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Modification of Titanium Dioxide with Platinum Ions and Clusters: Application in Photocatalysis

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TiO₂ (commercial-P25 and synthesized by sol–gel method) was surface modified with platinum ions or [Pt₃(CO)₆]_n^{2−} clusters to improve its photocatalytic activity. The physical properties of the synthesized photocatalysts were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD), and Brunauer, Emmett and Teller adsorption (BET) methods. To characterize the absorption ability of visible light, the diffusion reflectance spectra (DRS) were recorded. The charge-carrier lifetimes in TiO₂ after UV illumination were determined by microwave absorption experiments using the time-resolved microwave conductivity (TRMC) method. The photocatalyst activity was examined by degradation of exemplary aqueous phase pollutants, such as Rhodamine B and phenol. The impact of the adsorbates on the photocatalytic activity depends strongly on the titania precursor (commercial or synthesized), the irradiation wavelength (UV or visible), and the model compound (dye or phenol). The results show that it is possible to enhance the P25 photocatalytic activity under UV–visible light by doping it with Pt clusters. Also, P25 doping with Pt(II) or Pt clusters results in enhancement of the activity under visible light. Pt(IV)/TiO₂ synthesized by sol–gel method exhibits better photoactivity under UV–visible and visible light compared to the unmodified titania. In all mentioned systems, a positive effect of modification with platinum clusters and, in particular, an important enhancement in photocatalytic activity under visible light were obtained. These results are explained by enhancement in visible light absorption and inhibition of charge-carrier recombination.

1. Introduction

Photodegradation of various pollutants by photocatalysis, using wide band gap semiconductors, has been widely studied.^{1–9} Among them, titania, TiO₂, is known as a relatively inexpensive semiconductor exhibiting substantial photocatalytic activity, stability in aqueous solution, and nontoxicity.¹⁰ However, titania usage has a few shortcomings; e.g., TiO₂ absorbs only 2–3% of the solar light impinging on the Earth's surface as it can be excited only under UV irradiation with wavelengths shorter than 400 nm. Moreover, as in most semiconductors, a high rate of recombination between electrons and holes results in low quantum efficiency. In order to enhance the photocatalytic activity, modifications of crystalline anatase or rutile are, in general, involved.¹¹ Metallization of TiO₂ surface with noble metals such as Pt, Ag, and Au has been investigated from the early times of photocatalysis to increase the photocatalytic activity.¹² Different studies have shown that metal ion or metal doped semiconductor composites exhibit shifts in the Fermi level to more negative potentials. It must be noticed that one important factor that can influence the electronic properties of the TiO₂–metal composite is the size of the metal nanoparticles and the shift in the Fermi level is size-dependent.¹³ This shift enhances the efficiency in the interfacial charge transfer process and

improves the energetics of the composite system.^{14–16,24,35} In a photocatalytic process, the noble metal has the mediating role in storing and shuttling photogenerated electrons from the semiconductor to an acceptor.^{13,15}

Improving the activity can also be obtained by sensitizing titania for visible-light activity by doping with transition metal ions.¹⁷ Such an approach creates intra-band states close to the conduction or valence band edges which induce visible-light absorption at sub-band-gap energies.¹⁸ Films and powders of TiO_{2–x}N_x have also revealed an improvement over pure TiO₂ under visible light (wavelength <500 nm) in optical absorption and in photocatalytic activity.^{19,20} Similarly, doping with S and C have also resulted in better performance under visible light.^{21,22} However, the obtained photocatalytic activities under UV light were not improved by such doping.

Previous works on silver halides have shown that doping with [Pt₃(CO)₆]_n^{2−} (*n* = 3–10) clusters (called Chini clusters)²³ could enhance the photoconversion yield by inhibition of the electron–hole recombination.²⁴ In order to improve the photocatalytic efficiency by enhancing the charge separation^{25,26} and to sensitize titania for visible-light activity, we have modified titania with platinum ions (Pt(II) or Pt(IV)) or clusters ([Pt₃(CO)₆]_n^{2−}).

2. Experimental Section

The titania P25 (a mixture of about 75% anatase and 25% rutile) from Degussa was used as one of the starting materials. Titanium isopropoxide, ethanol, and phenol were purchased

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from Aldrich, H₂PtCl₆ and K₂PtCl₄ were purchased from Johnson Matthey, and Rhodamine B was purchased from Fluka.

The experimental procedure involved two steps: photocatalyst preparation and subsequent model wastewater degradation. In the photocatalyst preparation step, commercial photocatalyst (P25 with a specific surface area of 50 m² g⁻¹) or TiO₂ (in anatase form) synthesized by sol–gel hydrolysis precipitation of titanium isopropoxide (Ti(OCH(CH₃)₂)₄) followed by thermal treatment (24 h at 80 °C) and postcalcination (2 h at 450 °C)²⁷ was modified with noble metals by direct surface adsorption of Pt(IV) (PtCl₆²⁻) or Pt(II) (PtCl₄²⁻) in aqueous or mixed alcohol–water solutions (metal/TiO₂ = 1–2% w/w). TiO₂ was synthesized by a sol–gel method, according to the procedure described by Zhang.²⁷ It has been shown by X-ray diffraction (XRD) that the obtained titania samples generated through the thermal treatment were mostly anatase with a minor brookite component, and TiO₂ samples crystallized by calcination had a pure anatase phase.²⁷ Pt salts or clusters were put into contact with TiO₂ under stirring for several hours. Pt(IV) was introduced from aqueous solution (10⁻³ M) and stirred in the dark for 3 h. Pt(II) was dissolved (10⁻³ M) in equivolume ethanol–water solution and used as a source of Pt(II) surface adsorbent as well as a platinum metal cluster precursor. Pt(II) surface adsorption was carried out during stirring in the dark. Platinum clusters [Pt₃(CO)₆]_n²⁻ were used as surface adsorbents. These clusters were synthesized by radiolytic reduction (using a ⁶⁰Co γ-source of 3000 Ci, dose of 800 grays (Gy)) of Pt(II) in water/2-propanol solutions (10⁻³ M) under 1 atm of CO.^{28–30} The hydrated electrons and the reducing radicals (CH₃)₂C•OH produced during the radiolysis of the solvent are used to reduce the metal ions. Under CO atmosphere, the reduction of platinum salts leads to formation of [Pt₃(CO)₆]_n²⁻ (*n* = 2–10), with the nuclearity *n* being fixed by the dose.³⁰ The modified TiO₂ photocatalysts were separated by centrifugation and dried at 60 °C.

