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Studies on the Adsorption and Photocatalytic Degradation of an Eu^{III}(TTFA)₃(MePhTerpy) Complex on the TiO₂ Surface

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<u>Highlights</u>

- Eu^{III}(TTFA)₃(MePhTerpy) is adsorbed by the TTFA ligand on the TiO₂ surface.
- Upon UV illumination the TTFA ligand of the Eu^{III}(TTFA)₃(MePhTerpy) complex is degraded into trifluoroacetic acid, 2-thiophenecarboxaldehyde and 2thiophenecarboxylic acid.
- Eu^{III}(TTFA)₃(MePhTerpy) is proposed to be oxidized by photogenerated OH⁻ rather than by holes.

Abstract

The luminescent dye Europium^{III}(thenoyltrifluoroacetone)(4'-(4-methylphenyl)-2,2':6',2"terpyridine) (Eu^{III}(TTFA)₃(MePhTerpy)) has been proposed as a probe molecule for a fast photocatalytic test of TiO₂-materials. For an industrial application of this test method the underlying photocatalytic reaction mechanism and the degradation products of the dye need to be known. Hence, in this study the adsorption and the photocatalytic degradation of the luminescent dye on the TiO₂ surface were investigated by means of ATR-FTIR spectroscopy and GC/MS analysis. The dye is adsorbed by the thenoyltrifluoroacetone (TTFA) ligand on the TiO₂ surface as evinced by the respective ATR-FTIR spectra. It is assumed that TTFA and TiO₂ form hydrogen bonds. Upon UV illumination the ATR-FTIR spectra reveal a degradation of the TTFA ligand forming trifluoroacetic acid (TFAA) and 2thiophenecarboxylic acid (TCA). GC/MS analysis confirms the ATR-FTIR results because TCA and TFAA are also detected here. Additionally, 2-thiophenecarboxaldehyde is observed, which is proposed to be an intermediate that is further oxidized to TCA.

Keywords: Europium complex, luminescence, dye, degradation, TiO₂

Key Words: luminescent europium dye, photocatalytic activity, degradation mechanism, TiO₂, photocatalysis, ATR-FTIR, GC/MS

Introduction

In the last decades the amount of pollutants in air and in water has increased mainly due to the population increase and the industrial growth. Semiconductor photocatalysis might be a sustainable and environmentally friendly solution in order to decrease the amount of these pollutants. Herein, TiO₂ appears to be an ideal photocatalyst, since by UV illumination TiO₂ is able to catalyze the decomposition of organic compounds yielding CO₂ and H₂O and traces of mineral acids as reaction products.[1] Besides its high reactivity, it is a low cost material, it is nontoxic and prevalent. Hence, recently TiO₂ containing building materials in different types and forms such as tiles, paints or concrete have shown great potential.

Several standard methods already exist to test the photocatalytic activity of photocatalytic surfaces such as the degradation of NO_x (ISO 22197-1)[2] or acetaldehyde (ISO 22197-2)[3]. However, such methods require an expensive analytical equipment. Moreover, these setups do not have a high mobility, therefore measuring the photocatalytic activity of building materials outdoors still remains challenging.[4]

Böttger *et al.*[5] developed a new method to test the photocatalytic activity of photocatalytic surfaces based on a luminescent europium complex dye. In this work the dye Europium^{III}(thenoyltrifluoroacetone)(4'-(4-Methylphenyl)-2,2':6',2''-terpyridine) (Eu^{III}(TTFA)₃(MePhTerpy)) was investigated. Its molecular structure is shown in Figure 1. The dye can be excited by UV light at 365 nm, therefore the same excitation can be used to test the photocatalytic activity since both TiO₂ and the dye can be excited at the same wavelength. Upon UV light absorption the organic ligands are excited to the singlet S₁ state, immediately followed by a migration to the triplet state T_1 . Afterwards, the energy is transferred to the Eu³⁺ cation, thus Eu³⁺ is excited. Upon relaxation from the occupied electronic state to the ground state an emission at $\lambda_{max} = 617$ nm is induced.[6,7] When a decomposition of the complex by TiO_2 occurs, the interaction between the ligand and Eu^{3+} is weakened leading to a decrease in the emission intensity that can be detected.[5] Several dyes used for photocatalytic tests are already known from literature such as methyl orange, rhodamine B, or methylene blue (ISO 10678:2010).[8,9] However, using for example the methylene blue degradation as a standard method to test the photocatalytic activity is challenging because several assumptions (e.g. dye purity, pH of the solution or the stirring time) need to be considered, since all these processes influence the bleaching of the dye.[4] Furthermore, these dyes are only applicable to test the photocatalytic activity for water purification, therefore they cannot be applied for air purification tests.



