Visible-Light Detoxification and Charge Generation by Transition Metal Chloride Modified Titania

Ling Zang,[a] Wojciech Macyk,[a] Christian Lange,[b] Wilhelm F. Maier,[b] Christina Antonius,[c] Dieter Meissner,[c] and Horst Kisch*[a]

Dedicated to Professor Kurt Schaffner on the occasion of his 68th birthday

Abstract: Amorphous microporous metal oxides of titanium (AMM-Ti) modified with chlorides of Pt^{IV}, Ir^{IV}, Rh^{III}, Au^{III}, Pd^{II}, Co^{II}, and Ni^{II} have been prepared by the sol–gel method and characterized by various surface analytical methods. These hybrid AMM-Ti powders are catalysts for the photodegradation of 4-chlorophenol (4-CP) in aqueous solution when illuminated with visible ($\lambda \geq 400$ or 455 nm) or UV ($\lambda \geq 335$ nm) light. The initial rate depends on the dopant level and is highest at 3.0% Pt in the case of Pt^{IV}/AMM-Ti. When employed in a photoelectrochemical cell, the activity spectrum of the photocurrent extends downward to about 600 nm, as does the photodegradation of 4-CP. It is suggested that the metal salt acts as a redox-active chromophore, transmitting the photogenerated charges to the amorphous matrix.

Keywords: amorphous materials · photochemistry · photoelectrochemistry · sol–gel processes · titanium

Introduction

The preferential use of TiO_2 in the photocatalytic degradation of organic pollutants is based on its high oxidative power, photostability, and nontoxicity.[1–3] However, one severe disadvantage of this semiconductor material is the large bandgap, 3.2 eV for bulk TiO_2, which limits the photosensitivity to the UV region. Various methods have been applied to improve the response to visible light. Dye sensitization in photoelectrochemical systems has been explored extensively,[4] but cannot be used for detoxification of waste waters since the dye molecules would also be degraded. Coupling of TiO_2 with a small bandgap semiconductor[5–8] or doping with transition metal ions such as V, Cr, Mn, Fe, Co, Ni, or Cu[8, 9] extends light absorption into the visible region, but only in a few cases could a chemical reaction be driven for a prolonged time. Similarly, various Ti/Fe oxides initiate degradation of dichloroacetate[10] by visible light, but photocorrosion prevents a catalytic reaction pathway from being followed. The detailed effects of the dopant metal ions are still unclear.[2, 11] Although most reports state that the photocatalytic activity of TiO_2 is improved by doping with transition metal ions, some record the opposite result. In general, in all the cases mentioned above the *crystalline* anatase or rutile modifications were involved, the *amorphous* phase being known to be photocatalytically inactive.[12]

We reported previously[13] that an amorphous microporous titania modified with 1.1% (wt/wt) platinum(IV) (Pt^{IV}/AMM-Ti) was capable of catalyzing the photodegradation of 4-chlorophenol (4-CP) in aqueous solution upon illumination with visible light. Since platinum-free AMM-Ti was found to be almost inactive upon irradiation with UV or visible light, it was postulated that the excited state of the platinum(IV) chloride component initiated the reaction. To test this postulate we have prepared a series of AMM-Ti hybrid catalysts modified with various metal chlorides and investigated their photocatalytic and photoelectrochemical properties. 4-CP, the photodegradation of which has been studied extensively,[11] was used as a probe.

Results and Discussion

Characterization of hybrid AMM-Ti: Preparation of the sol–gel was exactly as reported for Pt^{IV}/AMM-Ti;[13, 14] care was taken to ensure that the sol remained clear and transparent

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[a] Prof. Dr. H. Kisch, Dr. L. Zang, W. Macyk
Institut für Anorganische Chemie der Universität Erlangen-Nürnberg
D-91058 Erlangen (Germany)
Fax: (+49) 9131-8527363
E-mail: kisch@anorganik.chemie.uni-erlangen.de

