



Visible light photocatalysis by a Titania–Rhodium(III) complex

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ABSTRACT

Titania hybrid photocatalysts containing 0.5, 1.0, 2.0, and 5.0 wt% of rhodium(III) were prepared by chemisorption of $\text{RhCl}_3 \times 3\text{H}_2\text{O}$ onto anatase hydrate powder (TH). Analytical data suggest that a titania–trichlororhodate complex is produced containing a $[\text{TiO}_2]\text{–O–Rh}$ bond.

Similar results are found in the case of modification by $\text{RhBr}_3 \times 3\text{H}_2\text{O}$. Diffuse reflectance spectra exhibit an absorption shoulder throughout the visible region down to 700 nm. Photoelectrochemical measurements indicate that the quasi-Fermi level of electrons is gradually shifted to more anodic potentials with increasing rhodium loading reaching a value of -0.34 V at pH 7 (vs. NHE) in the case of 5.0% RhCl_3/TH . This is more anodic by 210 mV as compared to unmodified TH. Upon visible light irradiation this photocatalyst induces a fast mineralization of 4-chlorophenol whereas cyanuric acid, which is known to be mineralized in the presence of the analogous Pt(IV) modified titania, is not degraded.

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1. Introduction

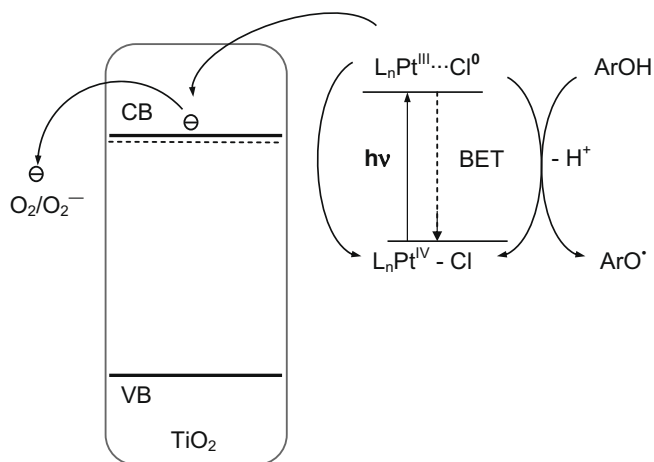
In many aspects titania is the most promising photocatalyst for small scale photooxidation reactions in basic and applied chemistry [1]. However, its utilization in solar chemistry is hampered by the fact that it absorbs only UV light which constitutes a very small part (2–3%) of the solar spectrum. Recently, we found that surface-modification of titania by platinum(IV) chloride affords photocatalysts active in the mineralization of 4-chlorophenol (4-CP) and many other pollutants with visible light ($\lambda \geq 455$ nm) [2,3a,3b]. These novel materials are easily obtained through stirring a suspension of anatase powder (TH) in hexachloroplatinate solution and subsequent thermal treatment. From desorption experiments it was concluded that chemisorption took place affording an oxygen bound surface complex of the proposed composition $\{[\text{Ti}]\text{OPtCl}_4\text{L}\}^n$, $\text{L} = \text{H}_2\text{O}, \text{OH}^-$, $n = 1, 2$ [3a,3b], abbreviated as Pt(IV)/TH in the following. Thus, the semiconductor may be considered as an unconventional ligand in a transition metal coordination complex. The quasi-Fermi level of electrons (nE_F) of this hybrid semiconductor was changed considerably as a function of surface-loading. At pH 7 the value of -0.54 V as found for the anatase hydrate powder TH was shifted to -0.49 , -0.45 , and -0.28 V (vs. NHE) when the surface was covered by 1.0, 2.0, and 4.0 wt% of platinum, respec-

tively. This resembles the corresponding anodic shift observed upon adsorption of fluoride ions [3c]. One of the most active photocatalysts in 4-CP mineralization was 4.0%Pt(IV)/TH, a high surface area ($260 \text{ m}^2 \text{ g}^{-1}$) material containing 4.0 wt% of platinum. Both upon visible and ultraviolet excitation this novel titania complex is a superior photocatalyst as compared to previously known titania materials. It even catalyzes the mineralization of cyanuric acid, which is usually the final product in atrazine degradation by titania and other advanced oxidation processes. Scheme 1 summarizes the proposed mechanism for the primary reaction steps [4]. According to this the excited platinum surface complex undergoes first homolytic $\text{Pt}^{\text{IV}}\text{–Cl}$ bond cleavage affording a Pt^{III} intermediate and a surface bound chlorine atom [5–9]. In the reductive reaction path the platinum(III) species injects an electron into the titania conduction band from where it is subsequently transferred to oxygen. Since the titania semiconductor ligand is covalently attached to the chloroplatinate chromophore, a strong electronic coupling is expected rendering this step fast enough to efficiently compete with the undesired back electron transfer (Scheme 1, process BET). In the oxidative reaction pathway 4-chlorophenol (ArOH) transfers an electron to the chlorine atom. As summary of both pathways the $\text{Pt}^{\text{IV}}\text{–Cl}$ fragment is reformed.