Titania was also doped inside during the synthesis with platinum salts and clusters. Platinum dopants dissolved in aqueous or alcoholic phases were introduced drop by drop during the titanium isopropoxide hydrolysis. To obtain well-crystallized titania in anatase form, all samples were calcinated after thermal treatment (24 h at 80 °C) during 2 h in oxygen atmosphere (450 °C).

The modified TiO₂ samples were examined by transmission electron microscopy (TEM). The morphology and structure analysis were determined with a JEOL 2000 FX microscope. XRD patterns were obtained using an X-ray diffractometer (Philips, X'Pert-MRD) with Cu target Kα radiation (λ = 1.5405 Å). The diffusion reflectance spectra of the modified TiO₂ samples were obtained using a Cary 5E spectrophotometer equipped with a Cary 4/5 diffuse reflection sphere. The baseline was recorded using a poly(tetrafluoroethylene) reference.

The specific surface of modified powders was determined by the BET method using nitrogen physisorption at 77 K (COULTER SA 3100): the surface area was around 50 m²/g for P25-based photocatalysts and between 100 and 120 m²/g for modified TiO₂ synthesized by the sol–gel method (Table 2).

The charge-carrier lifetimes in TiO₂ after UV illumination were determined by microwave absorption experiments using the time-resolved microwave conductivity method (TRMC), carried out at the Hahn-Meitner-Institut, Berlin.^{31–33} The incident microwaves were generated by a Gunn diode of the K_a band (28–38 GHz). The experiments were performed at 36.8 GHz. The pulsed light source was a Nd:YAG laser providing IR radiation at λ = 1064 nm. The full width at half-

TABLE 1: Coloration of Samples after Modification with Platinum

dopants	bare photocatalyst		
	commercial TiO ₂ (P25)	synthesized TiO ₂	
	modification location		
	surface	surface	during synthesis
none	white	white	white
Pt clusters	gray	gray	creamy
Pt(II)	creamy	creamy	light gray
Pt(IV)	creamy	creamy	creamy gray

maximum of one pulse was 10 ns; the repetition frequency of the pulses was 10 Hz. UV light (355 nm) was obtained by tripling the IR radiation. The light energy density received by the sample was 1.3 mJ·cm⁻².

The principle of TRMC and the experimental setup have been widely described in a previous paper.³¹ This technique is based on the measurement of the change of the microwave power reflected by a sample, Δ*P*(*t*), induced by its laser pulsed illumination. The relative difference Δ*P*(*t*)/*P* can be correlated, for small perturbations of conductivity, to the difference of conductivity Δσ(*t*) considering the following equation:³²

$$\frac{\Delta P(t)}{P} = A \Delta \sigma(t) = A e \sum_i \Delta n_i(t) \mu_i$$

where Δ*n_i*(*t*) is the number of excess charge carriers *i* at time *t* and μ_{*i*} is their mobility. The sensitivity factor *A* is independent of time, but depends on the microwave frequency and on the conductivity of the sample.

Considering that the trapped species have a small mobility which can be neglected, Δ*n_i* is reduced to mobile electrons in the conduction band and holes in the valence band. In the specific case of TiO₂, the TRMC signal can be attributed to electrons because their mobility is much larger than that of the holes.³⁴

The model wastewater containing Rhodamine B (RB) or phenol as pollutants was photodegraded in quartz cells under oxygen flow. Powdered photocatalyst in the amount of 0.5 or 1 g/L ((0.62 or 1.25) × 10⁻² M TiO₂) was suspended in aqueous solution of 10⁻⁴ M RB or 2 × 10⁻⁴ M phenol. Samples of 1 g/L of 1 or 2% w/w Pt on TiO₂ correspond to 5 × 10⁻⁵ or 10⁻⁴ M Pt vs 1.25 × 10⁻² M TiO₂, that is, 0.4 or 0.8 mol %. The suspension was magnetically stirred and irradiated for 20 min (under UV–visible light) or 120 min (under visible light >450 nm) with an Oriel 300 W xenon lamp. During UV or visible experiments, 0.5 mL samples were taken for analysis from the cell at 5 or 30 min intervals, respectively.

The RB concentration was determined by spectrophotometric method (at 550 nm) using an HP 8453 spectrophotometer, whereas phenol degradation was measured via high performance liquid chromatography (HPLC) (Beckman LC-126) equipped with a diode array detector (Beckman LC-168). The reaction products were separated on a reverse-phase column (C18), 5 μm, 100 Å (4.6 × 250 mm), using a mixture H₂O/CH₃CN = 70/30 (v/v) as eluent, at a flow rate of 1 mL/min. The product quantification was done with a detection at 214 nm.

3. Results and Discussion

All modified photocatalysts were gray or colored (Table 1). Surface modification with Pt clusters caused the gray color of the sample, which can be due to the presence of Pt⁰ or PtO₂.³⁵ Surface modification with Pt salts caused a yellow-creamy

