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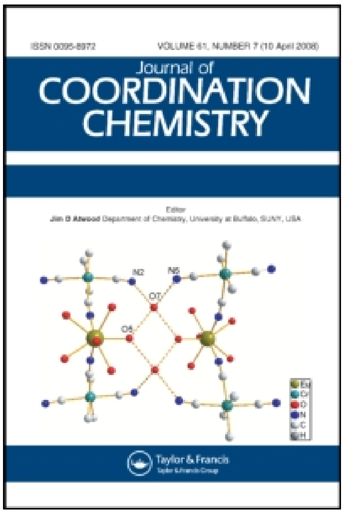

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Polyol-derived carbon-modified titania for visible light photocatalysis

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Modification of anatase by calcining titanium hydroxide or titania (UVLP) at 250°C in the presence of ethylene glycol and pentaerythritol afforded modified powders TiO_2-EG, UVLP-EG, and UVLP-PE, respectively, active in visible light mineralization of 4-chlorophenol. The presence of surface hydroxyl groups is necessary for the modification process, since their removal results in a photocatalyst of much lower activity. When UVLP-EG was calcined at 400°C, the resulting residue is of very low activity suggesting oxidative destruction of an organic photosensitizer. Quasi-Fermi levels of −0.58, −0.53, −0.52, and −0.46 V were observed for TiO_2-EG, $UVLP_{calc}$, UVLP-EG, and UVLP-PE, respectively. In attempts to desorb the photosensitizer, TiO_2-EG, UVLP-EG, and UVLP-PE were treated at 90°C with NaOH as recently performed with the commercial material VLP_{com}. Whereas the activity of the residual powder was strongly decreased in the case of TiO_2-EG, it did not change for UVLP-EG and UVLP-PE. Both the residues, $UVLP\text{-}EG_{res}$ and $UVLP\text{-}PE_{res}$, exhibited slightly enhanced mineralization activities as compared to the starting materials. Thus, different from VLP_{com} and TiO_2-EG, no sensitizer but only an organic impurity could be extracted. In agreement with this conclusion, the corresponding extracts had different emission spectra. Similarly, acidic desorption experiments on UVLP-EG again produced a very active residual powder. This inertness of UVLP-EG and UVLP-PE against alkali or acidic treatments suggests that the sensitizer is bound to the titania surface not through an ester bond as proposed for VLP_{com}.

Keywords: Carbon-modified titania; Ethylene glycol; Organic sensitizer; Visible light activity

1. Introduction

Carbon modification of titania, often referred to as "carbon-doping", may render this usually only UV sensitive semiconductor photocatalyst also active for visible light photocatalysis. Various modification procedures employing diverse carbon compounds have been reported in the literature. In most cases they consist of thermal treatment of titania or titania precursors with an organic carbon compound at 250–500°C in the presence of air. Typical carbon precursors employed are alcohols [1–3], sugars [4–7], adamantane [8], tetrabutylammonium hydroxide [9], *n*-hexane [10], 2,4-pentadione [11],

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oxalic acid [12], the alkoxide groups of titanium alcoholates [13–17], and even carbonic ink [18]. Another method is oxidative annealing of titanium carbide [19–23]. However, in all cases the nature of the carbon species in the resulting TiO_2–C powders, responsible for Vis light photooxidation of various pollutants, could not be unraveled. Proposals range from carbides [1, 8, 19–24], carbonates [1, 2, 12–16, 23], and aromatic hydrocarbons [4, 6, 10, 12, 14, 17] to oxygen vacancies [25, 26]. Further details are summarized in the reference [27].

All the above proposals were obtained from rather small experimental evidence based on mainly physical data, such as ambiguous carbon 1s binding energies. Contrary to this, we thought that the chemical data, such as stability against acids and bases may afford more valuable information. This was recently confirmed by the finding that the beige carbon-modified commercial titania visible light photocatalyst (VLP_{com}) [28] contains structurally unknown aromatic hydrocarbon compounds responsible for Vis light activity. Surprisingly, treating VLP_{com} with NaOH afforded a dark brown soluble organic photosensitizer ($Sens_{ex}$). The almost colorless residue $VLP_{com,res}$ induced only 18% mineralization of 4-chlorophenol (4-CP), in comparison with 70% observed for VLP_{com}. After re-assembling $Sens_{ex}$ with $VLP_{com,res}$, the resulting powder $VLP_{com,reas}$ had the same quasi-Fermi level of $-0.50\,V$ (*vs*. NHE) and the same Vis light activity in 4-CP mineralization like pristine VLP_{com}. Contrary to this, the much less active residue $VLP_{com,res}$ exhibited a quasi-Fermi level of $-0.56\,V$. From elemental analysis and the presence of intense peaks at 1580 and $1420\,cm^{-1}$ in the IR spectrum it was concluded that $Sens_{ex}$ contains organic carboxylate groups. Standard analysis by chromatography and NMR spectroscopy revealed that $Sens_{ex}$ is a multi-component mixture and all purification attempts failed [27].