To find out whether analogous surface-modification is feasible also with chlorides of other d^0 metals, we report here on the preparation and photocatalytic properties of a rhodium(III) chloride modified titania.

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Scheme 1. Mechanistic scheme of titania sensitization by platinum(IV) chloride complexes (according to Ref. [9]).

2. Results and discussion

The novel hybrid photocatalysts $x\% \text{RhCl}_3/\text{TiO}_2$ containing 0.5, 1.0, 2.0, and 5.0 wt% of rhodium were prepared by stirring a suspension of TiO_2 in a corresponding amount of aqueous rhodium(III) chloride and subsequent heating at 200°C . The best commercial titania material for this modification turned out to be the titania hydrate TH. Modified Hombikat and P25 exhibited less activity in the standard degradation of 4-CP. Therefore, in the following we will consider only TH modification. Maximum loading was observed at 5.0 wt% of rhodium since the use of higher metal chloride concentrations afforded powders from which excess rhodium is completely removed during washing (see Section 3). In order to understand the role of the halogen ligand, also $2.0\% \text{RhBr}_3/\text{TH}$ and $4.0\% \text{RhBr}_3/\text{TH}$ were synthesized.

RhCl_3/TH and RhBr_3/TH have a pink and a dark yellow color, respectively, and are surprisingly stable to desorption of the rhodium component as compared with the previously reported platinum modified TH [3a,3b,9]. In aqueous suspension upon stirring either in the dark or under irradiation with visible light, no dissolved rhodium complex was detectable by UV-Vis absorption spectroscopy. Although it is known that fluoride forms very stable Ti-F bonds, both $4.0\% \text{RhCl}_3/\text{TH}$ and $4.0\% \text{RhBr}_3/\text{TH}$ did not undergo desorption of the rhodium surface complex even after stirring for five days in the dark in 0.5 M KF. Thus, by analogy with Pt(IV)/TH one can conclude that Rh(III) is covalently bound to titania through a bridging oxygen ligand. This fluorinated sample, within experimental error, exhibited the same photoactivity as the unfluorinated samples in the standard degradation of 4-CP. Whereas in 0.1 mol dm^{-3} HCl the previously reported $4.0\% \text{Pt(IV)/TH}$ upon UV irradiation [3a], for 24 h suffers almost complete desorption to $[\text{PtCl}_6]^{2-}$, only 40% of $[\text{RhCl}_6]^{3-}$ were detectable in the case of $4.0\% \text{RhCl}_3/\text{TH}$. This difference may reflect the fact that the metal-oxygen bond is about 40 kJ mol^{-1} stronger in the case of rhodium [10]. However, in the presence of 6 mol dm^{-3} HCl complete desorption of the rhodium complex is observed. In strongly alkaline suspension the chloride ligands are completely displaced, as also observed for platinum(IV) chloride modified TH [3a]. Since from the amount of chloride produced in this experiment one can conclude that three chloride ligands are present in the surface rhodium complex, a composition of $\{[\text{TiO}_2]\text{-O-RhCl}_3(\text{H}_2\text{O})_2\}^-$ is suggested. An analogous structure is proposed for the RhBr_3/TH catalysts.

Comparison of the diffuse reflectance spectra of TH and $4.0\% \text{Rh(III)/TH}$ clearly indicates novel absorptions at 400–500 nm