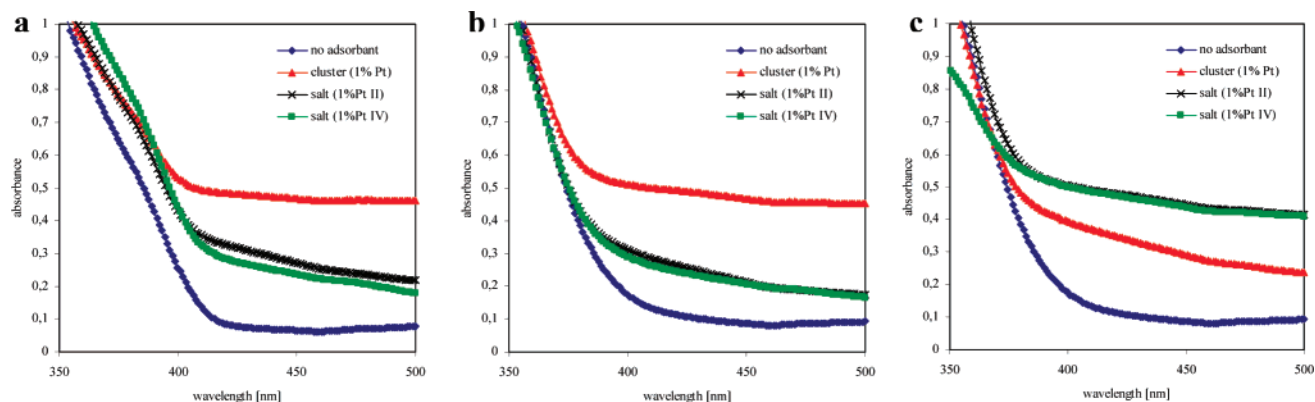


Figure 1. Diffuse reflectance spectra of pure or modified titania (modified and nonmodified TiO_2 with Pt salt (II), PtCl_4^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $[\text{Pt}_3(\text{CO})_6]^{2-}$): (a) P25; (b) surface-modified TiO_2 synthesized by sol–gel technique; (c) doped TiO_2 during sol–gel technique.

TABLE 2: Surface Area and Electronic Properties Measured by TRMC of Titania Powders

sample	I_{max} (mV)	$\tau_{1/2}$ (ns)	$\tau_{1/4}$ (ns)	$\tau_{1/8}$ (ns)	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)
P25, no adsorbate	69.8	60	670	15000	50
P25 clusters (1% Pt)	53.9	70	1500	17000	57
P25 salt (1% Pt(II))	62.4	40	160	1500	53
P25 salt (1% Pt(IV))	43.7	120	850	6100	52
TiO_2 , no adsorbate	21.5	30	200	1300	110
TiO_2 clusters (1% Pt)	21.4	25	100	2300	113
TiO_2 salt (1% Pt(II))	20.1	30	190	900	120
TiO_2 salt (1% Pt(IV))	20.0	20	80	500	123

coloration. Similar colored samples were obtained by Burgeth and Kisch after titania modification with Pt(IV).³⁵ Differences after modification during synthesis are surely caused by postcalcination processes. During calcination Pt^0 is oxidized to yellow Pt(II) and Pt(IV), whereas PtO_2 is generated from Pt salts during calcination under oxygen atmosphere.

Diffuse reflectance spectra of modified and nonmodified TiO_2 are shown in Figure 1. The spectra of the loaded samples show a slight shift in the band gap transition to longer wavelengths for both kinds of surface-modified photocatalysts (P25 and synthesized TiO_2). These results are different from those obtained by Macyk et al., where only modification of pure anatase photocatalyst led to a red shift of absorption, while the absorption spectrum of modified P25 (with 3% PtCl_4) showed a blue shift.³⁶ These differences can be due to the different methods used for the photocatalyst modification: in the case of Macyk's experiments the photocatalysts were prepared by grinding both components, instead of adsorption of metal from solution.

The red shift in the band gap transition revealed by diffuse reflectance spectra can be explained by the introduction of energy levels of the Pt ions or clusters into the band gap of TiO_2 . The presence of energy levels below the conduction band and above the valence band edge can influence the photoreactivity since the dopants can act as electron (or hole) scavengers enhancing the photoconversion yield.

The absorbance in the visible region is always higher than that of pure TiO_2 . The absorption in this spectral region is the most important in the case of Pt cluster/ TiO_2 , due to high absorption of platinum Chini clusters in the visible region.³⁰ $[\text{Pt}_3(\text{CO})_6]^{2-}$ is green and presents two specific narrow absorption bands at 430 and 802 nm. $[\text{Pt}_3(\text{CO})_6]^{2-}$ is sensitive to oxidation, and is probably partly oxidized to higher nuclearity clusters $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n > 6$) during the deposition on TiO_2 .³⁰ Kim et al. obtained similar absorption spectra of Pt^0/TiO_2 with a significant background in the visible region and Pt(IV)/ TiO_2 with much weaker intensity in the visible region.³⁷ The absorption properties of platinized titanium dioxide depends on

the optical properties of the metal, the matrix, and the volume fraction of the metal in the composite mixture. Driessen et al. showed that the absorption of Pt/ TiO_2 complex in the visible region predicted by Maxwell–Garnett theory increased as a function of platinum volume fraction, and for 2% Pt was nearly half as much as the intensity at the maximum (near 320 nm) due to the band gap absorption.³⁸ Our results are very similar, and for 1% Pt addition, the absorption of Pt^0/TiO_2 in the visible region reached more than 30% of the intensity at the maximum.

The photocatalytic activities of surface-modified photocatalysts are described below. The data of inside-modified photocatalysts are not presented here due to a lower photocatalytic activity.^{39,40}

3.1. Photocatalytic Activity of Surface-Modified Degussa P25 Photocatalyst. The photocatalytic activities of pure and modified P25 (with Pt(II), Pt(IV), or Pt clusters) have been compared. Curves in Figure 2a and 2b illustrate the photodegradation of RB using UV–visible and visible light, respectively, in the presence of the four photocatalysts. Figure 3 shows the photodegradation of phenol on modified and pure P25 under UV–visible and visible light. Doping with Pt(IV) does not improve the photocatalytic activity of P25 under UV–visible light for RB degradation. The same result under UV–visible light was also obtained by Kisch et al.^{18,35,41} According to the literature, Degussa P25 catalytic properties could not also be improved by Pt(IV) doping.³⁵

The yellow Pt(II)/P25 photocatalyst is more active in the visible but less in the UV, as compared with P25. Izawa et al. have shown that the presence of transition metal cations, such as $(\text{Pt}(\text{NH}_3)_2)^{2+}$, can act as a surface recombination center, leading to low photocurrent during photoelectrochemical oxidation of methanol.⁴² Our results indicate that Pt(II) adsorbed on P25 serves as a visible light absorbing sensitizer.

