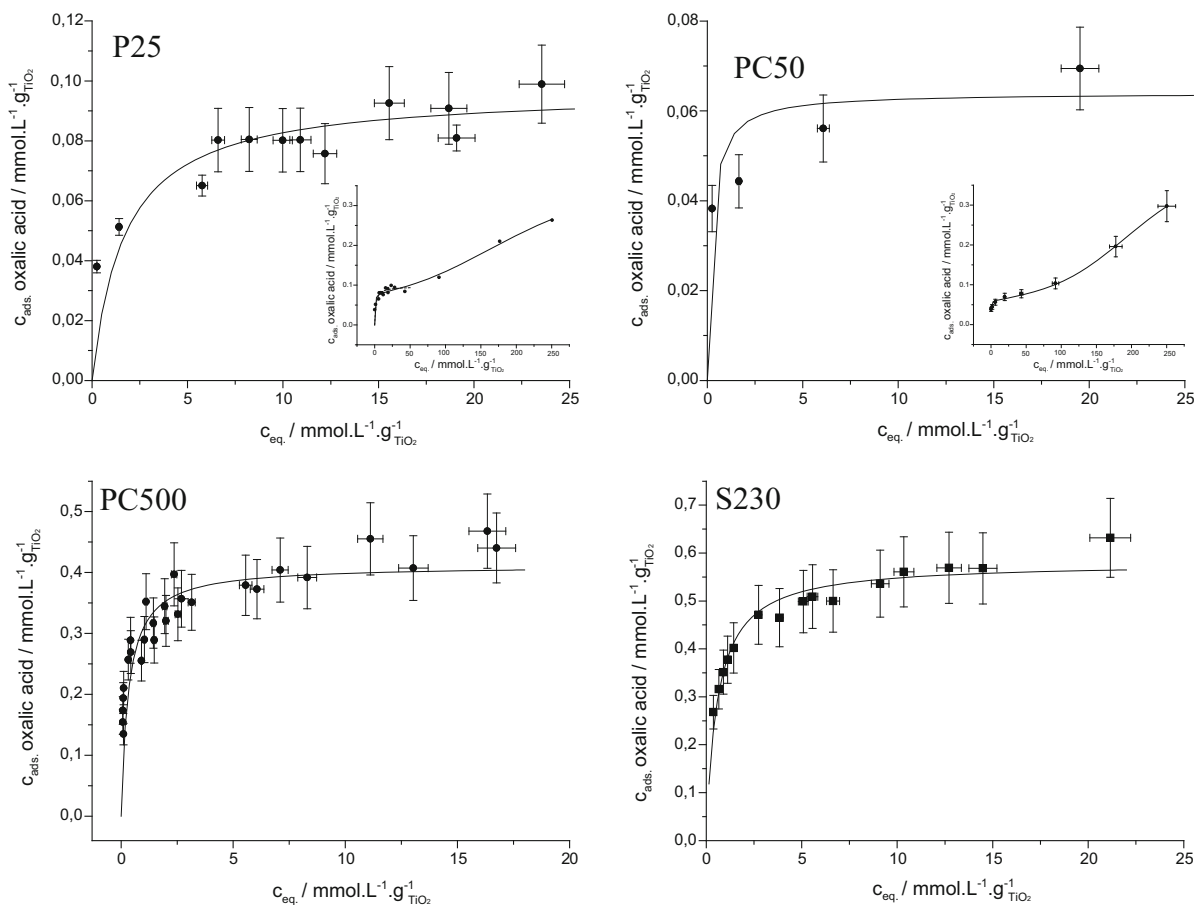
Fig. 2 Adsorption isotherms of oxalic acid on different TiO$_2$ powders, i.e., P25, PC50, PC500 and S230

of the very slow kinetic profile observed at longer irradiation times, i.e., after one or 2 h, for large or small particle sizes, respectively (Fig. 1a). In order to explain it, one may think of a system where the photocatalyst particles can be organized in such a manner that they are able to shield some OA molecules from the incoming light. Thus, the incomplete photocatalytic degradation observed for all TiO$_2$ studied here may be attributed to a collective phenomenon common to all type of TiO$_2$ samples. A collective phenomenon can be understood as an effect of several particles acting together. Because all TiO$_2$ samples are different, the single characteristic parameters, in particular their particle size and surface area, find as well a quite central role.

