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Photocatalytic and photoelectrochemical properties of titania–chloroplatinate(IV)

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Dedicated to Professor Dick Stufkens on the occasion of his retirement

Contents

Abstract

Rutile (Ald), anatase (TH), and the mixed anatase/rutile powder (P25) were surface modified by chemisorption of $H_2[PtCl_6]$ from aqueous solution. The resulting materials photocatalyzed the degradation and mineralization of 4-chlorophenol with visible light. Ald adsorbed only traces and was inactive, P25 adsorbed 1.1 wt.% and exhibited medium activity, whereas TH adsorbed 4.0% and was six times more active than P25. In neutral water 4.0%Pt(IV)/TH is stable towards thermal and photochemical desorption of platinate, even in the presence of strongly adsorbing fluoride ions. Contrary to this, complete photodesorption occurred in 0.1 M hydrogen chloride solution. It is postulated that adsorption affords a surface tetrachloroplatinate(IV) complex covalently linked to the titania surface through a [Ti]O–Pt bond. The flatband potential of 4.0%Pt(IV)/TH at pH 7 is determined as -0.28 ± 0.02 V (vs. NHE), which is more anodic by 260 mV as compared with unmodified TH. Solar experiments revealed that 4.0%Pt(IV)/TH is a much better photocatalyst than 1.1%Pt(IV)/P25, P25, and TH. It catalyzed the photodegradation also in diffuse indoor daylight, conditions under which all other tested materials were inactive. Upon UV excitation 4.0%Pt(IV)/TH is even more active than P25.

Keywords: 4-Chlorophenol; Photosensitization; Chloroplatinate(IV); Titanium dioxide; Flatband potential; Photomineralization; Solar detoxification

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1. Introduction

Both in basic and practical aspects of semiconductor photocatalysis, titania is the most commonly employed material [1]. This applies especially for the photodegradation of organic water pollutants. However, a serious problem for technical application is the fact that titania absorbs only 3% of solar light. Therefore, only a very small fraction of the solar energy can be utilized to drive a chemical reaction. Accordingly, many efforts have been made to sensitize titania for visible light induced photocatalytic reactions. Previously we have shown that simple inorganic compounds like $Na_2[PtCl_6]$, $AuCl_3$, and $RhCl_3$ introduced into the bulk of amorphous microporous titania [2–4] by sol–gel methods induce the photomineralization of 4-chlorophenol (4-CP) with visible light. Recently we found that photocatalysts of even better activity can be obtained by simple grinding crystalline titania, preferably anatase, with $PtCl_4$ or $H_2[PtCl_6]$ [5]. The most efficient photocatalysts contained up to 2 wt.% of Pt(IV). At higher surface loading the excess fraction of the complex is desorbed into the aqueous solution. As mechanistic hypothesis it was proposed that the excited platinum complex undergoes homolytic Pt–Cl cleavage affording a Pt(III) intermediate and an adsorbed chlorine atom. Electron injection into the titania conduction band reforms Pt(IV). The trapped conduction band electron reduces oxygen to superoxide and finally hydroxyl radicals as evidenced by scavenging experiments with benzoic acid and tetranitromethane. The adsorbed chlorine atom was assumed to oxidize 4-CP to the corresponding oxyl radical, which is eventually converted to CO_2 and HCl, by analogy with the photomineralization catalyzed by unmodified titania [6]. Adsorbed chlorine atoms were also proposed as intermediates in the photodegradation of trichloroethylene [7]. The surprising stability of these surface-modified materials suggested the platinum complex became chemisorbed during grinding. If so, then chemisorption from solution may offer a much better preparation method. In the following we report on the results of adsorption of $H_2[PtCl_6]$ onto three types of titania powders and on the catalytic activity of the resulting photocatalysts. One of the novel materials was more active than the corresponding material obtained by grinding. The analogous rhodium modified titania samples possess similar properties [8].

2. Results

2.1. Preparation and characterization of photocatalysts

Upon stirring the titania powders in the dark in an aqueous solution of $H_2[PtCl_6]$ different maximum amounts were adsorbed. Whereas 4.0 and 1.1% were taken up by the anatase and anatase/rutile samples TH and P25, respectively, only traces were adsorbed onto the rutile material Ald. In the case of 4.0%Pt(IV)/TH calcination induced a color change from slightly yellow to ochre. In contrast, a gray color developed during calcination of the P25 and Ald based materials. Adsorption from methanolic or ethanolic suspensions did not increase the total amount adsorbed but induced formation of a gray color.