Doping with platinum clusters $[\text{Pt}_3(\text{CO})_6]^{2-}$ enhances the photocatalytic activity under UV–visible and visible light. It has been shown that loading the TiO_2 surface with Pt nanoparticles creates a sink for the electrons, which facilitates the separation of photogenerated electron–hole pairs.⁴³ The en-

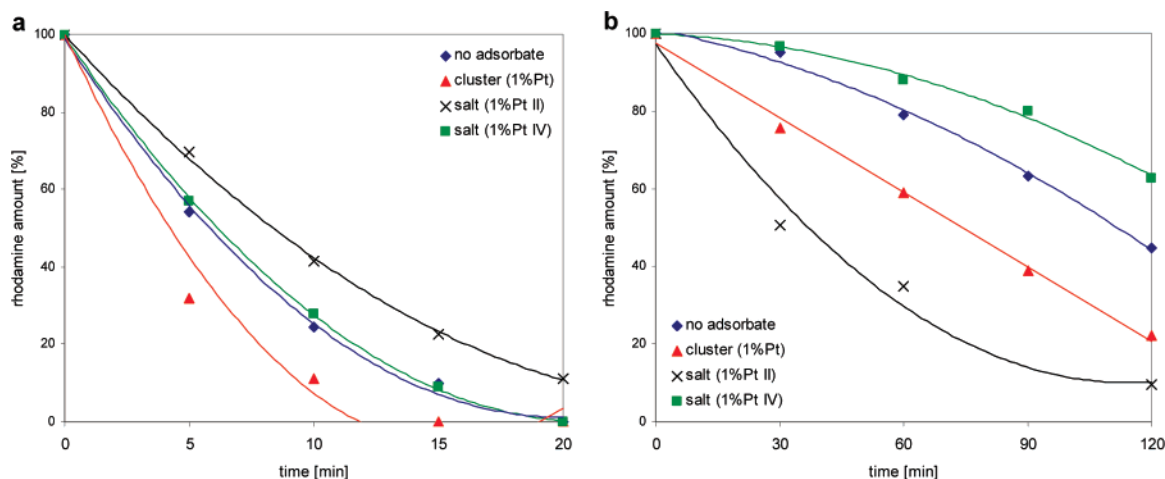


Figure 2. Degradation of RB (10^{-4} M RB initial concentration) with pure or modified P25 titania (1 g/L photocatalyst) (surface modified and nonmodified with Pt salt (II), PtCl_4^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $[\text{Pt}_3(\text{CO})_6]_6^{2-}$): (a) under UV/vis light; (b) under visible light >450 nm. The solid lines are just a guide for the eyes.

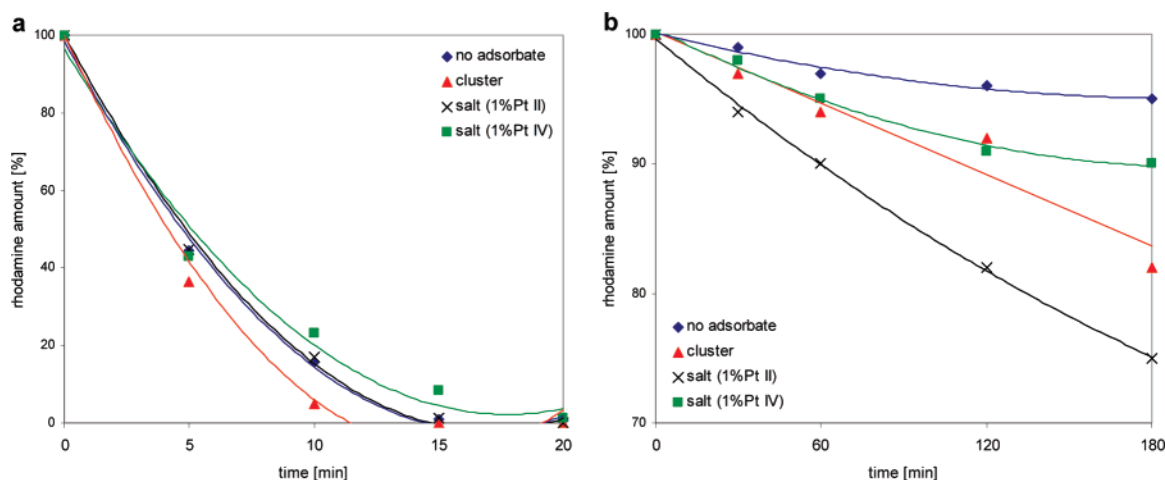


Figure 3. Degradation of phenol (2×10^{-4} M phenol initial concentration) with pure or modified P25 titania (1 g/L photocatalyst) (surface modified and nonmodified with Pt salt (II), PtCl_4^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $[\text{Pt}_3(\text{CO})_6]_6^{2-}$): (a) under UV/vis light; (b) under visible light >450 nm.

hancement of titania photocatalytic properties after Pt⁰ deposition was previously shown by Ohtani et al. in aqueous alcohols and amino acid solution and by Hwang et al. in photooxidation of CO.^{44,45} Platinization decreases the recombination probability of the holes with their counterpart (e^-_{CB} or e^-_{VB}) and increases the fraction of photoholes undergoing the oxidizing interfacial charge transfer reaction.^{43,46–48} Previous investigations have shown that $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 3–10$) clusters could act as weak hole scavengers and also as temporary electron scavengers³⁰ in other semiconductors such as silver halides.²⁴ Under visible light, Pt clusters act as sensitizers. Sensitization by electron transfer (ET) from an excited donor, such as a dye or a metal complex, is well-known, and in the case of Rhodamine, the pollutant itself acts as a sensitizer and visible light detoxification becomes feasible.

After P25 modification with 1wt % Pt (metal deposition), Tahiri et al. obtained a 2.5 times lower catalytic activity in the mineralization of chlorobenzoic isomers.⁴⁹ This activity decrease is explained by generation of recombination centers, with negatively charged platinum becoming attractive for photoinduced positively holes. Emelio et al.⁵⁰ also observed a decrease of the activity of Pt-modified P25 while the activity of other pure anatase commercial compounds such as Millennium PC50 increased with Pt modification.