and 500–700 nm (Fig. 1, curves a and c). The shoulder at about 500 nm compares well with the lowest d,d transition of $[\text{RhCl}_6]^{3-}$ observed in hydrochloric acid at 518 nm [11] (Fig. 2). At wavelengths shorter than about 550 nm a strong absorption increase suggests that it does not originate exclusively from the second d,d-transition occurring in $[\text{RhCl}_6]^{3-}$ at 410 nm with about the same intensity as the 510 nm band. It rather may originate from a rhodium-to-titanium charge transfer transition (MMCT) as also reported for other titania-metal-complex systems like $[\text{Fe}(\text{CN})_6]^{3-}/\text{TiO}_2$. [12] This is corroborated by the fact that the silica analogue $2.0\% \text{RhCl}_3/\text{SiO}_2$ does not exhibit a strong absorption increase at $\lambda \leq 550 \text{ nm}$, most likely because, different from titania, silica does not have a low lying conduction band (Fig. 3, curve b). In the corresponding difference spectrum an unsymmetrical absorption band is observed at a maximum at 380 nm. In the case of $2.0\% \text{RhBr}_3/\text{TH}$ a similar comparison with $2.0\% \text{RhBr}_3/\text{SiO}_2$ afforded the MMCT maximum at 390 nm (Fig. 4).

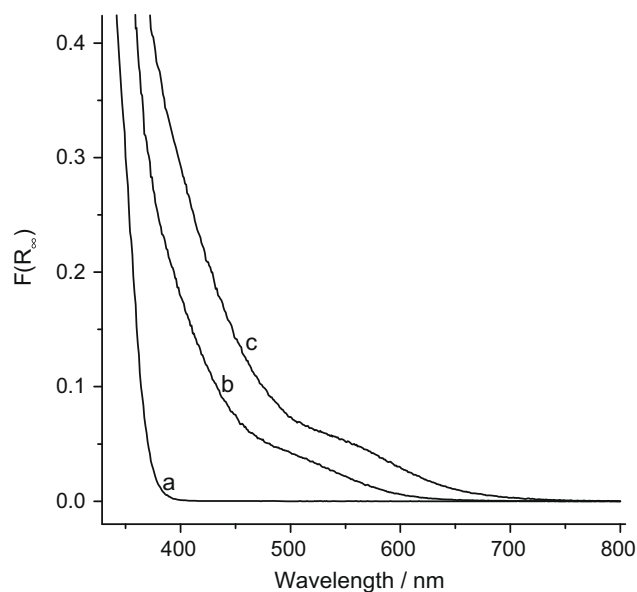


Fig. 1. Diffuse reflectance spectra of TH, $2.0\% \text{RhCl}_3/\text{TH}$ and $2.0\% \text{RhBr}_3/\text{TH}$. The Kubelka-Munk function, $F(R_\infty)$, is used as the equivalent of absorbance: (a) TH, (b) $2.0\% \text{RhCl}_3/\text{TH}$ and (c) $2.0\% \text{RhBr}_3/\text{TH}$.

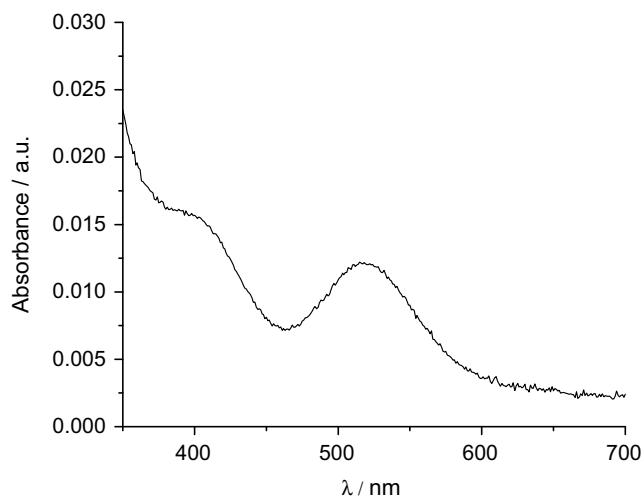


Fig. 2. Absorption spectrum of $[\text{RhCl}_6]^{3-}$.

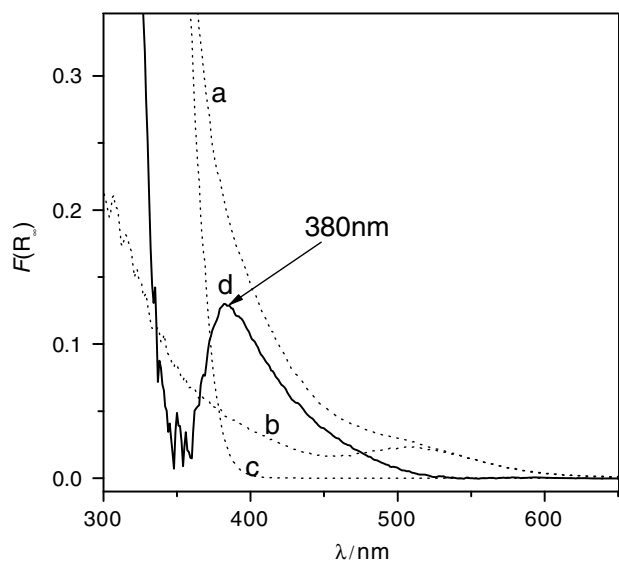


Fig. 3. Diffuse reflectance spectra of 2.0%RhCl₃/TH (a), 2.0%RhCl₃/SiO₂ (b), TH (c). Spectrum $d = a - (b + c)$.