The specific surface areas of unmodified P25 (50 m^2 g^{-1}) and Ald (3 m^2 g^{-1}) were not changed upon modification whereas the area of TH was decreased from 334 to 260 m^2 g^{-1}.

Since it is known that anions like dihydrogen phosphate and fluoride irreversibly adsorb onto titania through replacement of surface hydroxide [9], dark desorption experiments were performed in the presence of various fluoride concentrations. No desorption of $[PtCl_6]^{2-}$ was observable upon stirring 4.0%Pt(IV)/TH for 4 days in the presence of 0.01 M KF, whereas 2% were desorbed as $[PtCl_4]^{2-}$ indicating that partial reduction of Pt(IV) had occurred during calcination. At higher fluoride concentrations of 0.1 and 0.5 M, the amount of desorption increased to 21 and 31%, respectively. Since a suspension of 4.0%Pt(IV)/TH in water has a pH value of 3.4, adsorption of fluoride (0.5 M) was repeated after neutralizing with sodium hydroxide. The amount of desorbed complex decreased to only 2%.

When a photodesorption experiment ($\lambda \geq 455$ nm) with 4.0%Pt(IV)/TH was performed in water, no desorption occurred, whereas in the presence of 0.1 M HCl almost complete desorption of $[PtCl_6]^{2-}$ within 24 h irradiation time was observed; the same observation was made also upon prolonged stirring the acid solution in the dark. The remaining TH sample exhibited negligible photocatalytic activity. Only 1 and 0% were desorbed photochemically or thermally in 0.1 M HNO_3 and 0.1 M NaCl, respectively.

Diffuse reflectance spectra are summarized in Fig. 1a. From a plot of the modified Kubelka–Munk function versus the energy of the exciting light [10] bandgap energies of 3.27 and 3.21 eV were obtained for TH and 4.0%Pt(IV)/TH, respectively.

2.2. Determination of flatband potential

Previous attempts to measure the flatband potential of 2%Pt(IV)/P25, prepared by grinding, failed because under the experimental conditions reduction to elemental platinum took place [11]. Contrary to this, the chemisorbed catalyst 4.0%Pt(IV)/TH was stable enough to allow reproducible measurements. The method employed is based on the cathodic shift of the flatband potential of oxidic semiconductors upon increasing pH value of the suspension [12]. In the presence of a homogeneous pH-independent redox couple like methyl