[b] Dr. C. Lange, Prof. Dr. W. F. Maier
Max-Planck-Institut für Kohlenforschung
D-45470 Mülheim (Germany)

[c] Dr. C. Antonius, Dr. D. Meissner
Forschungszentrum Jülich
D-52425 Jülich (Germany)

throughout the preparation, so that it was reasonable to assume that the other metal chlorides employed in this study were also distributed homogeneously in the microporous TiO_2 matrix as their neutral salts. All materials exhibited large specific surface areas (about 200 m^2g^{-1}). X-ray diffraction (XRD) analysis of 1.1% Pt^{IV}/AMM-Ti showed the powder to be almost exclusively in the amorphous phase. Upon heating, the anatase pattern started to appear around 523 K, and at 923 K both anatase and rutile could be observed, but of these only rutile was detectable at 1173 K; meanwhile the amorphous phase was still dominant, as suggested by the low signal-to-noise ratio and the broadness of the peaks (Figure 1).

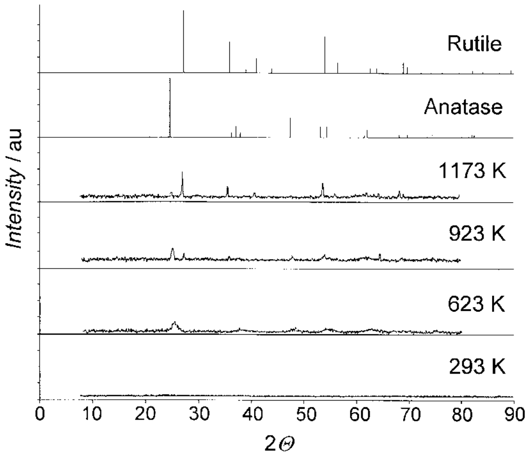

Figure 1. Temperature-dependent XRD patterns of 1.1% Pt^{IV}/AMM-Ti.

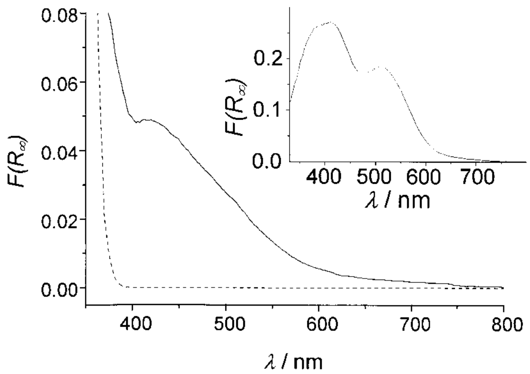

Figure 2. Diffuse reflectance spectra of P-25-TiO_2 (broken line) and Rh^{III}/AMM-Ti (solid line). The Kubelka–Munk function, $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, is used as the equivalent of absorbance. Insert: reflectance spectrum of solid $RhCl_3$.

In Figure 2 the diffuse reflectance spectra[15] of Rh^{III}/AMM-Ti and commercial P-25-TiO_2 are compared. The pronounced absorption of the modified material in the visible region was assigned tentatively to a ligand-field transition of the metal chloride, by analogy with solution spectra of corresponding chloro complexes.[16] Solid $RhCl_3$ has a similar reflectance spectrum (Figure 2, insert). Below 400 nm, a sharp increase in the absorption of the hybrid sample indicated bandgap absorption of AMM-Ti, as inferred from the absorption features of P-25-TiO_2.