Characteristic differences in the mechanism of RB degradation during UV–visible and visible irradiation could be observed by absorption spectrophotometry (Figure 4). For visible irradiation, the absorption maximum is shifted from 558 to 498 nm with irradiation time. It is known that the N-deethylation of RB causes the blue shift in the maximum absorption of the dye.^{51,52} The N-deethylation products of RB correspond to an optical absorption maximum at 498 nm. Similar observation has been noticed for another dye—methylene blue, where generation of N-demethylation products shifted the absorption maximum from 664 to 610 nm.⁵³ For UV degradation, the N-deethylation is not observed, while much faster degradation proceeds with additional decomposition of the aromatic ring ($\lambda = 260$ nm).

Enrichment of platinum content from 1% to 2% (0.4–0.8 atom %) has not improved much the photocatalytic efficiency of the photocatalyst. During the oxidation of formaldehyde, Zhang et al. found that the increase of platinum amount from 1 to 2% did not enhance the reaction rate (the optimal metal loading was thus 1%).⁵⁴ Similarly, Kim et al. reported that the optimum concentration of Pt ions for DCA and 4-CP degradation was 0.5 and 0.5–2 atom %, respectively.³⁷ In this regard, all the following experiments were carried out at 1% platinum loading.

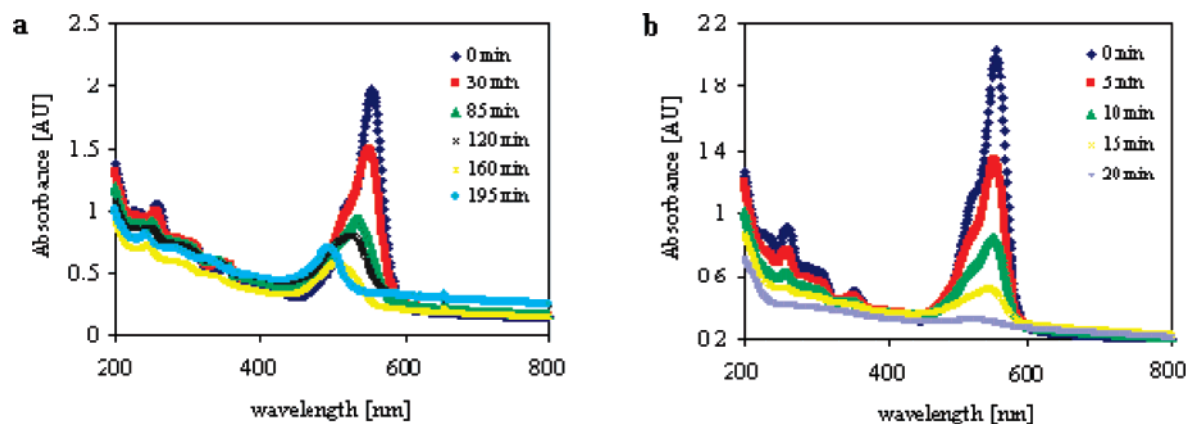


Figure 4. Examples of data of RB degradation with time under visible (a) and UV (b) irradiation (1 g/L photocatalyst). Modified titania with Pt clusters, synthesized by sol–gel method: (a) modified during synthesis; (b) surface modified after synthesis.

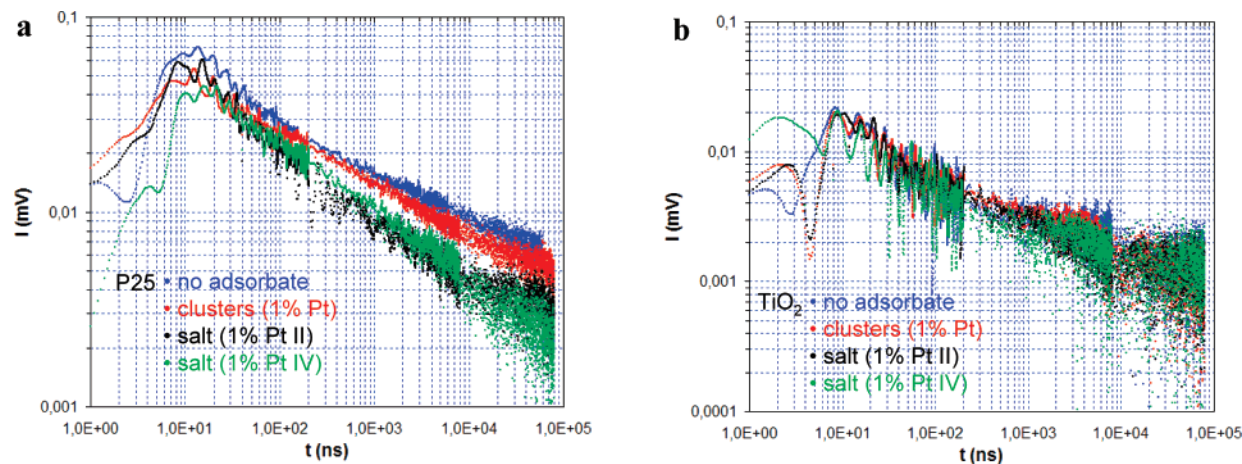


Figure 5. TRMC signals after excitation at 355 nm of pure or modified titania with Pt salt (II), PtCl_4^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $[\text{Pt}_3(\text{CO})_6]^{2-}$: (a) P25; (b) TiO_2 synthesized by sol–gel technique.

In the case of nonadsorbed pollutants such as phenol, and for activities in the UV range, the mobile charge carriers seem to be directly involved in the chemical reaction.^{50,55} In this case, TRMC measurements of charge-carrier lifetimes can be a useful tool for better understanding of the photoactivity mechanisms.³¹ TRMC results are gathered for three time ranges (0–250 ns, 0–10 μs , 0–100 μs) and are displayed in a double logarithm plot in Figure 5. The corresponding I_{max} , $\tau_{1/2}$, $\tau_{1/4}$, and $\tau_{1/8}$ values are gathered in Table 2 together with S_{BET} area values.