However, the results presented above clearly indicate that the Vis light activity of carbon-modified VLP_{com} is due to the presence of covalently attached organic photosensitizers generated during the modification reaction conducted at 250–500°C. The first step of the corresponding mechanism should be complexation of pentaerythritol by under-coordinated titania surface atoms. Corresponding coordination complexes between titania and various polyols are well known in the literature [29, 30]. Subsequent aerial oxidation of the polyol is expected to produce a mixture of carboxylic acids. Esterification of the latter with titania hydroxyl groups eventually affords VLP_{com}. From this, one expects that using ethylene glycol, an alcohol simpler than the employed tetra-alcohol but still capable of forming stable titania chelate complexes, may lead to a more selective modification reaction. This may generate only one unique photosensitizer enabling structural characterization. In the following sections, we report on the preparation of the corresponding modified titania powders, on their photoelectrochemical characterization, photocatalytic activity, and on their stability against alkali and acid treatments. For comparison, pentaerythritol was also employed as a modifier. Ethylene glycol was often used as a structural directing/modifying agent to obtain titania crystals of various morphology [31–37]. Its action is based on the selective formation of labile titanium–ethylene glycol coordination complexes. Only two papers dealing with polyols as modifiers were reported in the literature. In the first one, the modified sample was prepared by stirring a water suspension of commercial TiO_2 and glycerol at room temperature followed by calcination at 300°C [38]. According to the second paper ethylene glycol and citric acid were employed together with titanium isopropoxide in a special sol–gel method [39].

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2. Experimental

Diffuse reflectance spectra were obtained relative to $BaSO_4$ with a Shimadzu UV-Vis recording spectrophotometer equipped with a diffuse reflectance accessory. Samples were prepared by mechanical mixing of 2 g of $BaSO_4$ with 25 mg of the corresponding powder sample. Reproducibility of E_{bg} was better than ±0.05 eV. *Quasi-Fermi levels of electrons* (${}_nE_F{}^*$) were measured according to the literature [40]; 50 mg of catalyst and 10 mg of methylviologen dichloride were suspended in 50 mL of $0.1\,\mathrm{mol\,L^{-1}}$ KNO_3 in a 100 mL two-necked flask. A platinum flag and Ag/AgCl served as working and reference electrodes and a pH meter for tracing the proton concentration. Concentrated HNO_3 and NaOH (0.1, 0.01, and $0.001\,\mathrm{mol\,L^{-1}}$) were used to adjust the pH. The suspension was magnetically stirred and purged with nitrogen throughout the experiment. Before measurement the pH of the suspension was adjusted to pH 2. Irradiation was performed with the full light of an Osram XBO 150 W xenon arc lamp. Stable photovoltages were recordable about 30 min after changing the pH value. The pH_0 values obtained from the inflection points were converted to the Fermi potential at pH 7 by the equation ${}_nE_F{}^*$ (pH 7) $= -0.445\,\mathrm{V} + 0.059\,\mathrm{V}\,(pH_0 - 7)$ [40]. Reproducibility of ${}_nE_F{}^*$ was better than ±0.05 V. Reported values are the average of the three measurements. *Binding energies* were measured by X-ray photoelectron spectroscopy (XPS) with a PHI 5600 XPS instrument employing pressed powder pellets contacted by silver lacquer with an aluminum foil. Argon ion sputtering was performed using a Penning source, Specs PS IQP 10/63 ($p = 10^{-8}$ Torr; voltage = 3.5 kV) and the sputtering rate was estimated by calibration with a SiO_2 standard of known thickness. All XPS spectra were referenced to the C1s peak of adventitious hydrocarbon contamination located at 284.8 eV. Fitting of the XPS data was accomplished using XPSPEAK41 software. A Shirley-type background subtraction was used. X-ray diffractometry (XRD) measurements were performed with a Philips X'Pert PW 3040/60 diffractometer. *Emission and excitation spectra* were recorded by means of the spectrofluorometer *Jasco FP – 6200*. *UV-Vis spectra* were recorded on a Varian, Cary 50, UV-Vis Spectrophotometer. *Elemental analysis* (EuroVector, CHNSO, E.A. 3000 equipped with a GC detector) was conducted by dynamic spontaneous combustion. *Surface areas* were determined by the BET (Brunauer–Emmet–Teller) method using a Gemini 2360 V5.00 instrument.

