Iron(III) Phthalocyanine-Modified Titanium Dioxide: A Novel Photocatalyst for the Enhanced Photodegradation of Organic Pollutants

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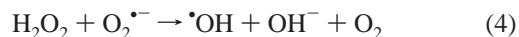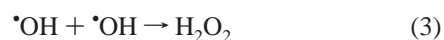
Iron(III) phthalocyanine modified titanium dioxide, $Fe^{III}Pc/TiO_2$, photocatalyst was prepared. The photocatalyst reveals enhanced activity for the degradation of organic pollutants as compared to nonmodified TiO_2. The photodegradation of *p*-aminobenzoic acid (**1**), *p*-nitrobenzoic acid (**2**), *p*-chlorophenoxyacetic acid (**3**), salicylic acid (**4**), and aniline (**5**) was found to be significantly enhanced in the presence of the $Fe^{III}Pc/TiO_2$ photocatalyst as compared with the nonmodified TiO_2 photocatalyst. The enhanced activity of $Fe^{III}Pc/TiO_2$ is attributed to the cooperative functions of the two components of the photocatalyst, Iron(III) phthalocyanine and the TiO_2 semiconductor in the generation of $^{\bullet}OH$ radicals.

Photocatalysis has been an area of rapidly growing interest over the past decade.[1–5] Semiconductor photocatalysis has been used successfully for water, air, and wastewater treatment.[6–9] The application of illuminated semiconductors for the remediation of contaminants has been used for a variety of compounds[10–15] such as alkanes, alkenes, phenols, aromatic carboxylic acids, dyes, surfactants, and pesticides as well as for the reductive deposition of heavy metals (e.g., Pt^{4+}, Au^{3+}, Rh^{3+}, Cr^{6+}, etc.) from aqueous solutions to surfaces.[16–19]

Several semiconductors have been employed as photocatalysts,[20] but TiO_2 has proven to be the benchmark semiconductor for effective degradation of organic pollutants. Photoexcitation of the semiconductor with light of energy that matches the band gap energy yields the electron–hole pair. The excited-state conduction band electrons can recombine with the holes and dissipate the input energy, react with electron donors and electron acceptors adsorbed on the semiconductor surface, or get trapped in surface states. For the effective utilization of the electron–hole pair in secondary catalytic transformations, their transfer to chemical substrates at the semiconductor interface is important. Hence, in order to compete with the electron–hole recombination and trap the conduction band electron or the valence band hole, the electron acceptor or donor should be confined to the semiconductor surface. Several methods have been suggested to control the interfacial electron transfer at the semiconductor–electrolyte interface. These include immobilization of semiconductor photocatalysts in redox-functionalized polymers,[21,22] electrostatic association of electron acceptors at the semiconductor surface,[23] and application of receptor-functionalized semiconductors.[24]

The mechanism of TiO_2 photocatalyzed reactions has been a subject of extensive research.[25–28] Although the detailed mechanism differs from one pollutant to another, it has been widely recognized that superoxide and, specifically, hydroxyl radicals $^{\bullet}OH$ act as active reagents for the mineralization of the organic compounds.[29] The radicals are formed by the scavenging of the electron–hole pair by molecular oxygen and water, eqs 1–4.
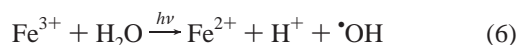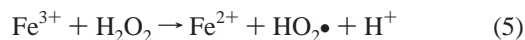
$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet-} \tag{1}$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{3}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{4}$$

Insertion of $^{\bullet}OH$ radicals into C–H bonds leads ultimately to the complete mineralization of the organic substrate. Indeed, complete mineralization of a variety of organic compounds, such as phenols, hydrocarbons, carboxylic acids, and chlorinated aliphatic and olefinic compounds, has been realized.[30–34] The reactive hydroxyl radicals can, however, recombine to yield H_2O_2. This leads to incomplete mineralization of the pollutant. Enhanced degradation of the pollutant can be realized by preconcentration of the pollutant at the semiconductor surface or by effective utilization of the $^{\bullet}OH$ radicals. Concentration of organic pollutants at the semiconductor surface was achieved by surface modification of the photocatalyst with chelating agents[35] or by the immobilization of hydrophobic layers.[34] Also, surface modification of the catalyst with electron groups that concentrate electron-donor pollutants via the formation of donor–acceptor complexes,[36] and the selective doping of TiO_2 with lanthanide oxides,[37] proved to concentrate the pollutants at the photocatalyst surface and to enhance their degradation yields.