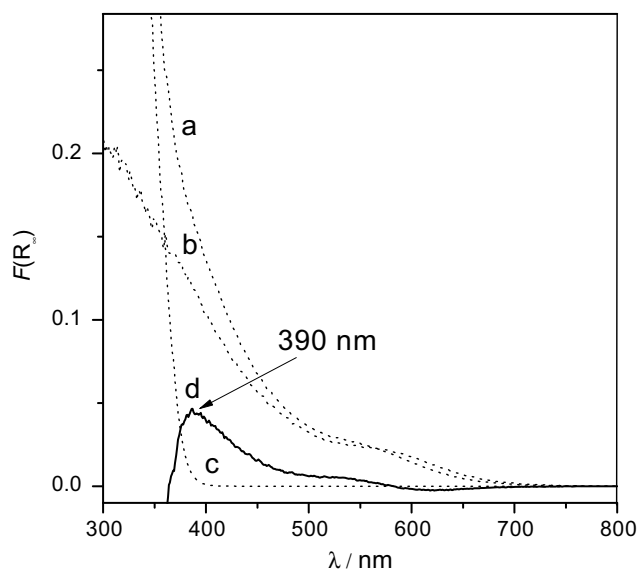


Fig. 4. Diffuse reflectance spectra of 2.0%RhBr₃/TH (a), 2.0%RhBr₃/SiO₂ (b), TH (c). Spectrum $d = a - (b + c)$.

Assuming that all samples are indirect crystalline semiconductors, as is anatase, the bandgap energy can be obtained by extrapolation of the linear part of a plot of $[F(R_{\infty})h\nu]^{1/2}$ vs. the energy of exciting light [13]. From this the bandgap of TH, 0.5, 1.0, 2.0, and 5.0%RhCl₃/TH and of 2.0%RhBr₃/TH, can be calculated as 3.29, 3.26, 3.25, 3.22, 3.21 and 3.1 eV, respectively (Fig. 5 and Table 1).

To investigate the photocatalytic activity, the disappearance and mineralization of 4-CP, an ubiquitous pollutant in water, was performed in the presence of air. Surprisingly, the activity of 5.0%RhCl₃/TH was very high and after 60 min of visible light irradiation ($\lambda \geq 455$ nm) 95% of 4-CP had disappeared whereas 75% of 4-CP were completely mineralized (Fig. 6). 2.0%RhBr₃/TH exhibited a photoactivity comparable to that of 2.0%RhCl₃/TH. The unmodified powders TH, Hombikat and P25 were inactive under these experimental conditions.

The photocatalytic activity increases with increasing rhodium loading, exhibiting the highest value for 5.0%RhCl₃/TH (Fig. 7). This

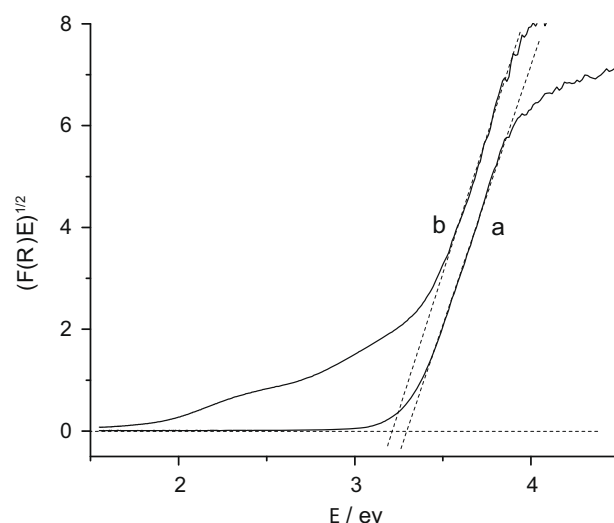


Fig. 5. Transformed diffuse reflectance spectra of TH and 5.0%RhCl₃/TH. The bandgap energy was obtained by extrapolation of the linear part: (a) TH and (b) 5.0%RhCl₃/TH.