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2.1. *Preparation of titanium hydroxide and titanium dioxide*

A solution of $0.25\,\mathrm{mol\,L^{-1}}$ $TiOSO_4$ (Alfa Aesar) was prepared by stirring the required quantity of $TiOSO_4$ in 1250 mL of doubly distilled water at room temperature until a clear solution was obtained. After heating to 80°C, a solution of $1.25\,\mathrm{mol\,L^{-1}}$ NaOH was slowly added until a pH of 5.5 was reached. The formed gel was kept at 80°C for 1 h under stirring followed by aging for 24 h at room temperature. Finally, titanium hydroxide was filtered off, washed with water, and dried under air at 70°C. To obtain titania, the required quantity of this powder was calcined in a rotating flask for 1 h at 250°C affording white TiO_{2calc} having a specific area of $68\,\mathrm{m^2\,g^{-1}}$ and anatase structure as indicated by XRD analysis.

2.2. *Preparation of UVLP-EG and TiO_2-EG*

UVLP-EG: 0.12 mL of ethylene glycol p.a. (Acros Organics) was diluted with 4.88 mL of doubly distilled water. Thereafter, the solution was added to 1 g of the commercial TiO_2 powder UVLP 7500 (Kronos Titan GmbH; abbreviated in the following as UVLP), followed by 30 min of sonication. After stirring for 24 h, the suspension was kept for 3 h at 120°C to evaporate water. The dried powder was ground and then calcined in a rotating flask for 1 h at 250°C. To remove inorganic and organic impurities, the powder was washed three times by centrifuging for 15 min in *ca* 50 mL of doubly distilled water. Final drying at 100°C for 1 h afforded beige UVLP-EG having a specific surface area of $175\,m^2\,g^{-1}$ and anatase structure as indicated by XRD analysis.

TiO_2-EG: 1 g of self-prepared titanium hydroxide was used instead of UVLP as described above affording slightly yellow TiO_2-EG having a specific surface area of $133\,m^2\,g^{-1}$ and anatase structure as indicated by XRD analysis.

2.3. *Preparation of $UVLP_{calc}$-EG*

As described above, but UVLP was calcined before use for 1 h at 250°C affording $UVLP_{calc}$ (C = 0.02; H = 0.39%) having a specific surface area of $112\,m^2\,g^{-1}$. After modification as described above, the creamy anatase-based powder $UVLP_{calc}$-EG (C = 0.67; H = 0.38%) was obtained.

2.4. *Preparation of UVLP-PE*

0.11 g of pentaerythritol (98%, Acros Organics) was diluted in 5 mL of doubly distilled water. Thereafter, the solution was added to 1 g of UVLP followed by 30 min of sonication. After stirring for 24 h, the suspension was kept for 3 h at 120°C to evaporate water. The dried powder was ground and then calcined in a rotating flask for 1 h at 250°C. To remove inorganic and organic impurities, the powder was washed as described above. Subsequent drying at 100°C for 1 h afforded brownish UVLP-PE (C = 2.24; H = 0.92%) having anatase structure.

2.5. *Elemental analyses, amounts of mineralization, and photoelectrochemical properties*

Catalyst	C (%)	H (%)	Mineralization (%)	E_{bg} (eV)	${}_nE_F$* (V)	E_{VB} (V)
TiO_{2calc}	0.07	0.56	20	3.06*	−0.59	2.47
TiO_2-EG	0.76	0.96	68	3.04*	−0.58	2.46
TiO_2-EG_{res}	0.67	0.85	37	3.18	−0.52	2.66
UVLP	0.04	1.14	60	3.22	−0.50	2.72
$UVLP_{calc}$	0.02	0.39	21	3.21	−0.53	2.68
UVLP-EG	1.05	0.76	63	3.19	−0.52	2.67
UVLP-EG_{res}	0.42	0.76	75	3.21	−0.55	2.66
UVLP-EG_{reas}	0.41	0.56	60	3.21	−0.55	2.66
UVLP-PE	2.24	0.92	70	2.97*	−0.46	2.51
UVLP-PE_{res}	0.49	0.90	83	3.16	−0.50	2.66

*Apparent bandgap; due to the presence of a broad shoulder the extrapolation of the linear absorption part may contain a large error.