Abstract in German: *Durch Chloride von Pt^{IV}, Ir^{IV}, Rh^{III}, Au^{III}, Pd^{II}, Co^{II} und Ni^{II} modifizierte amorphe, mikroporöse Metall(IV)oxide von Titan (AMM-Ti) wurden nach Sol–Gel-Verfahren hergestellt und durch diverse oberflächenanalytische Methoden charakterisiert. Diese Hybrid—AMM-Ti—Pulver besitzen Halbleitercharakter und katalysieren den Photoabbau von 4-Chlorphenol (4-CP), wenn sie in wäßriger Suspension mit sichtbarem ($\lambda \geq 400$ oder 455 nm) oder UV-Licht ($\lambda \geq 335$ nm) belichtet werden. Die Abbaugeschwindigkeit hängt vom Dotierungsgrad ab und durchläuft im Falle von Pt^{IV}/AMM-Ti ein Maximum bei 3.0% Pt. Eingesetzt in einer photoelektrochemischen Zelle, erstreckt sich das Aktionsspektrum des Photostroms bis zu 600 nm, in völliger Analogie zur Wellenlängenabhängigkeit des Photoabbaus von 4-CP. Als mechanistische Hypothese wird angenommen, daß das Metallsalz als Redoxchromophor wirkt, welcher die durch Lichtabsorption entstanden Ladungen an die amorphe Matrix weiterleitet.*

Photodegradation of 4-CP: To explore the general applicability of this new concept of titania sensitization, we have investigated the photodegradation of 4-CP catalyzed by AMM-Ti modified by various metal chlorides (Table 1).

Table 1. Initial rates [$\times 10^{-6}$ mol L^{-1} min^{-1}] of photodegradation of 4-CP catalyzed by various MCl_x/AMM-Ti catalysts upon illumination with UV and visible light.

Catalyst	$\lambda_{irr} \geq 335$ nm	$\lambda_{irr} \geq 400$ nm	$\lambda_{irr} \geq 455$ nm
P-25-TiO_2	12	0.4	≈0.1
AMM-Ti	<1.8	0.25	≈0.1
1.1% Pt^{IV}/AMM-Ti	6.3	4.1	3.4
1% Rh^{III}/AMM-Ti	5.3	3.0	1.5
1% Au^{III}/AMM-Ti	4.1	2.3	1.1
1% Pd^{II}/AMM-Ti	3.1	1.2	1.0
1% Ni^{II}/AMM-Ti	2.5	2.4	0.9
1% Co^{II}/AMM-Ti	1.4	1.2	0.8
1% Ir^{IV}/AMM-Ti	≈1.4		≈0.1

Although quantitative comparison of initial rates at the different irradiation wavelengths is impossible, the data clearly indicate that the activity of P-25-TiO_2 is dramatically lower for visible than for UV irradiation, whereas this is much less the case for the modified samples. Hence an activity pattern ($Pt^{IV} > Rh^{III} > Au^{III} > Pd^{II} > Ni^{II} > Co^{II} > Ir^{IV}$) can be derived for all three wavelength regions. This is demonstrated further by the decay curves (Figure 3). It is noteworthy that the unmodified AMM-Ti sample exhibited only negligible activity at all irradiation wavelengths. This is in accord with Ohtani et al.'s recent finding that amorphous TiO_2 did not photocatalyze the dehydrogenation of 2-propanol.[12] It was assumed that the abundant defects at the surface and in the bulk promoted efficient recombination of photogenerated charge carriers.

4-CP decomposition upon illumination at $\lambda \geq 400$ nm is shown in Figure 3 top. Whereas negligible reaction was observed for the two unmodified titania samples, AMM-Ti