The parameter I_{max} is the TRMC signal maximum value. I_{max} reflects the number of the excess charge carriers created by the UV pulse. It must be noted that this information is weighted by the influence of charge-carrier decay processes during the excitation, which means that recombination phenomena during the pulse may minimize the I_{max} value. The parameters $\tau_{1/2}$, $\tau_{1/4}$, and $\tau_{1/8}$ are the half-times of signal corresponding to the time necessary to reduce the intensity of the signal respectively to $I_{\text{max}}/2$, $I_{\text{max}}/4$, and $I_{\text{max}}/8$. These three parameters are important because the signal decay is not purely exponential; thus, the general decay shape is characterized by several half-time lives linked to charge-carrier lifetimes.

In previous works,^{50,55} the two linked parts of the photocatalytic mechanism were considered separately, in order to correlate structural, textural, and electronic properties of TiO_2 powders. The first part concerns phenomena related to the interaction of the semiconducting material with photons. The second part concerns the surface catalytic reactivity. For the first part, a high I_{max} value and a slow decay indicate a large amount of created charge carriers having long lifetimes and, thus, reveal

a high crystalline quality. For the second part, the specific surface area is the most relevant structural parameter because photocatalysis is an interfacial reaction: a higher specific surface area induces a higher number of accessible active sites and, consequently, a better reactivity.

In the present case, Pt surface modification does not influence in a significant way the surface area (Table 2) involving the second part of the mechanism; therefore, the photoactivity may be explained by modification of the photon–material interaction involving the first part of the mechanism.

In Emilio's work⁵⁰ the influence of P25 platinization on TRMC signal shows two main points. The signal is lowered (I_{max} value) because Pt acts as a shield and favors fast recombination processes. The signal decay is also accelerated, showing that Pt does not lead to better charge-carrier separation thus explaining the lower activity of the platinized form.

In this work, platinization always lowers the signal but the influence on the decay is variable and can be related to the activity in the case of phenol degradation with UV light. The decay is fully accelerated with Pt(II) and globally accelerated with Pt(IV) as shown by the very low value of $\tau_{1/8}$ (Table 2 and Figure 5a). This explains the lower activity of Pt(II)/P25 and Pt(IV)/P25 (Figure 3a) under UV–visible light. On the other hand, the surface modification by Pt clusters slow the I decay, showing a slower charge-carrier recombination that is beneficial to the photoactivity.

3.2. Photocatalytic Activity of Surface-Modified Synthesized TiO_2 . The sol–gel synthesis has given small and well-crystallized nanoparticles of 5–10 nm (Figure 6a). X-ray

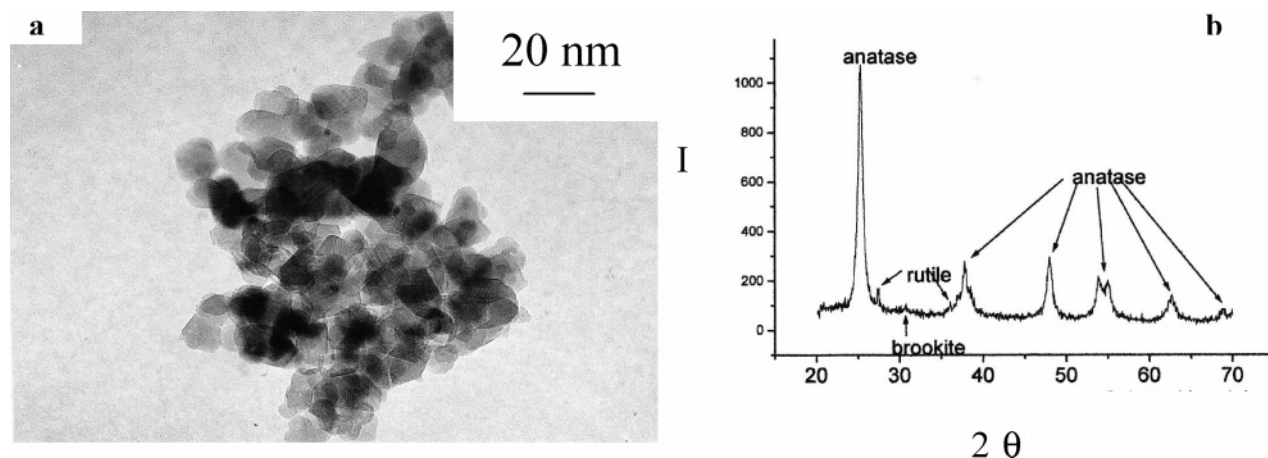


Figure 6. MET picture (a) and X-ray diffraction (b) of TiO₂ synthesized by sol-gel method followed by thermal treatment and calcination.

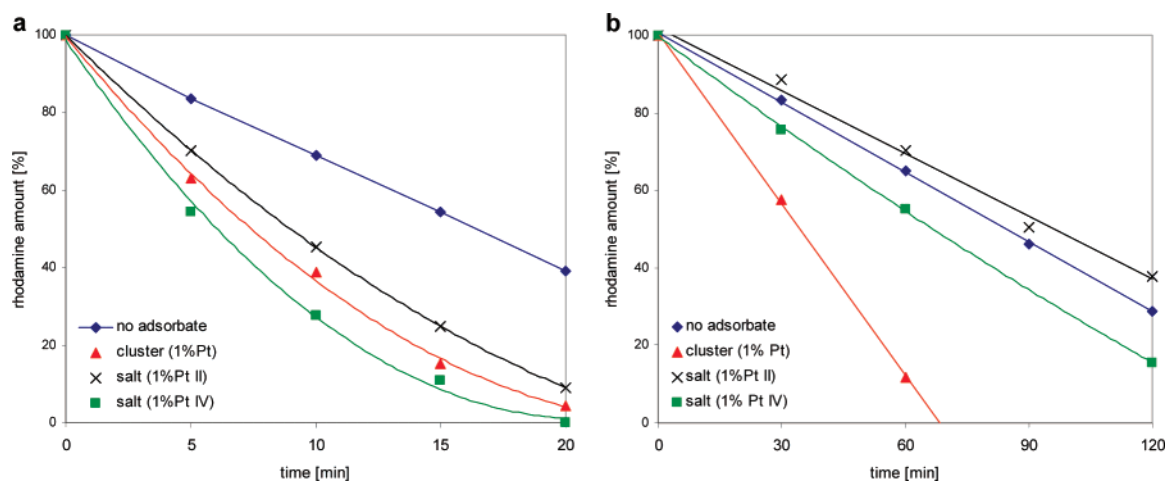


Figure 7. Degradation of RB (10^{-4} M RB initial concentration) with pure or modified titania synthesized by sol-gel method (1 g/L photocatalyst) (surface modified and nonmodified with Pt salt (II), PtCl_6^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $\text{Pt}_3(\text{CO})_6]_6^{2-}$): (a) under UV/vis light; (b) under visible light.

diffraction studies show that the titania is in a major part in the anatase form with a small amount of brookite and rutile (Figure 6b).