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2.6. *Attempted alkaline desorption of photosensitizer*

5 g of beige UVLP-EG was suspended in 50 mL of doubly distilled water and brought to pH 12 with 0.5 mol L^{-1} NaOH. Thereafter, the suspension was heated for 1 h at 90°C and kept overnight at RT under vigorous stirring. A brown supernatant (Org_{des}) and a beige powder were obtained after centrifugation. The solid was extracted three times using the same procedure and finally washed three times by centrifuging with doubly distilled water in order to remove organic and inorganic impurities affording a beige residue UVLP-EG_{res}, which was dried for 1 h at 100°C. The experiment was repeated as described above, employing only 0.2 g instead of 5 g of UVLP-EG.

As described above, but 0.5 g of UVLP-PE was used. UVLP-PE was extracted only once. After washing and drying the beige residue UVLP-PE_{res} was obtained.

As described above, but 0.3 g of TiO_2-EG was used. TiO_2-EG was extracted only once. After washing and drying the slightly yellow residue TiO_2-EG_{res} was obtained.

2.7. *Attempted acidic desorption of photosensitizer*

0.5 g of UVLP-EG was suspended in 50 mL of doubly distilled water and brought to a pH of ~2 with 1 mol L^{-1} HNO_3. Thereafter, the suspension was heated for 1 h at 90°C and kept overnight at RT under vigorous stirring. A colorless supernatant and beige powder were obtained after centrifugation. The solid was washed three times with doubly distilled water and dried for 1 h at 100°C affording UVLP-$EG_{res,acid}$ ($C = 0.90$; $H = 0.60\%$). Repetition was performed using 0.2 g instead of 0.5 g of UVLP-EG.

2.8. *Attempted re-assembling reaction*

50 mL of the brown extract Org_{des} obtained from the alkaline desorption experiment was acidified to pH~3 with 1 mol L^{-1} HCl. After adding of 1 g of UVLP-EG_{res} the pH of the suspension reached ~5.5. Therefore, it was not necessary to readjust the pH by addition of 1 mol L^{-1} HCl as reported recently in an analogous experiment [27]. Thereafter, the suspension was heated for 1 h at 90°C and stirred overnight at ambient temperature. The powder obtained after centrifugation was dried at 100°C for 1 h, calcined in a rotating flask for 1 h at 250°C, washed as described above, and dried again at 100°C for 1 h affording a beige UVLP-EG_{reas}.

2.9. *Attempted Lewis acid-catalyzed Ti–O–C cleavage*

0.1 g of beige UVLP-EG was suspended in 5 mL of CH_2Cl_2 p.a. (Fisher Scientific) and cooled in an ice bath [41]. Thereafter, 0.3 mL of BBr_3 (Acros Organics) was dropped into the reaction suspension affording an intense yellow solid. After addition of BBr_3, the reaction mixture was heated for 1 h at 80°C. Thereafter, 10 mL of dichloromethane was added and the suspension kept overnight under stirring at ambient temperature. The rest of solvent was removed by keeping for 1 h at 70°C. Thereafter, the residue was washed two times with dichloromethane and two times with doubly distilled water followed by 1 h drying at 70°C. The as-obtained material had a similar beige color like UVLP-EG before the BBr_3 treatment. The reaction was repeated with an excess of boron tribromide to exclude that only surface OH groups may have been reacting.

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In this experiment 0.2 g of UVLP-EG in 20 mL of CH_2Cl_2 p.a. and 2 mL of BBr_3 were used. The obtained residue was washed two times with dichloromethane affording a yellow supernatant, two times with methanol/water, and finally once with an ethanol/water mixture affording colorless washings in all cases. After 1 h drying at 70°C, a beige material was obtained (C = 0.98; H = 1.34%).