Figure 1: Molecular structure of Eu^{III}(TTFA)₃(MePhTerpy).

Eu^{III}(TTFA)₃(MePhTerpy)[10] can be used as a probe molecule to test the photocatalytic activity of building materials for air purification.[11] The idea is to link the dye on a foil and to bring the latter in contact to the surface of a building material. Upon UV illumination the dye is degraded and a decrease in emission can be detected.

For an industrial application of this dye as a test molecule the reaction mechanism of the decomposition by TiO_2 should be known. Hence, in this work the degradation of the dye was investigated using ATR-FTIR (Attenuated Total Reflection - Fourier Transform Infrared) spectroscopy and GC/MS (Gas chromatography - mass spectrometry) analysis. The obtained results of the measurements were correlated with each other. In this context the adsorption mode of the dye on TiO_2 was figured out and the degradation products were identified. To the best of our knowledge, herein the photocatalytic degradation mechanism of a luminescent europium complex by TiO_2 is investigated for the first time.

Experimental section

Materials

The commercial TiO₂ photocatalyst KRONOClean[®] 7050 was kindly provided by KRONOS[®]. Eu^{III}(TTFA)₃(MePhTerpy) and NaTTFA were synthesized at the Institut für Hochfrequenztechnik at the Technische Universität Braunschweig. Trifluoroacetic acid was supplied by Carl Roth[®] and 2-thiophenecarboxylic acid was purchased from Merck.

TiO₂ film preparation

A suspension of 5.75 g L⁻¹ KRONOClean[®] 7050 in deionized water was sonicated for 15 min in an ultrasonic bath. Subsequently, an aliquot of 400 μ l was placed on a ZnSe crystal and was distributed by gently balancing the crystal. After evaporation of the water, a homogenous film was obtained which had a coverage of 2.3 g m⁻² and a thickness of 1.7 ± 0.3 μ m according to Hug and Sulzberger.[12]

100 μ l of an 1 mM Eu^{III}(TTFA)₃(MePhTerpy) solution in acetonitrile was distributed over the TiO₂ film. After evaporation of acetonitrile, the dry film was analyzed by ATR-FTIR spectroscopy. The sample preparation of the other compounds was similar: 300 μ l TTFA (1 mM), 300 μ l TCA (1 mM) or 100 μ l TFAA (10 mM) in acetonitrile were deposited on the TiO₂ film.

ATR-FTIR spectroscopy

ATR-FTIR spectra were recorded on a Bruker IFS 66 equipped with a deuterated triglycine sulfate (DTGS) detector and an internal reflection element made of ZnSe with an angle of incidence of 45° and 9 reflections on the upper face. The interferometer and the infrared light path in the spectrometer were constantly purged with argon in order to avoid H₂O and CO₂ contamination. Each spectrum was an average of 300 scans with a resolution of 4 cm⁻¹. Before each experiment a blank spectrum of KRONOClean[®] 7050 was taken in the dark. Subsequently, spectra in the dark (2h) and upon UV illumination (6h) with Eu^{III}(TTFA)₃(MePhTerpy) were recorded. The final spectra were obtained by subtraction the blank from the ones with Eu^{III}(TTFA)₃(MePhTerpy). As UV light source a LED lamp was used, supplied from OMICRON with a wavelength of 365 nm and an intensity of 1 mW cm⁻². For equal reaction conditions a closed compartment made of Plexi-Glass[®] (PMMA, Polymethylmethacrylate) was attached to the upper part of the ZnSe crystal (see Figure 2), where a gas flow of 100 ml min⁻¹ (SIERRA[®]) of synthetic air was passed through.



Figure 2: Experimental set up for the ATR-FTIR measurement.

GC/MS analysis

50 mmol NaTTFA in acetonitrile (5 ml) mixed with K7050 (0.4 g/L) were illuminated by UV light (Philips CLEO 75 W) with an intensity of 1 mW cm⁻² for 12 h in the presence of O_2 .