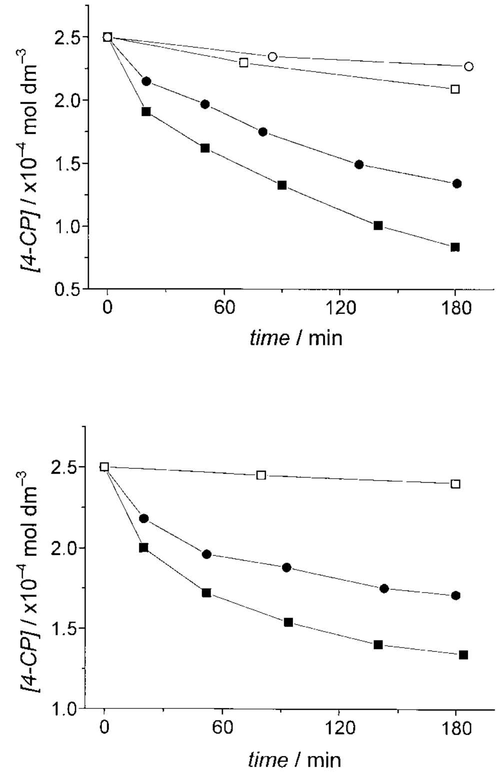

Figure 3. Comparison of photodegradation of 4-CP catalyzed by: (■) 1.0% Rh^{III}/AMM-Ti; (●) 1.0% Au^{III}/AMM-Ti; (□) P-25-TiO_2; (○) AMM-Ti; top: $\lambda \geq 400$ nm; bottom: $\lambda \geq 455$ nm.

and P-25-TiO_2, degradation of 4-CP occurred in the suspension of the two modified photocatalysts, Rh^{III}/AMM-Ti and Au^{III}/AMM-Ti, which have high activities under UV irradiation and were chosen to illustrate the activity in the visible region (Figure 3). Similar photodegradation behavior was observed previously in the case of Pt^{IV}/AMM-Ti.[13] The reaction rates are comparable with those in the UV region (Table 1).

The activity of modified AMM-Ti samples was also examined at $\lambda \geq 455$ nm, as the solar emission spectrum centers at $\lambda \approx 500$ nm. Photodegradation of 4-CP catalyzed by Rh^{III}/AMM-Ti and Au^{III}/AMM-Ti was compared with that catalyzed by P-25-TiO_2 (Figure 3 bottom). After 3 h of illumination about 50% of the 4-CP had been consumed in the case of Rh^{III}/AMM-Ti, whereas very little degradation was observed for P-25-TiO_2. Solar degradation was also demonstrated by illumination with diffuse sunlight. After 5 h of illumination under either a clear or a cloudy sky, 100, 85, and 70% of the 4-CP disappeared in the case of Pt^{IV}/AMM-Ti, Rh^{III}/AMM-Ti, and Au^{III}/AMM-Ti, respectively.

Formation of the final mineralization products CO_2 and HCl was confirmed by gravimetric and acidimetric methods, respectively. After 43 h of illumination at $\lambda \geq 455$ nm, 1.38×10^{-5} mol 4-CP (44% of theory) was degraded and 6.0×10^{-5} mol CO_2 (72%) was produced. Apparently, not all the 4-CP consumed was mineralized to CO_2, implying the presence of small amounts of intermediates in the reaction solution. Subsequent irradiation of the latter at $\lambda \geq 335$ nm for 20 h degraded almost all of the 4-CP left (1.41×10^{-5} mol) with formation of 1.2×10^{-4} mol CO_2. The production of excess CO_2 arises from the residual intermediates formed during illumination with visible light[13a] and the total amount of CO_2 (1.8×10^{-4} mol) is in good agreement with the amount of 4-CP (2.8×10^{-5} mol) degraded. This is also in accord with the pH change from approximately 7.0 initially to 2.5–3.0 finally, correlating well with the stoichiometric decomposition of 2.5×10^{-3} mol L^{-1} 4-CP to CO_2, HCl, and H_2O.

Dependence on dopant content: From the investigation described above, it is reasonable to suggest that the photoactivity of the hybrid titania is dependent on the content of the dopant metal salt. This was examined for Pt^{IV}/AMM-Ti, which has been characterized extensively.[13] After a steady increase in the initial rates of photodegradation of 4-CP with increasing weight content of the platinum salt (Figure 4), a maximum rate is observed around 3.0%, followed by a decrease at 4.0% Pt (vide infra). This decrease is assigned tentatively to increasing Pt–Pt interactions with increasing Pt content.