2.10. *Photomineralization of 4-CP*

20 mL of a photocatalyst suspension ($2.0\,g\,L^{-1}$) in aqueous 4-CP ($2.5 \times 10^{-4}\,mol\,L^{-1}$) was sonicated for 15 min before irradiating with visible light ($\lambda \geq 455$ nm, Osram XBO 150 W xenon arc lamp) for 3 h in a Solidex glass cuvette. All photocatalyst 4-CP suspensions needed addition of $1\,mol\,L^{-1}$ HCl to obtain a pH of 3.5–4.0, the optimum condition for the degradation process [42]. 2 mL of the suspension was withdrawn with a syringe both before and after 90 and 180 min of irradiation. Thereafter, the samples were filtered through a micropore filter (pore size 0.22 μm, Rotilabo Roth) and the total organic carbon (TOC = total carbon (TC) – total inorganic carbon (IC)) was obtained by measuring TC and IC by means of Shimadzu TC Analyzer TOC-500/5050 with an NDIR optical system detector. Amounts of mineralization given throughout this article refer to 180 min of irradiation time. Reproducibility of TOC values was in the range of ±10%.

2.11. *Photostability test*

A suspension of $2.0\,g\,L^{-1}$ of beige UVLP-EG in 190 mL of $2.5 \times 10^{-4}\,mol\,L^{-1}$ aqueous 4-CP was sonicated for 15 min in a 200 mL immersion lamp apparatus. After measuring the TOC value, the suspension was irradiated for 3 h with filtered light ($1\,mol\,L^{-1}$ solution of sodium nitrite, $\lambda \geq 400$ nm) of a tungsten halogen lamp. Subsequently, the TOC was again measured and new 4-CP solution was added. This procedure was repeated five times resulting in overall six degradation runs. Thereafter, the slightly yellow powder was washed as described above affording $\text{UVLP-EG}_{\text{res,washed}}$ (C = 2.18; H = 0.55%). When this material was employed in the standard photomineralization of 4-CP, it induced a decrease of the TOC value by 48% within 3 h.

3. Results and discussion

3.1. *Preparation and characterization of photocatalysts*

Slightly yellow TiO_2-EG, beige UVLP-EG, and brownish UVLP-PE were obtained by impregnating titanium hydroxide and the commercial titania powder UVLP with aqueous solutions of ethylene glycol and pentaerythritol, respectively, followed by removal of water and subsequent calcination in an open rotating glass flask at 250°C. Increasing the latter temperature to 350°C and 400°C decreased the visible light ($\lambda \geq 455$ nm) photomineralization rate of 4-CP. Elemental analysis revealed carbon contents of 0.76% for TiO_2-EG, 1.05% for UVLP-EG, and 2.24% for UVLP-PE (section 2). As indicated by XRD analysis of these powders and their derivatives

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(*vide infra*) they all are present in the anatase phase. Crystallite sizes of 15, 7, 13, 15, 17, 21, and 15 nm were obtained for TiO_{2calc}, TiO_2-EG, $UVLP_{calc}$, UVLP-EG, UVLP-EG_{res}, UVLP-EG_{reas}, and UVLP-PE, respectively, through application of the Scherrer equation to the diffraction peak at 25.3°. For the matter of comparison UVLP was calcined at 250°C in the absence of any precursor affording $UVLP_{calc}$ containing 0.02% carbon according to elemental analysis.

XPS spectra of $UVLP_{calc}$, UVLP-EG, and UVLP-PE were measured in the range of C1s binding energies. Curve fitting analysis revealed best results when the broad signal of $UVLP_{calc}$ was decomposed into four peaks located at 284.8, 285.6, 286.8, and 289.0 eV. After argon ion sputtering for 3 min, only a very weak signal remains at 286.0 eV. Unfortunately, the same result was obtained also for the modified sample UVLP-EG. Only in the case of UVLP-PE, the intensity of the peak at 285.6 eV observed after sputtering was a little higher. In view of these results, no firm conclusion on the nature of the carbon species is possible. It is noted that due to the relative large errors of up to 0.4 eV occurring in measurements of such binding energies [43], many assignments made in the literature for various carbon species in titania appear as questionable.

The diffuse reflectance spectra of TiO_2-EG, UVLP-EG, and UVLP-PE exhibit a significant absorption in the visible as displayed for the two latter samples in figure 1. It is absent in the case of $UVLP_{calc}$ and TiO_{2calc}. The stronger Vis light absorption of UVLP-PE as compared to UVLP-EG is in accord with its much higher carbon content.