In order to obtain a deeper insight, a thorough investigation of the OA adsorption at the surface of all employed TiO$_2$ powders has been carried out. Figure 2 shows the corresponding adsorption isotherms, and

Table 1 summarizes the best fits to two different adsorption models, i.e., Langmuir and Brunauer–Emmet–Teller (BET), respectively. The OA adsorption at rutile (110) and anatase (100) has been investigated previously (Ahtee and Unonius 1977; Friedmann et al. 2010), showing that several inner sphere complexes are formed differing in their adsorption geometry with bidentate or monodentate species being most stable on rutile (110) or anatase (100), respectively. Ref. (Ahtee and Unonius 1977) reports the Langmuir–Freundlich[3] adsorption parameters for OA on anatase S230 at pH 3.70 with the maximum number of adsorption sites (N) and the equilibrium constant (K) being 1320 ± 300 μmol g^{-1} TiO$_2$ and 5.5 ± 3.7 l mol^{-1}, respectively. In the present work, the same system was

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[3] The Langmuir–Freundlich isotherm, i.e., $y = \frac{N \times K \times x^{(1-C)}}{1 + K \times x^{(1-C)}}$, contains an experimental adjustable parameter C.

Table 1 Surface area, particle size and oxalic acid adsorption parameters for the different TiO_2 materials

TiO_2	Surface area/m^2 g^{-1}	Particle size/nm	Isotherm model	K and K'/l mmol^{-1}	N/μmol g^{-1}	l
P25 (anatase/rutile)	50	30	Langmuir	0.6 ± 0.2	97 ± 5	–
			BET	551 ± 208	79 ± 3	5.4 ± 0.5
PC50 (anatase)	50	40	Langmuir	4.3 ± 3.0	64 ± 7	–
			BET	1152 ± 507	60 ± 3	7.8 ± 0.4
PC500 (anatase)	340	7	Langmuir	3.0 ± 0.7	412 ± 14	–
S230 (anatase)	230	7	Langmuir	1.7 ± 0.2	580.00 ± 0.01	–

Single-point standard surface area measurements were carried out employing a Micromeritics AutoMate 23 instrument. The gas mixture used for the adsorption determinations was 30 % nitrogen and 70 % helium. Prior to the measurements the TiO_2 samples were heated to 150 °C for approximately 30 min in order to clean the surface from adsorbed organic compounds and to remove excess humidity. Desorption experiments were also performed in order to confirm the data obtained from the adsorption measurements

modelled by a Langmuir isotherm with the respective values being 580.00 ± 0.01 μmol g^{-1} TiO_2 and 1.7 ± 0.2 l mmol^{-1}. Fitting the experimental data by the "pure" Langmuir isotherm appears to be more suitable than employing the modified Langmuir–Freundlich model, not only because a "pure" Langmuir fit exhibits lower limits of error, but because the Langmuir–Freundlich isotherm is based on an experimentally adjustable parameter (the Freundlich parameter) which has no physical meaning. In addition, the rather small K value given in ref. (Ahtee and Unonius 1977) as compared to the equilibrium constants listed in Table 1 [note the units are (l mol^{-1}) and (l mmol^{-1}) for ref. Ahtee and Unonius 1977] and for this work, respectively) does not appear to properly describe the high sticking properties of OA as observed here.

Fitting the data by a Langmuir isotherm is further supported by the results of Weisz et al. (Weisz et al. 2002) who have modelled the OA adsorption on P25 employing a very different approach to the one used in the present work. In their work (Weisz et al. 2002), the adsorbed amounts of oxalate were measured directly by means of attenuated total reflection–Fourier transformed infrared (ATR-FTIR) spectroscopy. The equilibrium constant reported by Weisz et al. at pH 3.70, i.e., 3.0 l mmol^{-1}, is comparable to the value determined in the present work, i.e., 0.6 ± 0.2 l mmol^{-1} for the same system at the same pH.