Table 1

Bandgap energies and quasi-Fermi potentials of TH, 0.5%, 1.0%, 2.0%, 5.0%RhCl₃/TH and 2.0%RhBr₃/TH

Photocatalyst	E_{bg} (eV) ^a	nE_F^+ (pH 7, NHE) (V) ^b
TH	3.29	-0.55
0.5% RhCl ₃ /TH	3.26	-0.53
1.0% RhCl ₃ /TH	3.25	-0.48
2.0% RhCl ₃ /TH	3.22	-0.46
5.0% RhCl ₃ /TH	3.21	-0.34
2.0% RhBr ₃ /TH	3.1	-0.32

^a Reproducibility was better than ± 0.05 eV.

^b Reproducibility was better than ± 0.02 V.

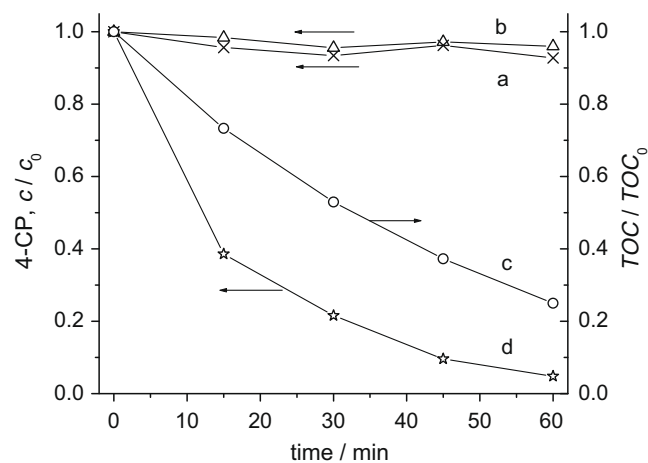


Fig. 6. 4-CP disappearance and mineralization upon visible light irradiation ($\lambda \geq 455$ nm); $c_0 = 2.5 \times 10^{-4}$ mol dm⁻³; photocatalyst dosage: 0.5 g dm⁻³; a: TH, b: P25, c and d: 5.0%RhCl₃/TH.

resembles our recent findings on the surface-loading of TH with [PtCl₆]²⁻ [3a,3b,9].

Photoelectrochemical measurements of the photovoltage as function of pH value [14] indicate that the quasi-Fermi level of electrons is shifted gradually more anodic upon increasing the rhodium loading. Thus, the value of -0.55 V (vs. NHE, at pH 7) as observed for unloaded TH is shifted to -0.53 , -0.48 , -0.46 , and