Assuming that TiO_{2calc}, TiO_2-EG, $UVLP_{calc}$, UVLP-EG, and UVLP-PE are indirect semiconductors like anatase, optical bandgaps of 3.06, 3.04, 3.21, 3.19, and 2.97 eV (figure 2), respectively, were obtained for these materials from a plot of the transformed Kubelka–Munk function *versus* the energy of absorbed light [44, 45]. Thus, carbon-modification does not significantly change the bandgap as also recently observed for commercially available VLP_{com} [27].

Measurement of the quasi-Fermi potentials by recording the photovoltage of the semiconductor suspension as a function of pH [40] afforded −0.58, −0.52, and −0.46 V for TiO_2-EG, UVLP-EG, and UVLP-PE at pH 7, respectively. The value of UVLP-PE is more positive by 0.04 V as compared to VLP_{com} suggesting the presence of different sensitizers in the two photocatalysts. UVLP-EG_{res} gave rise to a quasi-Fermi level of −0.55 V (figure 3).

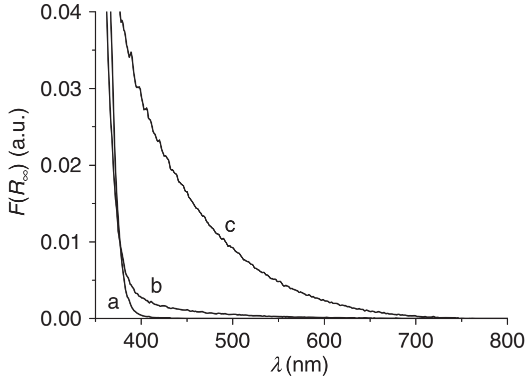

Figure 1. Diffuse reflectance spectra. A: (a) $UVLP_{calc}$, (b) UVLP-EG, and (c) UVLP-PE.

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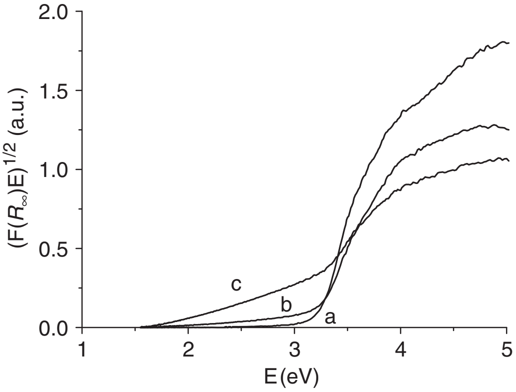

Figure 2. Plot of transformed Kubelka–Munk function *vs.* the energy of the light absorbed of (a) $UVLP_{calc}$, (b) UVLP-EG, and (c) UVLP-PE.

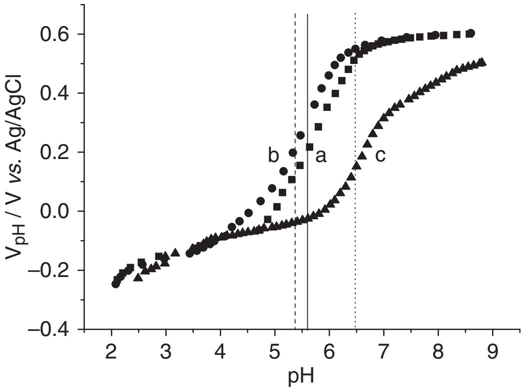

Figure 3. Variation of photovoltage with pH for a suspension of (a) UVLP-EG, (b) $UVLP\text{-}EG_{res}$, and (c) UVLP-PE in the presence of methylviologen dichloride. Solid (UVLP-EG), dashed ($UVLP\text{-}EG_{res}$), and dotted lines (UVLP-PE) indicate the pH value of inflection points from which the quasi-Fermi level can be calculated [40].

3.2. *Photomineralization of 4-CP*

The photocatalytic activity of the novel powders was tested in the mineralization of 4-CP at pH 3.5–4.0, the optimum pH value [42]. Unless otherwise noted, all activities refer to the TOC value measured after irradiating for 3 h at $\lambda \geq 455$ nm. It is further noted that due to the high catalyst concentration of $2\,g\,L^{-1}$, the amount of light absorbed is expected to be about the same in all experiments and, therefore, the reaction rates become comparable. The surprising activity of 60% mineralization measured for the as-received UVLP (C = 0.04%, see section 2.5) is due to formation of a charge-transfer (CT) complex as already observed with other titania samples, such as P25 [46–48]. Since the modified powders were prepared by calcination of UVLP in the presence of the carbon precursor, UVLP was analogously treated at 250°C in the absence of any additive in order to obtain the appropriate reference material $UVLP_{calc}$. The fact that the latter contained only 0.02% C but induced 21% of mineralization (figure 4a) is rationalized again by CT complex formation. Similarly, TiO_{2calc} (C = 0.07%) exhibited