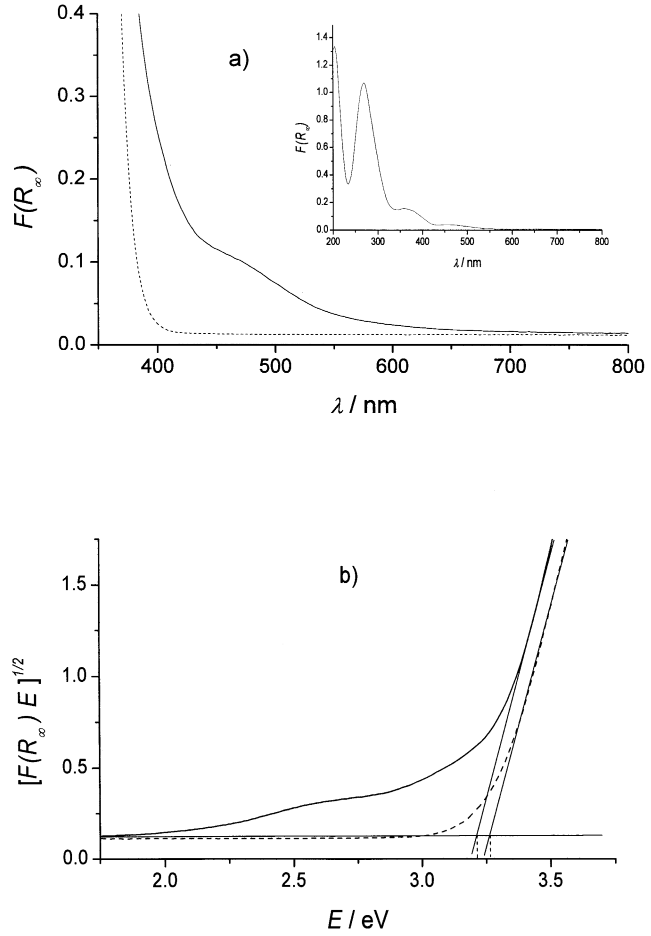


Fig. 1. (a) Diffuse reflectance spectra of TH (- -), 4.0%Pt(IV)/TH (—), and $H_2[PtCl_6] \cdot 6H_2O$ (inset); (b) plot of transformed Kubelka–Munk function vs. energy of light absorbed.

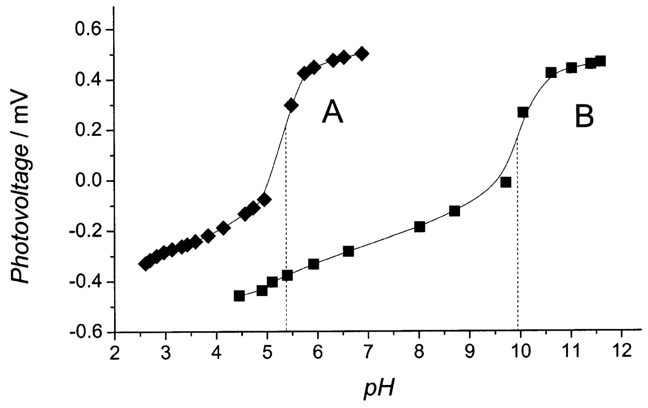


Fig. 2. Variation of photovoltage with pH for the suspension of TH (A) and 4.0%Pt(IV)/TH (B) in the presence of methyl viologen.

viologen a plot of photovoltage versus suspension pH value affords a pH_0-value from which the flatband potential at pH 7 can be calculated. Whereas the value of -0.54 ± 0.02 V (vs. NHE) measured for TH agrees well with anatase literature values, the potential of 4.0%Pt(IV)/TH was found to be shifted to -0.28 ± 0.02 V (Fig. 2).

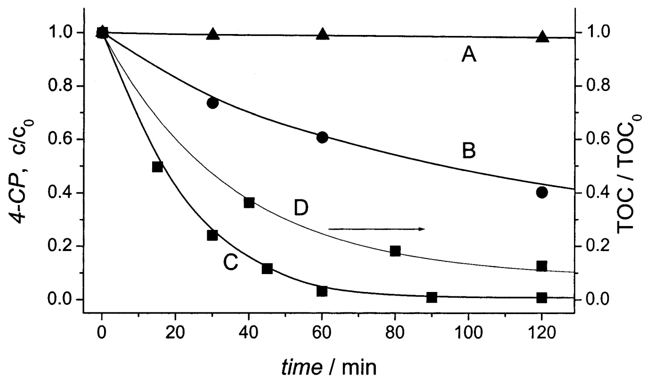


Fig. 3. 4-CP degradation upon visible light irradiation; λ ≥ 455 nm. (A) Pt(IV)/Ald, (B) 1.1%Pt(IV)/P25, (C) 4.0%Pt(IV)/TH, (D) 4-CP mineralization as catalyzed by 4.0%Pt(IV)/TH.

2.3. Photomineralization of 4-CP with visible light

Curves A–C of Fig. 3 illustrate the photodegradation of 4-CP with visible light (λ ≥ 455 nm) in the presence of the three photocatalysts. 4.0%Pt(IV)/TH also induced a fast mineralization as indicated by the TOC/TOC_0 values represented by curve D. Reaction rates increased with increasing catalyst concentration, reaching a constant value at 0.5–0.8 g l^{-1}.

A long-term irradiation was conducted in an immersion lamp apparatus (λ ≥ 400 nm) in the presence of 0.01 M $NaHCO_3$. In this experiment the concentration of 4-CP was re-adjusted to its original value when the c/c_0 values approached zero (Fig. 4).

Experiments at various pH values revealed that the amount of 4-CP reacted after 30 min has a maximum value at pH 5–7 (Fig. 5). Different from this, 4-CP degradation at unmodified P25 is accelerated at pH 8–12 [13]. However, for both catalyst systems the mineralization becomes slower at pH > 7.