The strong and positive influence of surface complexation on the reactivity is more significant for the synthesized TiO₂-based photocatalyst than for P25.

Under UV-visible light, the best results and 100% degradation of RB are achieved for Pt(IV)/TiO₂ after 20 min irradiation (Figure 7a). These results are in agreement with the results reported in the literature showing that surface modification with Pt(IV) of pure anatase can increase markedly the catalytic properties.^{35,57} Burgeth et al. showed that chemisorption of $[\text{PtCl}_6]^{2-}$ onto high surface anatase powder leads to formation of a covalently bound surface complex and this new modified semiconductor is an efficient photocatalyst. We have obtained similar results for phenol destruction (Figure 8a). For an initial concentration of 2×10^{-4} M, 100% degradation of phenol was achieved on Pt(IV) adsorbed photocatalyst after 15 min irradiation.

Surface modification with Pt(IV) induces an increase in photoactivity under both visible and UV-visible light (Figures 7 and 8). However, unmodified synthesized titania is less active than P25. This suggests that e^- - h^+ recombination is more important in synthesized titania. In that case, the inner filter effect should be less pronounced and more electron transfers arise from an additional contribution of the higher excited states of the platinum complex.

In the photodegradation there is a significant difference with visible light between the photocatalysts prepared by surface adsorption of P25 and sol-gel synthesized titania. Modification of synthesized titania leads to higher photocatalytic activity in the visible range than with modified P25. For example, total Rhodamine B degradation is obtained after 70 min of irradiation using Pt clusters, while the highest dye decay by P25 modified with Pt(II) after the same time of irradiation reached only 70%.

Electron-transfer sensitization was previously reported for titania containing up to 3% Pt(IV), Rh(III), or Au(III), either in the bulk or only at the surface.^{17,27,56,57} It has been shown that, in the case of PtCl_6^{2-} , the excited platinum complex first undergoes homolytic metal-chloride bond cleavage to yield a transient Pt(III) complex.¹⁸ Photochemical measurements indicated that the flat-band potential of this n-type semiconductor is shifted (to -0.30 V versus a normal hydrogen electrode, pH 7, compared to -0.53 V measured for pure titania). Therefore, this shift increases the driving force of electron injection from the platinum(III) intermediate and thus should improve the photocatalytic activity.¹⁸ Electron injection into the titania conduction band re-forms Pt(IV). In our case, as already obtained by Burgeth and Kisch,³⁵ such improvement of catalytic activity was achieved only for synthesized TiO₂ and not for P25. The high photocatalytic activity of P25 is often explained by the coexistence of anatase and rutile phases which can make possible an interphase charge transfer and in consequence leads to a partial inhibition of charge-carrier recombination.⁵⁸⁻⁶⁰

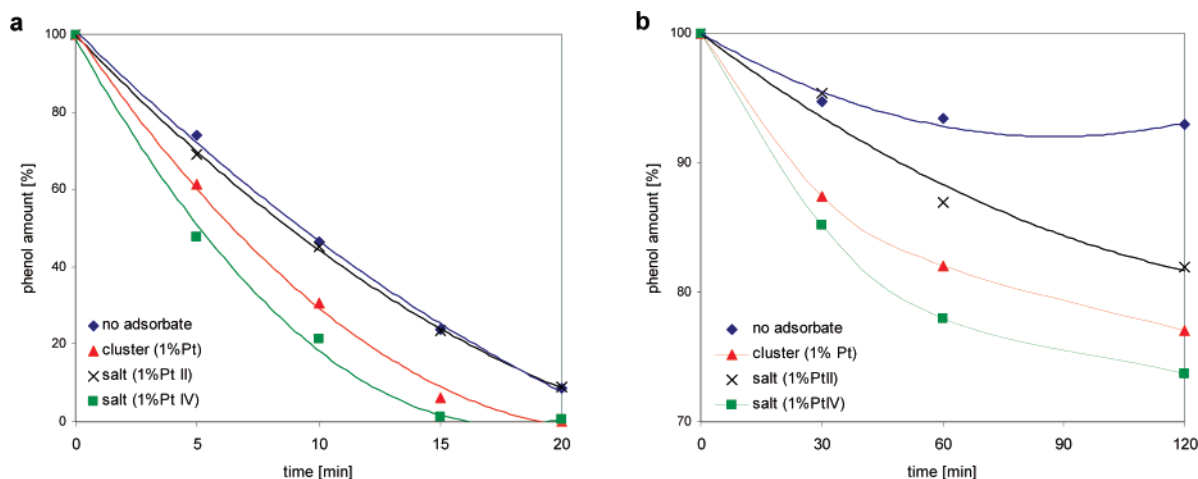


Figure 8. Degradation of phenol (2×10^{-4} M phenol initial concentration) with pure or modified titania (1 g/L photocatalyst) synthesized by sol-gel method (surface modified and nonmodified with Pt salt (II), PtCl_4^{2-} ; Pt salt (IV), PtCl_6^{2-} ; Pt cluster, $\text{Pt}_3(\text{CO})_6]_6^{2-}$): (a) under UV/vis light; (b) under visible light (>450 nm).