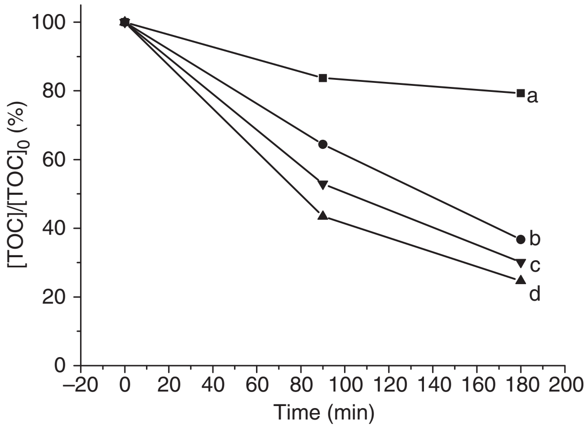

Figure 4. Photomineralization of 4-CP with visible light ($\lambda \geq 455$ nm) in the presence of (a) $UVLP_{calc}$, (b) UVLP-EG, (c) UVLP-EG_{res}, and (d) UVLP-PE.

an activity of 20%. Much higher values of 68%, 63%, and 70% were observed for TiO_2-EG, UVLP-EG, and UVLP-PE, respectively (figure 4b, d). The table in section 2.5 summarizes chemical and physical properties of the various photocatalysts.

3.3. *On the nature of the carbon sensitizer*

As summarized in section 1 we recently found that commercial VLP_{com} contains an alkali-soluble organic photosensitizer that can be easily desorbed [27]. To investigate if similar carbon species are present in the self-prepared photocatalysts TiO_2-EG, UVLP-EG, and UVLP-PE, the powders were subjected to the same and to two new desorption procedures.

After boiling TiO_2-EG at pH 12, a pale brown solution and a slightly yellow residue TiO_2-EG_{res} were obtained. The residue exhibited only 37% 4-CP mineralization as compared to 68% found for pristine TiO_2-EG. When UVLP-EG was analogously treated, again a brown solution (Org_{des}) and a beige residue (UVLP-EG_{res}) were obtained. Although UVLP-EG_{res} contained only 0.42% C as compared to 1.05% C found for UVLP-EG, its mineralization activity of 75% was even a little higher than that of the starting material (63%, figure 4b). Performing the re-assembling reaction gave rise to UVLP-EG_{reas} having about the same activity as UVLP-EG_{res}. In accord with this surprising result is the finding that both powders exhibited the same quasi-Fermi level of −0.55 V and the same carbon content of 0.42%. Thus, different from VLP_{com} [27], the photosensitizer cannot be desorbed from the titania surface through an alkaline treatment. But it could be removed by treating UVLP-EG in the presence of air at 400°C affording UVLP-EG_{400} ($C = 0.11\%$), which displayed no visible light absorption and induced only 9% mineralization, probably due to CT complexation of 4-CP (*vide supra*). The brown color of the desorbed species Org_{des}, therefore, is not related to the photosensitizer responsible for the visible light activity of UVLP-EG but to an impurity, the removal of which leads to a more efficient photocatalyst. Accordingly, different from VLP_{com}, where the Fermi level of the residue is shifted slightly cathodically by 0.06 V [27], it stays constant in the case of UVLP-EG.

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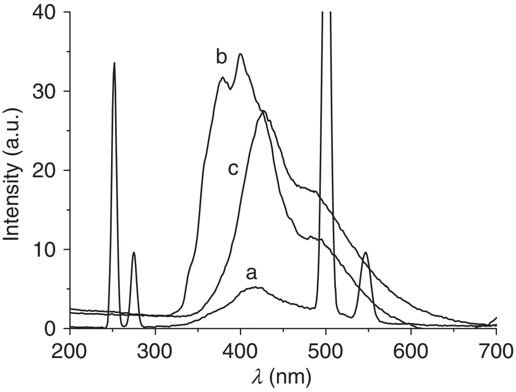

Figure 5. Emission spectra of (a) H_2O employed, (b) $Sens_{ex}$ at pH 12, and (c) Org_{des} at pH 12. $\lambda_{exc} = 254$ nm.