Afterwards the mixture was filtrated in order to remove TiO₂. The liquid extract was analyzed by GC/MS using a GCMS-QP5000 (Shimadzu) coupled with an AOC-5000 Plus auto sampler and employing parameters based on Method 8270D (SW-846): Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS). A capillary RXI[®]-5MS column (30 m × 0.32 mm, dF= 1 μ m, Restek) was used to perform the separation procedure. In a typical analysis 2 μ l of the liquid extract were injected in a split/splitless injector of the GC/MS system. The column oven was held at 40 °C for 4 min, followed by an increase in a rate of 10 °C/min to reach a final temperature of 270 °C. The temperature of both, the injection and the MS interface was adjusted to 280 °C. The MS scanned from 35 m/z to 500 m/z.

For the adsorption experiments solutions of TFAA (150 mmol) and TCA (25 mmol) in acetonitrile were prepared and analyzed by GC and GC/MS. K7050 (0.4 g/L) was added then to the solutions in order to allow TCA and TFAA to adsorb on the TiO₂ surface. After 2 h in the dark the suspensions were filtrated and the filtrate was analyzed again by GC and GC/MS. The GC used was a Shimadzu GC-2010 equipped with an AOC-20i autosampler und with a Rtx-5 (30m x 025 mm ID x 0.25 um) capillary column from Restek. A split injection mode was applied at 280 °C with a split ratio of 10 and a total flow of 19.1 ml/min with helium as carrier gas. The temperature of the column had been kept constant at 40 °C for 4 min before it was increased to 270 °C with a rate of 10 °C/min. TFAA was detected at a temperature of 300 °C by a flame ionization detector (FID).

Results and Discussion

In Figure 3 the ATR-FTIR spectrum (black) of the dye adsorbed on the TiO₂ surface is shown in the wavenumber range between 1100 and 1800 cm⁻¹. This fingerprint region has been analyzed since here the characteristic bands corresponding to the dye occur. Different bands are observed which are referred to specific molecular vibrations of the dye as listed in Table 1. The bands can be assigned to molecular vibrations of the TTFA ligand such as $v(CF_3)$, v(C-O) and $v(C_4H_3S)$. Since only the bands for TTFA appear, it is assumed that the dye is adsorbed by the TTFA ligand on the TiO₂ surface. For verification of this assumption, sodium thenovltrifluoroacetone (NaTTFA) was deposited on the anatase film and an ATR-FTIR spectrum was recorded (see Figure 3, red). The spectra of NaTTFA and the dye correlate with each other exhibiting equal band positions. Apparently, the dye is adsorbed on the TiO₂ surface by the TTFA ligand. A schematic illustration of the dye interacting with the TiO₂ surface is shown in Figure 4.[13] It is assumed that the dye shows rather a physical adsorption than a chemisorption on the TiO₂ surface due to steric hindrance and due to the molecular structure of the dye. As illustrated in Figure 4 a polar H-atom of the hydroxylated TiO₂ surface and a polar F-atom of the CF₃ group form hydrogen-bonds. Furthermore, the H-atom (marked in red) of the CH is acidic, because CH is located between two electron-withdrawing carbonyl groups causing a high negative inductive effect. Thus, the polarity of the H-atom increases favoring a hydrogen-bond formation to the O-atom of a hydroxyl group from the TiO₂ surface. Distinct polar atoms of the TTFA ligand form hydrogen-bonds with the OH groups of the TiO₂ surface, while the nonpolar MePhTerpy ligand has less contact to the polar TiO₂ surface.



Figure 3: Comparison between the ATR-FTIR spectra of the dye (black) and NaTTFA (red) deposited on the anatase film in the dark.

Table 1: Vibrational frequencies and mode assignments of the observed FTIR bands (cm⁻¹) of the dye and NaTTFA deposited on the anatase film in the dark.

Position / cm ⁻¹	Assignment[14,15]
1145	v(CF ₃) TTFA
1203	v(CF3) TTFA
1307	v(CF3) TTFA
1409	v(C4H3S) TTFA
1544	v(C ₄ H ₃ S) TTFA
1604	v(C-O) TTFA



Figure 4: Proposed adsorption mode of the dye on the TiO_2 surface based on the ATR-FTIR spectra.