The values of the Langmuir equilibrium constants determined for the four TiO_2 materials studied here (Table 1) are within the same order of magnitude, indicating that OA tends to adsorbs in a similar manner to the different surfaces exposed by each of the TiO_2 materials. Two groups of N values, small and large

values, correlate with the small and large BET surface area of the TiO_2 powders, i.e., the group P25 and PC50, and the group PC500 and S230, respectively. In the case of the small surface area TiO_2 materials an alternative adsorption model (BET) was used to fit the results obtained at high OA loadings, demonstrating that under such conditions several OA layers (parameter l, see Table 1) can be formed upon adsorption (see insets in Fig. 2). The thus determined number of layers is 5 and 8 for P25 and PC50, respectively. It is important to note that independently on which model was employed to fit the data for a given TiO_2 material, i.e., Langmuir or BET, the thus obtained N values are similar. This supports the notion that OA forms inner sphere surface complexes within the first monolayer, i.e., in its chemisorbed state (Mendive et al. 2008, 2009). The K and K' values arising from the two different models are, on the other hand, quite different in both cases, i.e., for P25 and for PC50. Since the BET isotherm is usually applied to model the adsorption from the gas phase, although some authors used it to explain the multilayer adsorption in aqueous phase (Ebadi et al. 2009; Maurya and Mittal 2006; Rangabhashiyam et al. 2014), it is expected that the interpretation of K' as a thermodynamic parameter indicating the sticking property of the adsorbate at the surface will be highly affected by the conditions given by the aqueous phase environment, as well as by the condensation induced within the multilayer adsorption. It must be noted that the term condensation should not be rigorously taken as a gas to liquid transformation, but rather as the formation of a condensed, and to some extent, ordered system close to the particle surface, different to the randomly

dispersed molecules in the liquid bulk solution. As Ebadi et al. (2009) reported, K' contains the information of the equilibrium constant for the first monolayer as well as that for upper layers. This is, moreover, also evinced in the large uncertainties for the determined K' (BET) values.

Studying high loadings of OA on the large surface area TiO_2 materials was limited by the solubility of OA in water [143 g/l at 20 °C Smith and Martell 1979]. Hence, it was not possible to explore whether or not there is a multilayer adsorption of oxalate on these materials.

An explanation of the data shown in Fig. 1 taking into account the above described adsorption features of OA is the following. The central concept of the suggested collective phenomenon is the formation of stable agglomerates of several TiO_2 particles by the adsorption of OA. Pettibone et al. confirmed that the uptake of OA on the surface of TiO_2 nanoparticles increases their aggregation (Scaife 1980). We therefore suggest that upon bandgap irradiation only those OA molecules adsorbed at the outermost particles of the agglomerates will be degraded photocatalytically since only these particles will absorb the incoming photons. In this manner, it will prevent the charge carrier formation in the inner particles. The degraded oxalate molecules will then be replaced by oxalate dissolved in the aqueous phase resulting in the decay of the concentration of oxalic acid as monitored by the chromatographic measurements (Fig. 1b). In this sense, the outer layer of particles could be described as a shield of the particles inside the agglomerate. And since the latter remain in the darkness, the oxalic acid molecules adsorbed at their internal surfaces will not be degraded photocatalytically. The pH-stat technique yields a mass balance of the total amount of oxalic acid molecules present in the system, i.e., the sum of adsorbed and dissolved molecules, and therefore accounts for the presence of these remaining oxalic acid molecules (Fig. 1a).

It is assumed that every single particle represents a system able to absorb one photon with the photogenerated electron–hole pair being able to attack oxalic acid molecules adsorbed at any site of its surface.