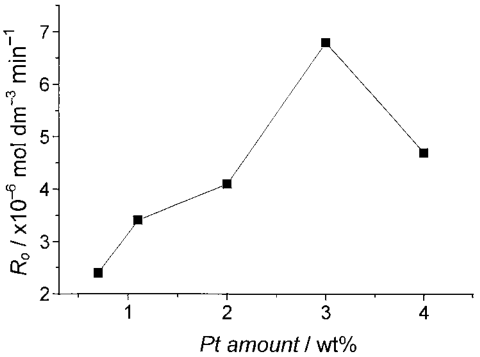

Figure 4. Dependence of the initial rate (R_0) of photodegradation of 4-CP on the weight content of the dopant platinum(IV) chloride in Pt^{IV}/AMM-Ti; $\lambda \geq 455$ nm.

Figure 5 illustrates the wavelength dependence of 4-CP disappearance for the 3.0% Pt^{IV}/AMM-Ti sample. Even at wavelengths as long as $\lambda \geq 530$ nm photodegradation still occurred steadily. The reaction in all illumination wavelength regions obeyed first-order kinetics (Figure 5, insert). This can be rationalized by a modified Langmuir–Hinshelwood model

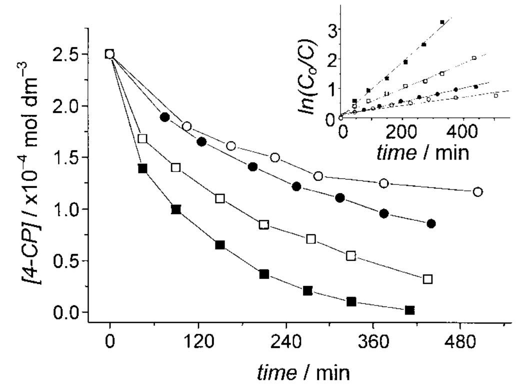

Figure 5. Photodegradation of 4-CP catalyzed by 3.0% Pt^{IV}/AMM-Ti upon illumination in various regions of the visible spectrum: (■) $\lambda \geq 400$ nm; (□) $\lambda \geq 455$ nm; (●) $\lambda \geq 495$ nm; (○) $\lambda \geq 530$ nm. Insert: the corresponding first-order plot.

[Eq. (1), where k_r is the reaction rate constant, θ the fraction of the catalyst surface covered by 4-CP, K the adsorption coefficient of 4-CP, C the concentration of 4-CP, K_s the adsorption coefficient of the solvent, and C_s the concentration

$$R = -\frac{dC}{dt} = k_r\theta = \frac{k_rKC}{1+KC+K_sC_s} \approx \frac{k_rK}{1+K_sC_s}\cdot C \qquad (1)$$

of the solvent], by analogy with the known kinetics of the UV photodegradation catalyzed by unmodified crystalline TiO_2.[17–19] Considering the low concentration and the weak adsorption of 4-CP on TiO_2, the approximation $KC \ll K_sC_s$ is plausible. This suggests that the photocatalysis initiated by the new amorphous hybrid catalyst is mainly a surface process, as is also observed for crystalline TiO_2.

Photocurrent action spectra: When a conducting glass electrode covered with 1.1 % Pt^{IV}/AMM-Ti, 1.0 % Rh^{III}/AMM-Ti, or 1.0 % Au^{III}/AMM-Ti was irradiated in a photoelectrochemical cell at different wavelengths, a photocurrent in the visible region was also observable, in distinct contrast to the case of commercial P-25-TiO_2. The photocurrent spectra of all three materials are shown in Figure 6, at two resolutions. They are presented as the incident photon-to-current efficiency (IPCE), the ratio of the measured photocurrent density to the incident photon density as determined with a calibrated photodiode. The photocurrent was controlled so as to be proportional to the incident light intensity. It is evident that the IPCE spectra reflected well the absorption behavior of these materials.