As adsorption mode of the dye on the TiO₂ surface was clarified, the decomposition of the dye and the formation of intermediates and products were investigated by ATR-FTIR spectroscopy upon UV-light illumination. For this purpose the complex was deposited on the TiO₂ surface and was illuminated by UV light for 6 h. Figure 5 illustrates the ATR-FTIR spectra of the dye before (red) and after 6 h of UV illumination (black). The intensity of the bands characteristic for distinct molecular vibrations of the dye such as the v(C-O) at 1604 cm⁻¹, the v(C₄H₃S) at 1544 cm⁻¹ and the v(CF₃) at 1307 cm⁻¹ strongly decrease indicating a nearly complete decomposition of the TTFA ligand. Furthermore, the intensity of the band of v(CF₃) at 1203 cm⁻¹ increases and the band maximum of v(CF₃) at 1145 cm⁻¹ is shifted to higher wavenumbers. Additionally, a new band appears at ~1670 cm⁻¹. These changes are highlighted by arrows in Figure 5. The results indicate a decomposition of the TTFA ligand accompanied by the formation of intermediates and products on the anatase surface.



Figure 5: ATR-FTIR spectra of the dye deposited on the anatase film before (red) and after 6 h of UV ilumination (black). The arrows show the formation of intermediates/products, indicated by a shift of a band, an increase in intensity of bands and the new appearance of bands.

Potential reaction products formed from the complex were deposited on the TiO₂ surface and ATR-FTIR spectra were recorded in order to compare them with the spectrum of the dye. Figure 6 demonstrates the spectrum of the dye after 6 h of UV illumination, of trifluoroacetic acid (TFAA) and of thiophenecarboxylic acid (TCA). A correlation between the spectrum of TFAA and the dye is observed because the v(CF₃) bands at 1150 cm⁻¹ and 1203 cm⁻¹ appear similar in position and in intensity. Furthermore, the band at 1670 cm⁻¹ can be probably referred to the v(C-O) of TFAA.[16] Consequently, the formation of TFAA as a product of the dye degradation could be proven which is accumulated on the anatase surface. When comparing the spectra of the dye before and after UV illumination (see Figure 5) a small increase in intensity at ~1380 cm⁻¹ and at ~1420 cm⁻¹ is observed. These bands can be referred to TCA (see Figure 6).[17] However, a clear correlation between TCA and the dye is difficult because of the small changes in intensity of the bands of the dye.



Figure 6: ATR-FTIR spectra of the dye after 6 h upon UV illumination, of TFAA and of TCA deposited on the anatase film.

For the identification of the further reaction products GC/MS measurements were performed. The ATR-FTIR analysis already evidenced that the TTFA ligand of the dye was decomposed, therefore a reaction suspension containing NaTTFA and TiO₂ in acetonitrile was illuminated by UV light for 12 h. Subsequently, the filtrated liquid extract was analyzed by GC/MS. For comparison a liquid sample before UV illumination was also analyzed by GC/MS. In Figure 7 the GC/MS chromatograms of the liquid extract before (inset) and after UV illumination are shown. The peaks separated by GC were further analyzed by mass spectrometry to assign them to the related compounds. The MS spectral patterns were compared with standard mass spectra of the National Institute of Standards and Technology (NIST) library. The corresponding mass spectra together with the observed compounds are shown in Figure 8. Table 2 presents an overview of the different degradation products of NaTTFA determined by the GC/MS analysis, their retention times and their spectral matching to the mass spectra of the NIST library. The peak in the inset as well as the one with a retention time (RT) of 15.7 min in Figure 7 is referred to the educt TTFA because the mass spectra highly correlate with the standard TTFA (see Table 2). After 12 h of UV illumination the intensity of the TTFA peak strongly decreases from 40 to 1 revealing the photocatalytic degradation of TTFA. The most intense peak in the GC/MS chromatogram with a RT of 15.3 min is referred to TCA with a high similarity of 87 % of the mass spectra of the compound and the standard TCA. Hence, the GC/MS analysis confirms the assumption derived from the ATR-FTIR results that TCA is formed as a degradation product. The second intense peak that elutes at a RT of 11.1 min shows matching with 2-thiophenecarboxaldehyde. It is assumed, that 2thiophenecarboxaldehyde is an intermediate which can be oxidized forming TCA. Furthermore, at a RT of 9.6 min a peak with small intensity is observed showing the highest