In agreement with the conclusion that the sensitizer could not be desorbed is also the difference in the emission spectra of the two extracts. Whereas the brown solution $Sens_{ex}$ as obtained from VLP_{com} exhibited two maxima at 380 and 400 nm and shoulders at 428 and 488 nm (figure 5b), brown Org_{des} extracted from UVLP-EG showed only one maximum at 428 nm and a shoulder at 488 nm (figure 5c). The fact that the maximum of $Sens_{ex}$ at 380 nm is absent in the spectrum of Org_{des} suggests that this signal originates from the photosensitizer.

Surprisingly, in contrast to VLP_{com} also the activity of the self-prepared pentaerythritol-derived photocatalyst UVLP-PE did not change after a corresponding alkaline desorption treatment. This may be due to the slightly different starting titania materials and differences in the details of the modification procedures. As mentioned above the density of surface hydroxyl groups should significantly influence the structure and reactivity of the initially generated titanium-polyol surface complexes. It seems unlikely that this surface property is identical for the two titania powders. Furthermore, the amount of aerial oxygen available for generation of the carboxylic acid strongly depends on reactor geometry and other technical details. It is very unlikely that they are the same in the commercial and home-made reactor.

This inertness of UVLP-EG and UVLP-PE against alkali treatments suggests that the organic sensitizer is not bound to the titania surface through an Ti–O–C(O)Ar group as proposed for VLP_{com} [27]. An alternative binding could occur *via* a Ti–OAr bond, more susceptible to an electrophilic cleavage. Therefore, UVLP-EG was refluxed in acidic solution of pH 2. However, no significant decrease of activity was observable for the obtained solid residue containing 0.90% C. Even a vigorous treatment with the strong Lewis acid BBr_3 [41] was not successful. The remaining beige residue (C = 0.98%) had about the same activity as the starting material.

These results suggest that the mutual Ti–OAr bond is of unusual inertness or that the organic sensitizer forms a Ti–C bond stable under the applied desorption conditions. Eventually, it may be insoluble under alkaline or acidic conditions and not chemically bound to the titania surface. This seems rather unlikely since removal of surface OH groups by precalcining UVLP at 250°C before the treatment with ethylene glycol decreased the amount of mineralization to 27%, indicating that these groups are involved in the modification reaction.

To address the problem of sensitizer photostability, an 18-h photomineralization of 4-CP in the presence of UVLP-EG was performed in an immersion lamp apparatus. After every third hour the irradiation was interrupted for the TOC measurements followed by addition of a new portion of 4-CP solution and subsequent irradiation and TOC determination. Whereas in the first cycle, 64% of the pollutant was mineralized, only 28% were found after the second 4-CP addition. This decrease continued and the oxidation completely ceased after the fifth addition suggesting photocorrosion of the photocatalyst. Most likely this is due to accumulation of colored intermediates preventing light absorption by the photocatalyst as suggested by a color change from beige to yellow. Accordingly, when the residue after the sixth degradation cycle was washed with water, mineralization increased to 48%.

4. Conclusions

Slightly yellow TiO_2-EG, beige UVLP-EG, and brownish UVLP-PE carbon modified anatase are prepared by calcining titanium hydroxide or the commercial titania powder UVLP at 250°C in the presence of ethylene glycol or pentaerythritol. These surface-modified titania materials photocatalyze the visible light mineralization of 4-CP. Removal of surface hydroxyl groups from titania before the modification process results in a photocatalyst of much lower photocatalytic activity, suggesting that these groups are involved in the reaction with the polyol. Different from the pentaerythritol-derived commercial photocatalyst VLP_{com}, self-prepared UVLP-PE and ethylene glycol derived UVLP-EG contain a sensitizer, which cannot be desorbed from the titania surface either under severe alkaline or acidic reaction conditions. Whereas no significant difference is observable between the diffuse reflectance spectra, quasi-Fermi levels of -0.58, -0.52, and -0.46 V were measured for TiO_2-EG, UVLP-EG, and UVLP-PE, respectively. However, when UVLP-EG is treated at 400°C in the presence of air, the visible light absorption disappears and activity strongly decreases, pointing to oxidation of a carbon sensitizer. Surprisingly, TiO_2-EG as prepared from titanium hydroxide loses a significant part of its activity after alkaline treatment. This emphasizes an important role of the nature of the titania precursor on the stability of carbon-modified titania photocatalysts.

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