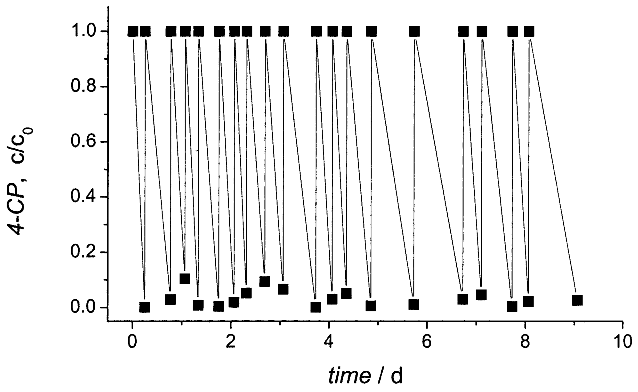


Fig. 4. Long term visible light degradation of 4-CP in the presence of 0.01 M $NaHCO_3$; λ ≥ 400 nm; for details see text.

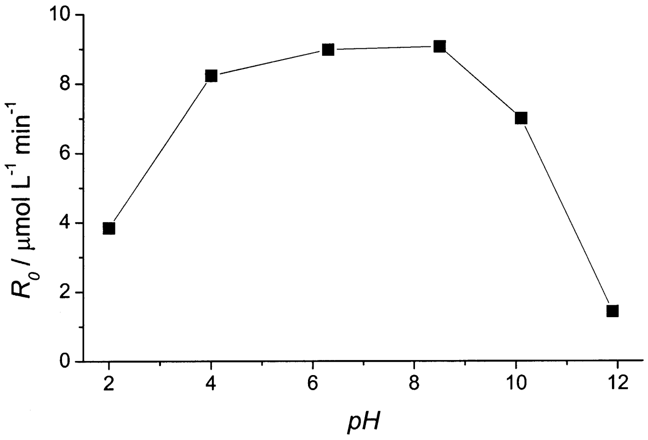


Fig. 5. Dependence of initial degradation rate of 4-CP on pH value of suspension; $\lambda \geq 455$ nm.

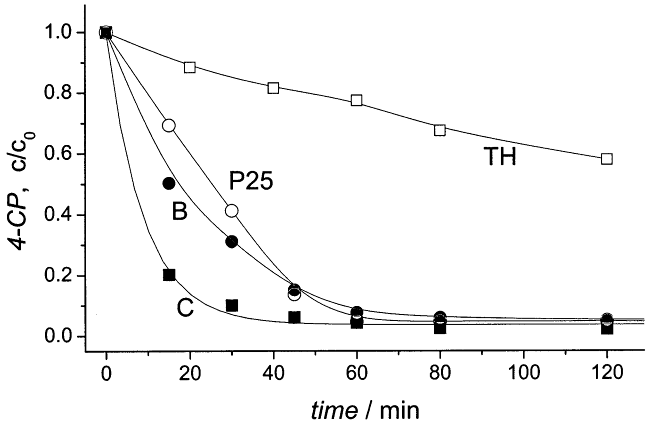


Fig. 6. Sunlight induced degradation of 4-CP in the presence of TH, P25, 1.1%Pt(IV)/P25(B), and 4.0%Pt(IV)/TH(C).

2.4. Solar photodegradation

Since under solar irradiation the previously reported 2%Pt(IV)/P25 photocatalyst, prepared by grinding of the two components, was less active than unmodified P25 [5], the novel materials were investigated also under these reaction conditions (Fig. 6).

3. Discussion

Transmission electron microscopy and X-ray powder diffraction of 4.0%Pt(IV)/TH revealed the presence of about 200 nm large aggregates consisting of 2–4 nm sized anatase crystallites [14].

The diffuse reflectance spectra of 4.0%Pt(IV)/TH and 1.1%Pt(IV)/P25 are a superimposition of TH and P25 with $H_2[PtCl_6]$ as indicated by Fig. 1. They do not differ significantly from the less loaded samples prepared by grinding [5].