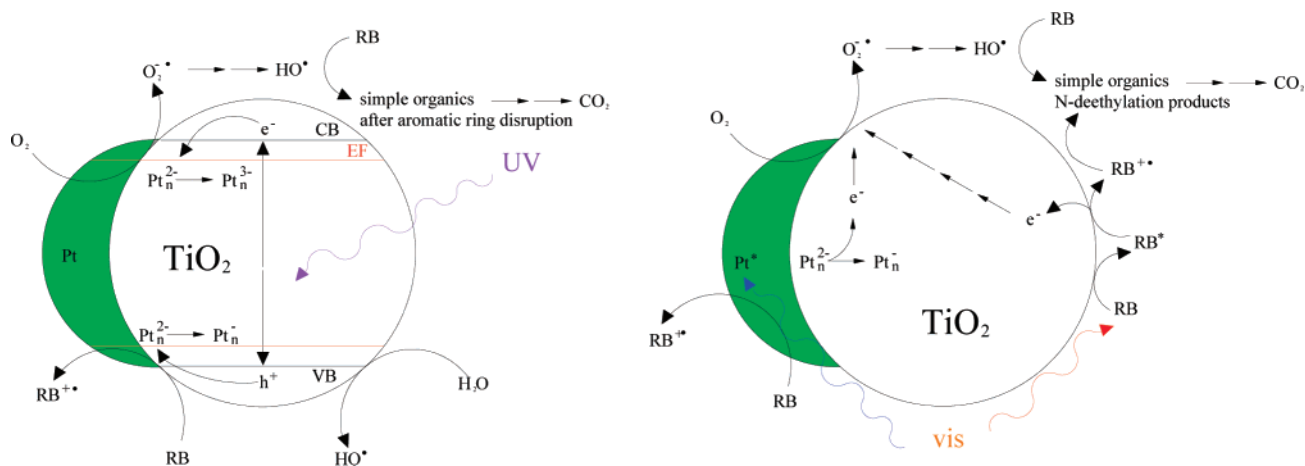


Figure 9. Schematic mechanism of RB degradation under UV (left) and visible (right) irradiation on TiO₂ modified with Pt clusters. EF refers to the Fermi level.

Zhang et al. consider such a high photocatalytic activity of P25 to be also caused by a small amount of Fe^{3+} (0.012%) which can inhibit surface recombination of e^-/h^+ .²⁷ In this regard, modification of P25 often leads to a decrease of the catalytic activity, due to disturbance of natural charge transfer in the bare P25.

In the case of synthesized TiO₂, Figure 5b shows that surface modification with Pt(II) or Pt(IV) has a very weak influence on the TRMC signal. The pure and doped compounds present quite the same signal. Detailed values of Table 2 show a small lowering of the I_{max} values and small differences in decays which cannot be used to understand the good activity of Pt(IV)/TiO₂. These weak influences on signal may not be important enough to be significant for activities. However, Pt clusters slow the I decay, indicating a slower charge-carrier recombination resulting in an enhancement of the photocatalytic activity under UV light. Surface-loaded TiO₂ with a small amount of Pt clusters creates a sink for electrons and/or holes, which facilitates the electron-hole pair separation and increases the fraction of photoholes undergoing the oxidizing interfacial charge transfer reaction.

Note that, in the case of silver halides, an enhancement in the photosensitivity was obtained by doping with platinum clusters.²⁴ A double action of platinum clusters as an irreversible hole scavenger and a reversible electron scavenger was found.³⁰ Probably here also the clusters protect electrons from recombination and can also act as an electron relay.

Doping TiO₂ (sol-gel synthesized) with Pt(IV) or Pt clusters probably induces a shift in the Fermi level to more negative potentials and enhances the efficiency in the interfacial charge transfer process. The visible activity of Pt(IV)/TiO₂ and $\text{Pt}_n^{2-}/\text{TiO}_2$ is ascribed to the role of doped Pt ions or clusters as charge generation centers, which produces free and trapped charges.

In summary, a schematic mechanism of RB degradation under UV and visible light on titanium dioxide modified with Pt clusters is shown in Figure 9. Under UV irradiation there are two main mechanisms for RB oxidation: direct oxidation by photogenerated h^+ and indirect oxidation by generated oxidizing agents, such as $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ and HO^{\bullet} radicals. Titania loading with platinum clusters causes the inhibition of charge-carrier recombination, when both holes and electrons could be trapped by $[\text{Pt}_3(\text{CO})_6]_6^{2-}$ clusters, leading to formation of oxidized and reduced forms, such as $[\text{Pt}_3(\text{CO})_6]_6^-$ and $[\text{Pt}_3(\text{CO})_6]_6^{3-}$ clusters, respectively.^{24,30} Under visible irradiation, RB can be destructed directly by a sensitization mechanism and on the surface of platinum as a result of electron escape, as well as indirectly by photogenerated oxidizing radicals: $\text{O}_2^{\bullet-}$, HO_2^{\bullet} , and HO^{\bullet} . Oxygen not only acts as a major acceptor of conduction band electrons, but also plays an important role in the photochemical N-deethylation process.^{51,61} In the case of organics different from dyes, e.g., for phenol, all the drawn mechanisms, except dye sensitization, are the same and could be shown similarly.

4. Conclusion

The effect of the adsorbates on the photocatalytic activity depends on the origin of titania. The commercial TiO₂ (Degussa P25) surface modified with platinum clusters exhibits the best efficiency in photocatalytic decomposition for RB dye and phenol under UV–visible light. Pt clusters/P25 and Pt(II)/P25 exhibit a visible light activity for both phenol and RB degradation. Surface modification of sol–gel synthesized titania with Pt(IV) and Pt clusters leads to enhancement of the photocatalytic activity under UV–visible and visible light. An important enhancement in photocatalytic activity under visible light is obtained with surface modification of titania with Pt clusters.

Titania surface modification with platinum clusters ([Pt₃(CO)₆]^{2−}) enables the increase of the photocatalytic activity both under UV and visible irradiation. Under UV irradiation platinum acts as a charge scavenger hindering charge recombination. Under visible light irradiation a sensitization mechanism should be considered: dye sensitization and absorption of light by platinum clusters and salts.

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