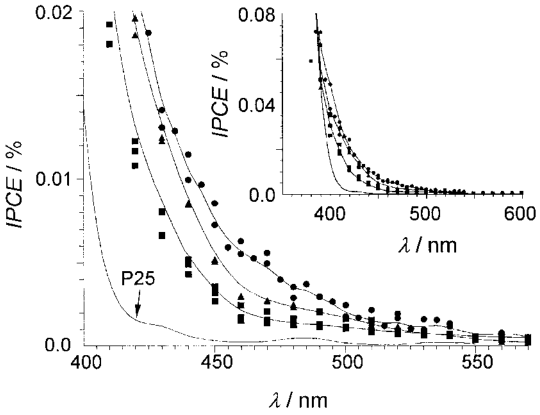

Figure 6. Photocurrent action spectra obtained from photoelectrodes prepared by casting films of pure P-25-TiO_2 (—) , 1.1 % Pt^{IV}/AMM-Ti (●), 1.0 % Rh^{III}/AMM-Ti (▲), and 1.0 % Au^{III}/AMM-Ti (■). The spectra were measured under potentiostatic control at a potential of +0.5 V (Ag/AgCl). Solution: 0.1 molL^{-1} NaOH.

The data shown were recorded under potentiostatic control at a potential of 0.5 V (Ag/AgCl) without addition of a redox couple to the 0.1 M NaOH solution. However, they were confirmed by measuring the somewhat noisier short circuit photocurrent as well as the photovoltage spectra in a two-electrode setup with a platinum counter-electrode. They were also controlled by adding the Fe^{3+}/Fe^{2+} redox couple or methanol as a current-doubling agent. In the latter experiment a current multiplication factor of approximately 2 was obtained in the visible spectral region, whereas a much higher factor could be obtained for direct TiO_2 absorption below 390 nm, as was previously reported for nanoporous TiO_2 films.[20] Current/voltage curves in a two-electrode setup are shown in Figure 7 for the rhodium-doped sample. Strong hysteresis occurred between forward and backward scans, even for scan rates as low as 10 mVs^{-1} (Figure 7, insert). However, a true primary positive photocurrent was obtained even when the applied voltages were negative, as shown here for the voltage scan in the negative direction.

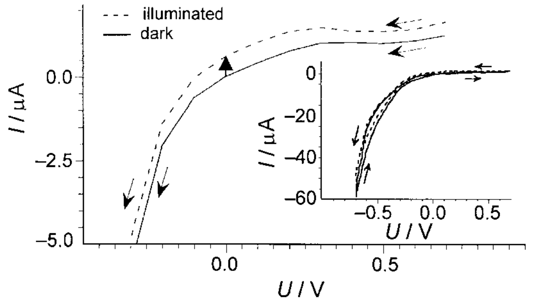

Figure 7. Current/voltage characteristics of the 1.0 % Rh^{III}/AMM-Ti electrode obtained by scanning, in the negative direction, the voltage in a two-electrode setup with a platinum counter-electrode. Solution: 0.1 molL^{-1} NaOH. Insert: scans in both voltage directions.

Mechanism: It is evident from the results that the photocatalytic activity of the gold- and rhodium-modified AMM-Ti samples is due to local excitation of the dopant metal chloride, as proposed previously for the platinum-doped sample.[13] Also, homolytic cleavage of the metal–chloride bond in these new hybrid materials most probably produces reducing and oxidizing surface sites from which reduction of oxygen and oxidation of 4-CP occur.[13a] Subsequently, a series of redox reactions involving the superoxide ion O_2^- and 4-$CP^{+\bullet}$ affords CO_2, HCl, and H_2O, as is known to occur in the reaction photocatalyzed by crystalline TiO_2. The indispensable role of O_2 in such a process is confirmed by the finding that no photodegradation of 4-CP takes place in the absence of O_2. Since metal chlorides in aqueous solution are known to undergo homolytic bond cleavage,[21–24] we irradiated dissolved $PtCl_4$ in the presence of 4-CP under experimental conditions identical to those in the heterogeneous system. Photodegradation occurred, but was much slower and only stoichiometric with respect to platinum chloride. This result supports the mechanism postulated for the titania hybrid photocatalysts. According to Figure 4 the optimum platinum content was around 3.0 %. The initial rate increase can be explained by considering the increased light absorption by the platinum(IV) chloride units, whereas the decrease in the later stage can be attributed to the enhancement of the intermolecular recombination of chlorine atoms and Pt^{III} species due to their relatively high local concentration. The mechanism of the Co^{II}-, Ni^{II}-, and Pd^{II}-modified samples may be similar.