Attempts to increase absorbance in the visible region by increasing the amount of adsorbed platinate through the use of more concentrated complex solutions, failed. In this case the excess complex remained quantitatively in solution. The almost four times larger amount of adsorbed chloroplatinate, as compared with 1.1%Pt(IV)/P25, agrees with the ca. four times larger surface area of TH. Calcination in general afforded more photostable materials. The gray color developed during this procedure most likely is due to formation of Pt^0 or PtO_2. Gray powders were less active in 4-CP photodegradation as also observed for amorphous titania modified in the volume with PtO_2 or Pt^0 [3]. Since 4.0%Pt(IV)/TH turned out to be the most active photocatalyst, the following experiments were conducted with this material, unless otherwise noted.

The novel photocatalyst is stable towards desorption of chloroplatinate. In aqueous suspension, either in the dark or under irradiation no dissolved platinum complex was observable by UV spectroscopy. This suggests that the complex is attached to the surface through a TiO–Pt bond. Irreversible adsorption of $[PtCl_6]^{2-}$ onto titania was also postulated from XPS analysis of platinum species remaining on the surface after a commonly employed photoreduction procedure [15].

However, complete photodesorption of $[PtCl_6]^{2-}$ occurred in hydrochloric acid. From this and the amount of chloride released into solution after stirring with NaOH in the dark, it is estimated that the surface complex has the composition $\{[Ti]OPtCl_4L\}^{n-}$, L = H_2O, OH^-, $n = 1, 2$ [16]. Since only 1% was desorbed in nitric acid and 0% in sodium chloride solution, it follows that both the presence of protons and chloride ions favor an efficient photodesorption process. It is known that chloride dark adsorption onto titania is favored at low pH values [9c,9d]. Accordingly, also fluoride at high concentration desorbed only 2% of $[PtCl_6]^{2-}$ at pH 7 as compared with 31% at pH 3.4.

To estimate the fraction of surface OH groups, which have reacted with $H_2[PtCl_6]$, it was assumed that TH contains 5 OH groups per nm^2, the higher limit of values reported for anatase [9a]. About half of them, 8×10^{20} g^{-1}, have basic character [9c,9d] and, therefore, may be susceptible to displace a chloro ligand in the dissolved platinum complex. However, only about 15% react in this way as can be estimated from the comparison with the surface concentration of platinum atoms (1.2×10^{20} g^{-1}) in 4.0%Pt(IV)/TH.

Large differences in the visible light ($\lambda \geq 455$ nm) induced catalytic activity are observed for the three photocatalysts. Whereas the rutile based Pt(IV)/Ald was inactive (Fig. 3curve A), in accord with only the trace amounts of adsorbed chloroplatinate, 1.1.%Pt(IV)/P25, and 4.0%Pt(IV)/TH were active, inducing 50% degradation after 95 and 15 min, respectively (Fig. 3curve C).

4.0%Pt(IV)/TH also initiated a fast mineralization as indicated by curve D in Fig. 3.

Since the mineralization process produces CO_2, H_2O, and HCl, the initial pH value of 3.4 decreased to 3.0 at 120 min irradiation time. These conditions should favor photodesorption (vide supra) and, therefore, a long-term irradiation was conducted in the presence of $NaHCO_3$ to neutralize the acid generated. Whereas in the absence of bicarbonate the activity decreased to 50% of its original value already at the third cycle, it changed only little even after 19 cycles when bicarbonate was present. Whereas in the sixth cycle an irradiation time of 7.5 h was required to obtain 98% degradation, in the 16th cycle only half an hour longer was necessary to reach a value of 95% (Fig. 4).

In the photodegradation with sunlight a significant difference between the photocatalysts prepared by adsorption from solution and by grinding [5] becomes apparent. Contrary to the ground material 2%Pt(IV)/P25 which is less active than P25 [5], the sample 1.1%Pt(IV)/P25, as prepared by adsorption, induces a slightly faster reaction as illustrated in Fig. 6(curves B and P25). The strong and positive influence of surface complexation is more significant for the TH based photocatalyst (curves C and TH Fig. 6).

The superior photocatalytic activity of 4.0%Pt(IV)/TH became even more evident, when the reaction was conducted in diffuse indoor laboratory daylight. Under these conditions both unmodified P25 and TH are inactive whereas the surface modified counterparts exhibit 10% degradation after 420 and 120 min, respectively (Fig. 7).