The existence of agglomerates in TiO_2 suspensions is widely known, as well as the fact that aggregation does not impact the organic acid uptake by TiO_2 particles (Pettibone et al. 2008) because the agglomerates are permeable for the solution through the space left in between the loosely attached particles. For instance, Brunelli et al. (2013) show that a 10 mg l^{-1} aqueous

suspension of P25 at the pH of pure water and after 25 h of equilibration forms stable agglomerates of 627 ± 25 nm, in agreement with the results of Pettibone et al. (2008) who report 500 nm size agglomerates formed from anatase nanoparticles of 5 nm particle size at pH 2. The results of Pettibone et al. also show that agglomerates of 5 nm anatase particles are within a range of 1–2 μm at low pH and that upon saturation with oxalic acid the agglomerate size is independent from the TiO_2 particle size. The manufacturer of the products PC50 and PC500 report an agglomeration size in pure water of 1.5 and 1.2–1.7 μm (Carneiro et al. 2010). Dynamic light scattering measurements taken for the specific TiO_2 suspensions employed in this work show at least two or three sizes of agglomerates of 500–5000 nm, with a huge distribution of sizes (broad bands). Such uncertainties did not allow specifying agglomerate sizes with accuracy.

But, as a rough approximation, assuming closed packed spherical particles forming a spherical agglomerate, the number of particles present in one agglomerate of 1 μm will be around 9×10^4 and 6×10^6, for particles of 30 and 5 nm diameter, respectively. Acting in a similar way like a sponge, such an agglomerate may therefore have the capacity for retaining oxalic acid molecules as evinced by the pH-stat measurement results.

Since oxalic acid adsorbs strongly at the TiO_2 surface, i.e., exhibits high K values (Table 1), and it is able to adsorb with a mono- or a bidentate structure (Mendive et al. 2009), the possibility that one molecule could bind to the surface of two very closely attached different particles within an agglomerate may play an important role in reinforcing its stability. Agglomerates of similar sizes made of smaller TiO_2 particles, i.e., PC500 or S230, will consequently contain many more particles and the space left between them will be considerably smaller than in the case of bigger particles. In addition, taking into account the ability of oxalic acid to build multilayers (at least on the larger TiO_2 particles), in which the interaction between the molecules is given by hydrogen bonds via their carboxylic terminations,[4] the OA

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[4] Solid oxalic acid in both forms, anhydrous and dihydrated, reveals the disposition of the molecules interacting via the carboxylic groups on both sides directly, or mediated by two water molecules, forming chains along the C–C bond Jayatilaka and Grimwood (2001), Grimwood and Jayatilaka (2001).

Fig. 3 Upon bandgap irradiation, deaggregation of particle agglomerates allows the photocatalytic degradation of the content
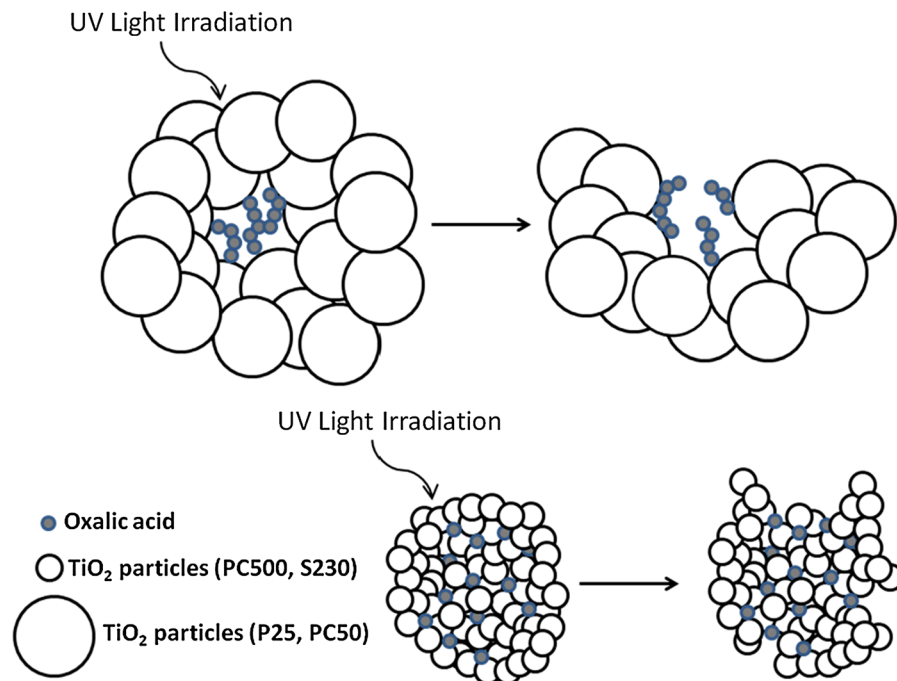
molecules encapsulated in the agglomerates of P25 or PC50 will likely form short chains of approximately 5–8 units (according to l, the number of adsorbed layers) that not only will maintain the connection between the particles, but may appear as small reservoirs of OA within the agglomerate (Fig. 3). This situation is not exactly the same in agglomerates of smaller TiO_2 particles, i.e., PC500 and S230, in which the OA molecules will be more homogeneously distributed throughout due to the considerably reduced space in between the particles and therefore a less favoured formation of multilayers of adsorbed molecules.