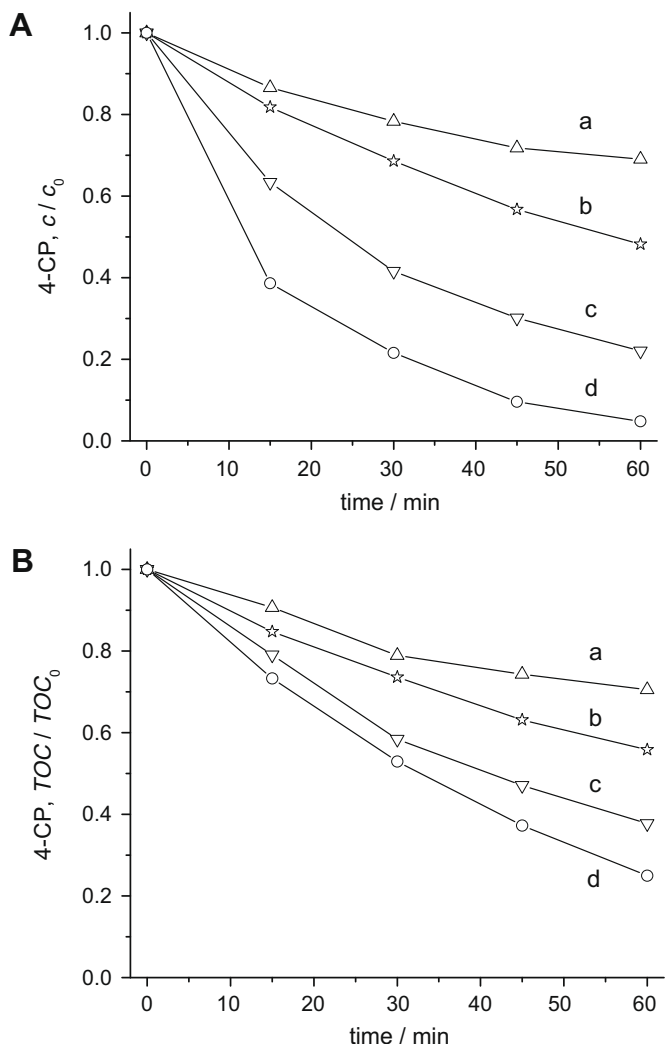


Fig. 7. 4-CP disappearance (A) and mineralization (B) as function of rhodium content; $\lambda \geq 455$ nm; $c_0 = 2.5 \times 10^{-4}$ mol dm $^{-3}$; photocatalyst dosage: 0.5 g dm $^{-3}$; (a) 0.5%RhCl $_3$ /TH, (b) 1.0%RhCl $_3$ /TH, (c) 2.0%RhCl $_3$ /TH and (d) 5.0%RhCl $_3$ /TH.

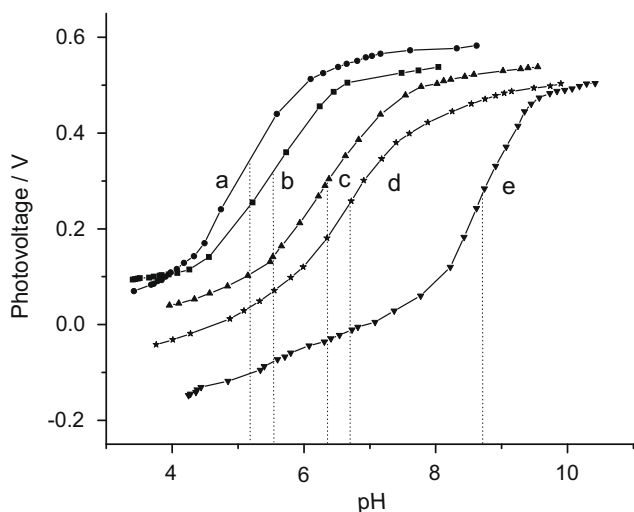
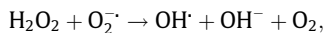
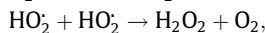
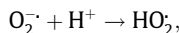
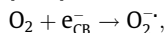
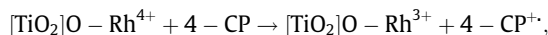
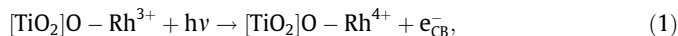


Fig. 8. Photovoltage recorded for 20 mg of TH (a) and 20 mg of 0.5% (b), 1.0% (c), 2.0% (d), and 5.0% RhCl $_3$ /TH (e) suspended in 100 cm 3 of 0.1 mol dm $^{-3}$ KNO $_3$ in the presence of 15 mg of methylviologen dichloride and irradiated with UV light ($\lambda \geq 320$ nm); The position of the inflection point pH $_0$ is marked with a dotted line.

–0.34 V upon loading with 0.5%, 1.0%, 2.0%, and 5.0% of rhodium, respectively (Fig. 8 and Table 1). In the case of 2.0%RhBr $_3$ /TH the quasi-Fermi level was found at –0.32 V.

To obtain experimental evidence for a mutual formation of OH radicals under visible light irradiation ($\lambda \geq 400$ nm), the photodegradation of benzoic acid in the presence of 4.0%RhCl $_3$ /TH and oxygen was investigated by monitoring the production of salicylic acid [2,15,16]. Surprisingly, no salicylic acid was detectable in solution. A likely reason for this could be a fast photodegradation of small amounts of initially produced salicylic acid. To test this hypothesis, photodegradation of salicylic acid was carried out under identical experimental conditions. It turned out that salicylic acid is efficiently adsorbed onto 4.0%RhCl $_3$ /TH (ca. 63% after 12 h of dark adsorption from a 1.0×10^{-4} mol dm $^{-3}$ solution) and that its photodegradation is very fast. About 96% of salicylic acid had disappeared after 10 min of irradiation. These results suggest that salicylic acid formed from benzoic acid largely remains adsorbed and is efficiently decomposed before being desorbed into solution.