Experimental Section

Materials: 4-CP, titanium isopropoxide, and all the other agents were of analytical grade and were used without further purification. P-25-TiO_2

powder, consisting mainly of anatase, was obtained from Degussa. Triply distilled or Milli-Q (Millipore) water was used throughout this study.

AMM-Ti materials were prepared by a sol–gel procedure through slow hydrolysis of titanium isopropoxide in the presence of various metal chlorides in strong acidic aqueous media.[13, 14] Dissolution of $Ti(OC_3H_7)_4$ (12 mL, 0.04 mol) in ethanol (50 mL) and stirring for 30 min were followed by slow addition of HCl (0.1 mL, 8 M). Concentrated HCl (0.1 mL after 5 min, 0.3 mL after 10 min, and 0.3 mL after a further 10 min) was added. Thereafter an appropriate amount of the corresponding metal chloride dissolved in ethanol (10 mL) was added slowly. The clear solution obtained was stirred at room temperature for one day. The loosely covered sol gelled within six days when it was then left to stand at room temperature without stirring. For further mild drying, the gel was kept uncovered in a hood for another 10 days, after which it had turned hard and brittle. The solidified gel was heated at 0.1 $K\,min^{-1}$ to 338 K, kept at this temperature for 100 min, heated at the same rate to 523 K, kept at this temperature for 300 min, and then allowed to cool at 0.5 $K\,min^{-1}$ to room temperature. The unmodified titania (AMM-Ti) was prepared by the same procedure but without addition of metal chlorides. Before use the material was ground in a ball mill, affording small particles suitable for suspension in water.

The metal chlorides of Pt^{IV}, Ir^{IV}, Rh^{III}, Au^{III}, Pd^{II}, Co^{II}, and Ni^{II} were used to prepare the hybrid titania. Except Pt^{IV}/AMM-Ti all the other samples were made with the same weight content (1.0%) of metal cation. A series of Pt^{IV}/AMM-Ti with platinum contents from 0.7% to 4.0% were prepared and used for comparative investigations.

Characterization of materials: Powder X-ray diffraction (XRD) patterns were recorded using the Debye–Scherrer technique on a Stoe Stadi 2/PL diffractometer with $Cu_{K\alpha}$ radiation in the range $10^\circ \leq 2\theta \leq 80^\circ$ and the area detector PSD1. The temperature dependence of the patterns was recorded in the range 293–1173 K, with a stepwise increase of 50 K before each measurement. Specific surface areas were determined by the Brunauer–Emmet–Teller method as described recently.[13a] Diffuse reflectance spectra of the powders were measured on a Shimadzu UV-3101PC, UV/Vis–NIR scanning spectrophotometer equipped with a diffuse reflectance accessory. The samples were spread onto an Al_2O_3 plate, the background reflectance of which had been measured. The reflectance data were converted by the instrument software to the $F(R_\infty)$ values according to Kubelka–Munk theory.[15]

Photodegradation procedure and product analysis: The photocatalytic degradation of 4-CP was carried out in a jacketed cylindrical quartz cuvette (15 mL) attached to an optical train, which was equipped with an Osram XBO 150 W xenon arc lamp ($I_0(400-520\,nm) = 2.0 \times 10^{-6}$ $Einstein\,s^{-1}cm^{-2}$) installed in a light condensing lamp housing (PTI, A1010S). When necessary, a cut-off filter was placed in front of the cuvette. Running water was circulated through the jacket to cool the reaction mixture, which was stirred magnetically.