The exact amount of OA retained in the different agglomerates will vary according to the capacity of every particular system forming these agglomerates. For instance, experimental factors such as the stirring force or the temperature may slightly alter the conditions, hence affecting the agglomeration. Additionally, the concentration of OA inside the agglomerates will also be affected provided that the so-called antenna mechanism (Wang et al. 2006) is operative. In this case, some of the OA molecules adsorbed at an inner particle of the agglomerate will also suffer from photocatalytic degradation if they are adsorbed to a particle belonging to a chain of topotactically attached

particles, where at least one of them is part of the most outer layer of the agglomerate. We assume that agglomerates build randomly, leading to a non-constant and rather reduced number of topotactic attachments.

Since the amount of adsorbed OA is negligible at high pH (results not shown), a drastic pH increase was used as a tool to promote desorption. Then, after the photocatalytic degradation was performed, the suspension was brought to pH 13.0, allowed to equilibrate over 12 h, and the concentration of the OA in solution was subsequently measured. The concentrations of dissolved OA increased from 0.72 to 1.13 $\mu m\ l^{-1}$ for P25 and from 0.44 to 1.48 $\mu m\ l^{-1}$ for PC500 (see Table 2). The results prove that there was indeed an amount of OA present in the system which the chromatographic method could not account for if the pH was not raised and desorption was not promoted (Fig. 1b). Nevertheless, the amount desorbed by the pH increase, both for P25 and for PC500, was rather small (note the units: $\mu mol\ l^{-1}$) as compared to the amount that was retained as indicated by the pH-stat method (Fig. 1a), i.e., 0.5–1.4 $mmol\ l^{-1}$ (see column "first cycle" in Table 2). These results strongly suggest that the apparently complete photocatalytic degradation as depicted by the chromatographic

Table 2 Oxalic acid concentration measured by chromatography (HPIC) or by the pH-stat technique upon withdrawal of an aliquot of the suspension: after the photocatalytic degradation was carried at pH 3.7 (column pH 3.7), after 12 h equilibration at pH 13.0 right after the photocatalytic degradation has been carried at pH 3.7 (column pH 13.0), after two consecutive cycles (by duplicate), in which 2 mM was the initial concentration, and an amount of oxalic acid was added before starting the second cycle in order to reach 2 mM without taking into account the remaining oxalic acid that had not been degraded

TiO_2	$C_{OA}/\mu mol.l^{-1}$ (chromatography method)		$C_{OA}/mmol\ l^{-1}$ (pH-stat method)	
	pH 3.7	pH 13.0	First cycle pH 3.7	Second cycle pH 3.7
P25	0.72	1.13	0.8	0
			0.5	0
PC500	0.44	1.48	1.4	1.0
			1.0	1.0

method was not real (Fig. 1b) and that a considerable amount of OA remained in the system, "hidden" inside the agglomerates functioning like capsules that cannot be broken.