To test if the photocatalytic activity of RhCl $_3$ /TH is also initiated by a homolytic M–Cl bond cleavage, as proposed previously for platinum(IV) chloride modified TH [2,9], the photodegradation of phenol under visible light irradiation ($\lambda \geq 455$ nm) was carried out. Formation of chlorophenol would evidence the presence of intermediate chlorine atoms. However, no significant amount of chlorophenol was detectable [17]. This differs from Pt(IV)/TH, in which case chlorophenol formation was observable [2]. Furthermore, cyanuric acid, a molecule which is mineralized in the presence of platinum(IV) modified TH [9], is not decomposed by 4.0%RhCl $_3$ /TH. These significant differences indicate that in the case of rhodium(III) modification visible light induced cleavage of the metal–halogen bond is not a major primary photoprocess. More likely seems a mechanism as proposed for UV light induced oxidation reactions in the presence of Rh(III) doped titania colloids [18].



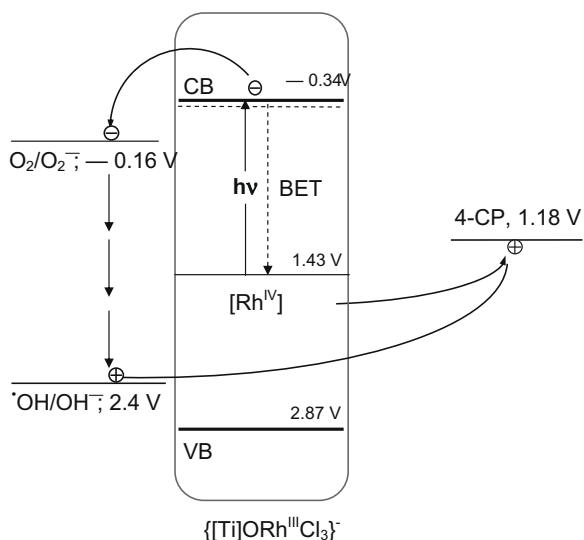
Visible light excitation within the MMCT band of RhCl $_3$ /TH (Figs. 3 and 4) affords as primary products an electron in the titania conduction band and a Rh(IV) center (Eq. (1)). The energetic position of the latter can be estimated by adding the energy of the Vis absorption onset (1.77 eV) to the quasi-Fermi level as depicted in Scheme 2 [19].

The resulting potential of 1.43 V is positive enough to oxidize water or more likely 4-chlorophenol to the radical cation (Eq. (2)), which finally breaks down to CO $_2$, HCl, and H $_2$ O, as well known from the UV photodegradation in the presence of unmodified TiO $_2$ [4]. The electron generated in the conduction band reduces oxygen to superoxide (Eq. (3)) produces an OH radical through the reaction sequence according to Eqs. (4)–(7) [20a–c] which in turn induces oxidation of 4-CP.

3. Experimental

3.1. 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



Scheme 2. Mechanistic scheme of titania sensitization by rhodium(III) complexes. Depicted values apply for 5.0%RhCl₃/TH at pH 7.

BaSO₄ 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 $F(R_{\infty})^{1/2}$ vs. energy of exciting light assuming that TH and 5.0%Rh(III)/TH are indirect crystalline semiconductors. 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, NaHCO₃/NaCO₃ = 0.001/0.0035 M as eluting agent).

3.2. Determination of absorptivity of [RhCl₆]³⁻

22.5 mg of pure RhCl₃ × 3H₂O was dissolved in 100 cm³ of 6 M HCl, and then refluxed to keep equilibrium for 4 h. Under these conditions, almost all of rhodium is in the form of [RhCl₆]³⁻. The resulting solution was diluted with 6 M HCl to a volume of 250 cm³. Thereafter the absorbance of [RhCl₆]³⁻ was measured by UV–Vis spectroscopy at the maximum of the LMCT band at 252 nm. The absorptivity of [RhCl₆]³⁻ at 252 nm at 20 °C was determined as $1.97 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. In the same spectrum one can observe the two weak bands at 410 and 518 nm corresponding to ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ²T_{2g}, respectively.

Similar procedure was performed to obtain absorption spectrum of [RhBr₆]³⁻.