In a typical experiment, a suspension (14 mL, 0.5 $g\,L^{-1}$) of pure TiO_2 or hybrid AMM-Ti containing 4-CP (2.5×10^{-4} $mol\,L^{-1}$) was sonicated for 15 min and then transferred to the cuvette. Before illumination, the suspension was stirred magnetically for 20 min to ensure complete adsorption of phenol. During a run, samples (approximately 1.0 mL) of the reaction solution were taken at given time intervals. Each sample was filtered through a Millipore membrane filter (0.22 μm pores). 4-CP and aromatic intermediates in the samples were analyzed by HPLC (Kroma-System 2000 controller, Kontron 320 autosampler, 430A photodiode array detector). A reverse-phase C_{18} column (Kontron, Spherisorb 5 ODS 2) and water–methanol eluent (50:50) were employed. The concentration of 4-CP was determined from the absorbance at 280 nm.

The procedure described above was also applied to the experiment on $PtCl_4$-assisted photodegradation of 4-CP. In this case the aqueous solution containing $PtCl_4$ (1×10^{-4} $mol\,L^{-1}$) and 4-CP (2.5×10^{-4} $mol\,L^{-1}$) was used instead of a TiO_2 suspension. The $\lambda \geq 455$ nm cut-off filter was applied during irradiation. The 4-CP concentration [$\times 10^{-4}$ $mol\,L^{-1}$] decreased by 0.43, 0.63, 0.75, 0.83, and 0.93 after 2, 4, 6, 10, and 15 h, respectively.

For the gravimetric measurements of CO_2, oxygen was slowly bubbled through the reacting suspension (Pt^{IV}/AMM-Ti, 0.5 $g\,L^{-1}$; 4-CP solution, 12.5 mL at 2.5×10^{-3} $mol\,L^{-1}$) and subsequently through a 10^{-2} $mol\,L^{-1}$ Ba^{2+} solution at pH 10–11. $BaCO_3$ was filtered off, washed, and dried at 60°C for three days. The formation of HCl was confirmed by measurement of the pH change in the reaction solution.

Sunlight experiments: Illumination by sunlight was carried out around midday in early October in Erlangen (latitude 49.5° N). Three samples (0.5 $g\,L^{-1}$) modified with Pt^{IV}, Rh^{III}, and Au^{III} were used as catalysts in a solution of 4-CP (40 mL, 2.5×10^{-4} $mol\,L^{-1}$) in a Pyrex glass reactor with magnetic stirring. The final reaction solution was subjected to HPLC analysis.

Photoelectrochemical measurements: Photoelectrochemical measurements were carried out in a conventional three-electrode cell equipped with a quartz window, a large platinum foil counter, and a saturated Ag/AgCl reference electrode connected through a freshly filled chloride-free salt bridge. The working electrode was prepared by casting a suspension of the doped AMM-Ti materials in ethanol onto ITO-covered glass slides (Balcatron, Balzers, Liechtenstein) and drying in air. A porous film was thus formed which allowed the electrolyte to penetrate into the bulk of the electrode. NaOH solution (0.1 $mol\,L^{-1}$) was used as the standard electrolyte. To investigate current-doubling effects, a small amount of ethanol was added forming an alkaline solution (about 0.01 $mol\,L^{-1}$). Current/voltage curves and most of the action spectra were measured in a standard three-electrode setup controlled by a Schlumberger 1286 Electrochemical Interface (Schlumberger, Munich) connected with a Macintosh II computer. Illumination was performed with a 1000 W Xe lamp (XBO, Osram, Munich, Germany) in a Mueller housing (Mueller, Moosinning, Germany) equipped with a standard water filter. Spectra were recorded using a Metrospec monochromator (AMKO, Tornesch, Germany) and gray filters, and normalized to a constant light intensity after it had been confirmed that the photocurrent was proportional to the light intensity.

To exclude pure photoconductivity effects, the photocurrent spectra were carefully cross-checked by measuring the true short circuit current in a two-electrode setup with the platinum counter-electrode. Measurements using the $Fe^{3+/2+}$ redox couple were also performed. In these experiments the photocurrents were measured with a Keithley 617 Electrometer (Keithley, Germering). Thus it was possible to confirm that the photocurrents observed at wavelengths above 420 nm were true primary ones. Their effect was also confirmed by recording photovoltage spectra.

Acknowledgments

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