similarity to TFAA. Apparently both ATR-FTIR and GC/MS analyses evince the formation of TFAA. TFAA seems to be strongly adsorbed on the TiO₂ surface while TCA does not show such a high interaction because the intensity of the peaks observed by GC/MS is much smaller for TFAA than for TCA. For verification of these assumptions, adsorption experiments in the dark with TCA and TFAA were performed. For this purpose solutions of TCA (25 mmol) and TFAA (150 mmol) in acetonitrile were prepared and analyzed by GC/MS and GC, then TiO₂ was added allowing TCA and TFAA to adsorb on the TiO₂ surface. After 2 h in the dark the suspensions were filtrated and the filtrate was analyzed again by GC/MS and GC. When comparing the peaks before and after the dark adsorption (see Figure S1 and Figure S2), the intensity of the peak of TFAA disappears after the dark adsorption therefore confirming the ATR-FTIR results of a strong adsorption of TFAA on the TiO₂ surface. The intensity of the peak of TCA also decreases to 32 % of its original value after the dark adsorption, indicating a partially adsorption of TCA on the TiO₂ surface. As illustrated in Figure 9 TFAA and TCA are both probably adsorbed in a bidentate coordination on the TiO₂ surface.[18,19] However, TFAA is a rather small molecule having one polar CF₃ group left, while TCA has a nonpolar thiophene rest which should not interact with the polar surface. Hence, the interaction between TFAA and the TiO₂ surface is stronger as compared to that of TCA with TiO₂.



Figure 7: Gas chromatogram of NaTTFA before (inset) and after UV illumination for 12 h.



Figure 8: Mass spectra of TFAA (RT 9.6 min), 2-thiophenecarboxyaldehyde (RT 11.1 min), TCA (RT 15.3 min) and TTFA (RT 15.7 min).

Retention	Name	Chemical	Molecular	Similarity
Time / min		Structure	weight / gmol ⁻¹	
9.6	Trifluoroacetic acid	F ₃ C OH	114	81
11.1	2-Thiophene- carboxaldehyde	S H	112	77
15.3	2-Thiophene- carboxylic acid	S OH	128	87
15.7	Thenoyltrifluoro- acetone	CF ₃	222	87

Table 2: Degradation products of NaTTFA identified by GC/MS.

Figure 9 summarizes the ATR-FTIR and GC/MS results in form of a reaction scheme. It is most likely that upon UV illumination the dye is oxidized by the OH⁻ radicals rather than directly by holes since in the latter case a strong interaction between the dye and the TiO₂ surface is required.[20] Accordingly, the generated OH⁻ first attacks the acidic CH group of the TTFA ligand forming a TTFA radical. In the next reaction steps it is assumed that OH⁻, O₂⁻⁻ and O₂ are involved in the reactions attacking the carbonyl groups rather than the thiophene, because the detected reaction intermediates still contain thiophene. In addition CO₂ should be released because TTFA contains one C-atom more than TFAA and TCA.



Figure 9: Photocatalytic degradation of the dye in the presence of TiO₂ forming TCA, TFAA and 2-thiophenecarboxaldehyde as concluded from the ATR-FTIR and GC/MS results.

Conclusions

In the present study, for the first time, the adsorption and the photocatalytic degradation of the luminescent dye Eu^{III}(TTFA)₃(MePhTerpy) on the TiO₂ surface was investigated by ATR-FTIR spectroscopy and by GC/MS analysis. The dye is found to be adsorbed through the TTFA ligand on the anatase surface. It is most likely that distinct polar atoms of the TTFA ligand form hydrogen bonds with OH groups of the TiO₂ surface. Upon UV illumination the ATR-FTIR spectra reveal a decomposition of the TTFA to TFAA and TCA, with the former being generated predominantly. The formation of these products could be confirmed by GC/MS analysis. Furthermore, 2-thiophenecarboxaldehyde is identified which is proposed to be an intermediate that is further oxidized forming TCA. TFAA is detected only to a small extent because it is strongly adsorbed on the TiO₂ surface. It is proposed here that upon UV illumination the dye is not directly oxidized by holes, but that rather the photogenerated OH⁻ favorably attack the acidic CH group. In the next step, an oxidative attack of the carbonyl group of the TTFA ligand occurs. Additionally, CO₂ should be generated through the decarboxylation of TTFA which has one C-atom more than the products TFAA and TCA.

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