3.3. Preparation of photocatalysts

To a suspension 1.0 g of titania (TH, Titanhydrat-0, Kerr-McGee) in 10 ml of H₂O were added appropriate amounts of RhCl₃ × 3H₂O or RhBr₃ × 3H₂O followed by sonication for 10 min. A pH value 3–4 was measured for these suspensions. After stirring for 24 h in the dark, water was removed in vacuo and the residue was dried under vacuum at room temperature for 3 h. Careful washing with water removed physisorbed rhodium chloride as indicated by UV–Vis absorption spectroscopy. The resulting powder was heated in air for 2 h at 200 °C, washed four times with 50 ml portions of doubly distilled water affording acidic solutions of pH 1–2. Drying as described above and a subsequent second heating for 2 h at 200 °C, gave pink RhCl₃/TH and a dark yellow RhBr₃/TH having a specific surface area of 230 m²/g as obtained from BET measurements. The amount of rhodium present in the RhCl₃/TH powder was determined as follows. 80 mg of RhCl₃/TH were suspended in 30 cm³ of

6 M HCl, and then refluxed for 4 h. The resulting suspension was diluted with 6 M HCl to a volume of 50 cm³. After filtration of the photocatalyst with a Millipore membrane filter (0.22 μm, Merck), the filtrate was analyzed as described above.

3.4. Preparation of 4.0%RhCl₃/TH and charge transfer absorption

Attempts to modify SiO₂ (Silica gel 60, Merck) through the procedure described above for TiO₂ failed. In fact, during washing the surface complex was almost removed, affording very weak colored powders. Therefore, modification of SiO₂ was accomplished by grinding opportune quantity of RhCl₃ × 3H₂O with SiO₂ to obtain 4.0%RhCl₃/SiO₂. Diffuse reflectance spectrum of 4.0%RhCl₃/SiO₂ was multiplied by the factor 2.3 in order to obtain the same Kubelka–Munk function measured for 4.0%RhCl₃/TH at λ = 518 nm.

3.5. Determination of Cl/Rh ratio

60 mg of 5.0%RhCl₃/TH (0.029 mmol Rh) were suspended in 40 ml of concentrated NaOH and refluxed for 24 h. After filtration 5 ml of the solution were neutralized with 0.1 ml of concentrated sulfuric acid. Quantitative determination by ion chromatography afforded 0.081 mmol/40 ml of chloride from which a Cl/Rh ratio of 2.79 is obtained.

3.6. Measurement of quasi-Fermi potentials

Quasi-Fermi levels of electrons were measured according to the literature [14]. 20 mg of TH (a) and 20 mg of 0.5% (b), 1.0% (c), 2.0% (d), 5.0% RhCl₃/TH (e) and suspended in 100 cm³ of 0.1 M KNO₃ in the presence of 15 mg of methylviologen dichloride irradiated with UV light (λ ≥ 320 nm, the light source was the same as used in the photodegradation). Suspensions were stirred and bubbled with N₂ prior to and during the measurement. The pH was adjusted with HNO₃ and NaOH solutions and monitored with a pH – meter. A large surface platinum flag (5 cm²) and Ag/AgCl were working and reference electrodes, respectively. Stable photovoltages were recorded about 2 min after adjusting the pH value. In the case of 2.0%RhBr₃/TH the electron acceptor used was DP²⁺. The measured pH₀ values were converted to the Fermi potential at pH 7 by the equations $E_F(\text{pH } 7) = -0.44 + 0.059 (\text{pH}_0 - 7)$ and $E_F(\text{pH } 7) = -0.27 + 0.059 (\text{pH}_0 - 7)$ when MV²⁺ and DP²⁺ were used, respectively.

3.7. Desorption experiments

Suspension of 5.0%RhCl₃/TH (30 mg) in 0.1 M HCl (15 cm³) was irradiated with UV light (λ ≥ 320 nm) for 24 h as described below. After filtration of the photocatalyst with a Millipore membrane filter (0.22 μm, Merck), the filtrate (10 cm³) was added to 12 M HCl (10 cm³) and then refluxed and analyzed as described above.

3.8. Photodegradation procedure and product analysis

The photocatalytic degradation of 4-CP was carried out in a jacketed cylindrical 15 cm³ quartz cuvette attached to an optical train. Irradiation was performed with an Osram XBO 150 W xenon arc lamp (I_0 (400–520 nm) = $2 \times 10^{-6} \text{ Einstein s}^{-1} \text{ cm}^{-2}$) installed in a light condensing lamp housing (PTI, A1010S) on an optical train. A water cooled cylindrical 15 cm³ 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, 15 cm³ of 0.5 g l⁻¹ powder suspension containing $2.5 \times 10^{-4} \text{ mol l}^{-1}$ of 4-CP was sonicated for 15 min and then transferred to the cuvette. During an illumination run ca. 1.2 cm³ 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 and TOC analysis. The same procedure was applied in the photocatalytic degradation of cyanuric acid followed by TOC measurements. The starting suspension was adjusted to pH 9 with NaOH followed by irradiation with visible light ($\lambda \geq 455 \text{ nm}$).

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