3.1. Irradiations with UV light

As expected, the higher photocatalytic activity of modified TH materials as compared with P25 was even more pronounced when the solar irradiation was replaced by artificial UV light. 2.0%Pt(IV)/TH induced 90% degradation already after 12 min, the time by which only 50% were degraded by P25 (curves D and P25 Fig. 8). Under these reaction conditions the ground material 2%Pt(IV)/P25 led to only 30% degradation (curve E Fig. 8). In the case of 4.0%Pt(IV)/TH only traces of 4-CP could be detected after this period of time (curves C Fig. 8).

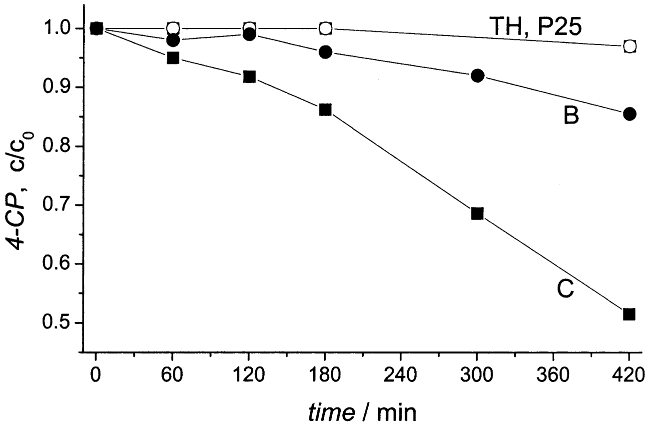


Fig. 7. Diffuse daylight induced degradation of 4-CP in the presence of TH, P25, 1.1%Pt(IV)/P25(B), and 4.0%Pt(IV)/TH(C).

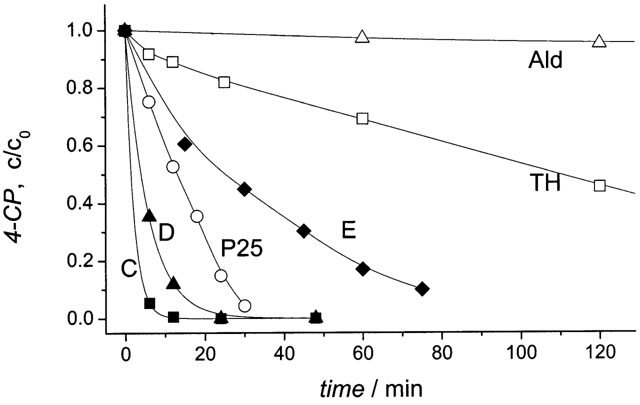
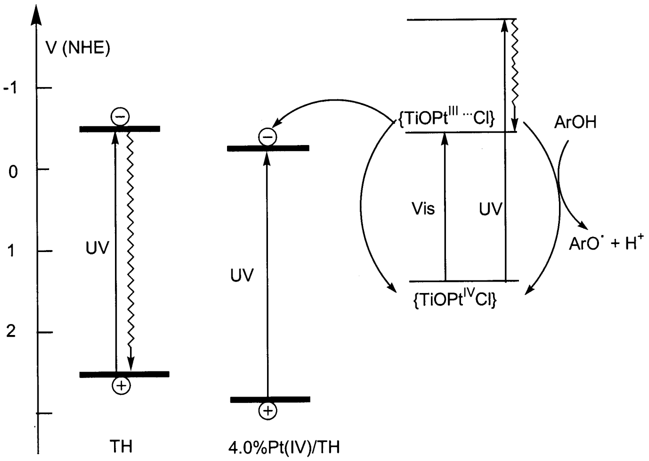


Fig. 8. 4-CP degradation upon UV irradiation; $\lambda \geq 320$ nm. 4.0%Pt(IV)/TH (C), 2.0%Pt(IV)/TH (D), ground sample 2%Pt(IV)/P25 (E).



Scheme 1. Schematic representation of primary photoprocesses upon visible and UV excitation. The bold lines correspond to the potentials of conduction and valence band edges.