For the case of P25, Table 2 shows that after a longer period of irradiation, i.e., after a second photocatalytic cycle, when an additional amount of OA equal to the initial one was added, the total photocatalytic degradation of OA can be achieved. Moreover, not only the retained OA concentration, i.e., 0.8 or 0.5 mmol l^{-1} measured in two independent experiments (duplicate), is completely mineralized, but also the entire newly added concentration, 2 mmol l^{-1}, is photocatalytically degraded without any OA retention in the system. On the contrary, in the case of PC500, the retained amount of OA within the agglomerates remained rather the same during the second experimental cycle. These results suggest that stability of the agglomerates in these systems appears to be related to the TiO_2 particle size.

After two consecutive cycles, the agglomerates of P25 are able to loose their structure in a way that the encapsulated OA becomes available for photocatalytic degradation. In this sense, the agglomerates of P25, as compared to those of PC500, cannot be well stabilized by adsorbed multilayers of OA molecules. In the case of PC500, a monolayer of OA molecules suffices to form strong bonds to more than one TiO_2 particle.

Since no chemical changes, i.e., pH or ionic strength, were made, but only irradiation was provided to the system, a plausible explanation for the rupture of the agglomerates could be given by the deaggregation mechanism (Mendive et al. 2011) taking place at the same time the photocatalytic reaction proceeds. In brief, the deaggregation mechanism upon UV irradiation assumes that the thermal energy liberated non-adiabatically upon recombination of the electron–hole pairs may break the hydrogen bonds between the TiO_2 particles that form the agglomerates. Since the photonic efficiency for TiO_2 P25 in the present system is 4–7 % (Ivanova et al. 2013), it can be readily calculated that 93–96 % of the initially formed electron–hole pairs recombine. Hence, the energy liberated in this reaction is more than sufficient to break the rather weak bonds between TiO_2 particles, thus promoting deaggregation (see Fig. 3). If the particles are large, already a few deaggregation steps may lead to the destabilization of the whole agglomerate. In this situation, the content will be exposed to the solution and to the incoming light accessible to photocatalytic degradation. On the contrary, agglomerates of small TiO_2 particles under the same conditions will hardly allow the exposition of their oxalic acid content as their respective degree of deaggregation needs to be much higher to produce the same effect (Fig. 3).

The remarkably good performance of P25 as a photocatalyst is a rather complex property, i.e., it is likely the result of the combination of several mechanisms that enhance its capacity for degrading the target pollutants. Therefore, the deaggregation mechanism operating on systems that have the capacity of encapsulating molecules, as in the case of oxalic acid in aqueous suspensions of P25, could be responsible for, at least, some part of the remarkably good performance of this photocatalyst.

Conclusions

The simultaneous bimodal study of the photocatalytic oxalic acid degradation by aqueous TiO_2 suspensions revealed the incompleteness of this reaction. While measurements of the oxalic acid concentration in the bulk liquid phase indicated completed photocatalytic degradation, in situ pH-stat measurements allowed the quantification of the amount of oxalic acid remaining

within the system in areas where light could apparently not access. An explanation for this phenomenon is that these molecules are located inside the TiO_2 agglomerates adsorbed at the aggregated particles. In other words, they may be regarded as encapsulated and thus protected from photocatalytic degradation. When the particles are small (PC500, S230) the available surface area inside these agglomerates is high and the oxalic acid distributes homogenously enhancing the strength with which the particles are "glued" together, i.e., increasing the stability of the agglomerate. On the contrary, bigger particle agglomerates (P25, PC50) could not be stabilized so effectively by oxalic acid because they host adsorbed multilayers that also may function as chains between particles. Only the latter situation finally allows the complete photocatalytic degradation provided that the deaggregation mechanism operates breaking agglomerates. In this case, the encapsulated oxalic acid is exposed to the solution and, consequently, to the action of light for its photocatalytic degradation. Because this property of encapsulating pollutant molecules by small surface area photocatalytic systems is a reversible phenomenon, Aeroxide TiO_2 P25 appears to be more convenient and advantageous as compared to the use of large surface area photocatalysts from the viewpoint of technological applications.

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