Whereas the results obtained for the photodegradation with visible light ($\lambda \geq 455$ nm, Vis in Scheme 1) can be rationalized within the previously proposed mechanism as summarized in Section 1, [5] this is not possible for the observations made during the UV experiments ($\lambda \geq 320$ nm, UV in Scheme 1). As mentioned above, surface modification of P25 by grinding produced a catalyst more active in the visible but less in the UV, as compared with P25. This was rationalized by an 'inner filter effect' of the metal complex, thus diminishing band-to-band excitation of the unmodified P25 surface and, therefore, the steady-state concentration of the reactive e^-/h^+ pairs. The same argument should hold also for the comparison of 2.0%Pt(IV)/TH with TH. However, in this case the modified material is more active also upon UV irradiation. This significant difference can be rationalized by first recalling that unmodified TH is much less active than P25 (curves TH and P25 in Fig. 8), suggesting that electron–hole recombination is much stronger in TH. Accordingly, the inner filter effect should be much less pronounced and may be overruled by a more efficient electron transfer arising from an additional contribution of the higher excited states of the platinum component (Scheme 1).

4. Conclusion

Chemisorption of $[PtCl_6]^{2-}$ onto high surface anatase powder leads to formation of a covalently bound surface complex. This novel hybrid semiconductor is an efficient photocatalyst for the mineralization of 4-CP both with visible and UV light. Activity is even retained in diffuse indoor light.

5. Experimental

5.1. Materials

4-Chlorophenol (4-CP, Fluka) was purified by distillation at low pressure. The fraction boiling at 355 K ($p = 5$ Torr) was collected. Triply distilled water was used during all manipulations. The titania samples P25 (a mixture of about 70% anatase and 30% rutile, Degussa), Ald (rutile, Aldrich), and TH (anatase, Titanhydrat-0, Kerr-McGee) were used as received. Crystal modifications were identified by XRD diffractograms. As an example 4.0%Pt(IV)/TH exhibited peaks at 2θ values of 26, 38 and 48°.

5.2. Instruments

Diffuse reflectance spectra of the solids were recorded on a Shimadzu UV-2401PC UV–vis recording spectrophotometer. Samples were spread onto $BaSO_4$ plates, the background reflectance of $BaSO_4$ was measured before. Reflectance was converted by the instrument software to $F(R_\infty)$ values according to the Kubelka–Munk theory. The bandgap was obtained from a plot of $F(R_\infty)^{1/2}$ versus energy of exciting light assuming that TH and 4.0%Pt(IV)/TH are indirect crystalline semiconductors [10]. XRD diffractograms were recorded on a Philips X'Pert PW 3040/60. An HPLC (KromaSystem 2000 controller, Kontron 320 autosampler with 430A photodiode array detector) was used to determine concentrations of 4-CP. A reverse-phase C-18 column (Kontron, Spherisorb 5 ODS 2) and water–methanol eluent (50/50, v/v) were employed. Absorbencies at 220 nm were measured for the detection of 4-CP. A Shimadzu UV-3101PC UV–vis–NIR scanning spectrophotometer was used for recording the electronic absorption spectra. TOC measurements were made on a Shimadzu Total Carbon Analyzer TOC-500/5050 with NDIR optical system detector. Chloride was measured by ion chromatography (Dionex-120, Ion Pac AS 14 column, conductivity detector, $NaHCO_3/NaCO_3 = 0.001/0.0035$ M as an eluating agent). Specific surface areas have been determined with a Gemini 2370 instrument according to Brunauer–Emmett–Teller theory.

5.2.1. Preparation of photocatalysts

To a suspension 0.5 g of titania in 30 ml of H_2O were added various amounts of $H_2[PtCl_6] \cdot 6H_2O$ (Degussa). After stirring for 24 h, water was removed in vacuo and the residue was dried under vacuum at room temperature (r.t.) for 3 h. The resulting powder was calcined in air for 2 h at 200 °C, washed five times with 30 ml portions of water, dried as described above and again calcined for 2 h at 200 °C. The washings were collected and checked for the presence of $[PtCl_6]^{2-}$ through measuring the absorbance at the maximum of the LMCT band at 262 nm ($\varepsilon = 11.8 \times 10^{-3}$ mol^{-1} dm^3 cm^{-1}). At this wavelength $[PtCl_4]^{2-}$ has only a very small absorption coefficient of 400 mol^{-1} dm^3 m^{-1}. From these measurements the amount of adsorbed platinum complex was obtained and is given throughout this paper as wt.% of Pt(IV).

5.2.2. Measurement of flatband potentials

According to the literature [12], 20 mg of TH or TH/4.0%Pt(IV) and 30 mg of methyl viologen dichloride were suspended in a 100 ml two-necked flask in 50 ml of 0.1 M KNO_3. A platinum flag and Ag/AgCl served as working and reference electrodes and a pH meter for following the proton concentration. HNO_3 (0.1 M) and NaOH were used to adjust the pH value. The suspension was magnetically stirred and flushed with dinitrogen throughout the experiment. In general the starting suspension had pH 3.3. The light source was the same as used in the photodegradation (see below). Stable photovoltages were recorded about 2 min after changing the pH value. The measured pH_0 values were converted to the flatband potential at pH 7 by the equation $U_{fb}(\mathrm{pH}\ 7) = -0.44 + 0.059\ (\mathrm{pH}_0\ -7)$ [12]. Reproducibility of pH_0 was better than 0.3 pH units.

5.2.3. Desorption experiments

4.0%PT(IV)/TH (20 mg) were suspended in 10 ml of water or KF solutions of different concentrations (0.01–0.5 M KF), then sonicated for 15 min followed by stirring in the dark for 4 days. After separation of the catalyst by filtration or centrifugation, 9 ml of the solution was acidified with 1.5 ml of fuming HCl to a final concentration of 2 N HCl. After standing 4 days for thermal equilibration the platinum content was analyzed by UV–vis spectroscopy as described above.

Photodesorption was measured by suspending 14 mg of 4.0%Pt(IV)/TH in different solutions (H_2O, 0.1 M NaCl, 0.1 M HCl, 0.1 M HNO_3) and irradiating as described below for 24 h. After separation of the catalyst the platinum content was analyzed as described above.

5.2.4. Photodegradation procedure and product analysis

The photocatalytic degradation of 4-CP was carried out in a jacketed cylindrical 15 ml quartz cuvette attached to an optical train. Irradiation was performed with an Osram XBO 150 W xenon arc lamp (I_o (400–520 nm) $= 2 \times 10^{-6}$ Einstein s^{-1} cm^{-2}) installed in a light condensing lamp housing (PTI, A1010S) on an optical train. A water cooled cylindrical 15 ml quartz cuvette was mounted at a distance of 30 cm from the lamp. Appropriate cut-off filters were placed in front of the cuvette. The suspension was stirred magnetically.

In the standard experiment, 14 ml of 0.5 g l^{-1} pure or modified TiO_2 suspension containing 2.5×10^{-4} mol l^{-1} of 4-CP was sonicated for 15 min and then transferred to the cuvette. When required, $NaHCO_3$ or NaCl were added. In the pH dependent studies 0.1 M NaOH or HNO_3 were employed for pH adjustment. During an illumination run ca. 1.0 ml of the reaction solution was sampled at given time intervals. The samples were filtered through a Millipore membrane filter (0.22 μm) and then analyzed by UV–vis spectroscopy or HPLC.

5.2.5. Long term irradiation

4.0%Pt(IV)/TH (150 mg) suspended in 150 ml of water containing 2.5×10^{-4} M of 4-CP and 0.1 M of $NaHCO_3$ were sonicated for 15 min prior to irradiation with a tungsten–halogen lamp in an immersion lamp apparatus. A 1 M $NaNO_2$ filter solution was used to cut off wavelengths shorter than 400 nm. Samples of 1.4 ml were withdrawn at intervals of 6–8 h except for some unfavorable night-hours. 4-CP and TOC were determined as described above. After each withdrawal 375 μl of a 0.1 M solution of 4-CP were added, followed by readjustment to the initial reaction volume through the addition of water.

Solar irradiations were carried out simultaneously on a day of August in Erlangen (49.5° N Lat., on the roof of the institute). Ten milligrams of the catalysts were suspended with 20 ml of 4-CP solution in 100 ml Erlenmeyer flasks. After sonication for 15 min in the dark, the suspensions were stirred magnetically in the sunlight. Decrease of 4-CP concentration was measured as described. *Diffuse daylight irradiations* were conducted as described above except that the Erlenmeyer flasks were placed on a laboratory bench, ca. 4 m distant from the window.

Acknowledgements

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