A further means to increase the degradation yields of organic pollutants involves the enhanced production of hydroxyl radicals,

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which are the reactive species in the degradation of organic pollutants. The addition of hydrogen peroxide considerably enhanced the photodegradation rate of phenols and organohalide compounds in a suspension of titanium dioxide.[38-40] The increase in the rate was attributed to the increase in the number of hydroxyl radicals formed on illuminated TiO_2. Another method to realize the enhanced production of hydroxyl radicals involves the application of the photo-Fenton reaction.[41-43] The mechanism of the Fenton reaction (eq 5) has been known for some time.[44] The reaction was, however, found to be enhanced in the presence of UV/vis irradiation, i.e., photo-Fenton reaction (eq 6). By this reaction, hydroxyl radicals are generated via photoinduced electron transfer from water to excited Fe^{3+}.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad (5)$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^\bullet OH \qquad (6)$$

The Fe^{2+} generated by the photoinduced electron transfer, eq 6, can additionally produce $^\bullet OH$ radicals via the dark reduction of hydrogen peroxide, eq 7.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (7)$$
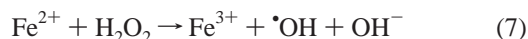
The photocatalytic activity of TiO_2 is limited only to the UV region, and hence solar energy cannot be effectively harnessed. Dye sensitization of TiO_2 extends the light absorption and conversion capacity of TiO_2 to the visible spectral region. Several dyes, exhibiting high absorptivity in the visible region, such as ruthenium(II) trisbipyridine, rhodamine, cyanines, and metal phthalocyanines, have been used as sensitizers for TiO_2.[45-48] Photosensitization of TiO_2 by a dye proceeds by the initial excitation of the dye, eq 8, followed by electron injection to the semiconductor conduction band, eq 9.

$$dye \xrightarrow{h\nu} {}^*dye \qquad (8)$$

$${}^*dye + (SC) \rightarrow dye^+ + e^-_{cb}(SC) \qquad (9)$$
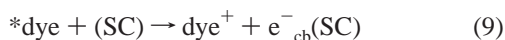
Metallophthalocyanines are very stable metal complexes and a number of properties contribute to their extraordinary versatility.[49,50] These include their redox activity, high thermal stability, and nontoxicity. Potential applications include electrochromic devices, sensors for industrial and environmental applications, and photocatalytic processes, including solar energy conversion.[51-54] In fact, metallophthalocyanines such as iron(III) phthalocyanine or manganese(III) phthalocyanine were employed for the catalyzed oxidation of organic pollutants in the presence of H_2O_2.[55,56] For example, the oxidation of trichlorophenol by H_2O_2 was promoted by iron(III) phthalocyanine.[57] It was suggested that oxene type intermediates such as Fe(IV)=O or Fe(V)=O phthalocyanines (metal oxene intermediates) or Fe(III)−OH phthalocyanine (metal peroxo intermediate) act as the reactive species in the mineralization of the organic compounds.[57] A further aspect relates to the possibility for axial ligation of electron donor functionalities to the central Fe(III) ion of the metal phthalocyanine. This enables the concentration of the organic pollutant at the photocatalytic interface. Thus, the incorporation of iron phthalocyanine in a TiO_2 matrix could enhance the photostimulated degradation of a pollutant by several complementary means: (i) The iron(III) phthalocyanine could participate in photo-Fenton type reactions that enhance the photoinduced formation of $^\bullet OH$. (ii) The iron-(III) phthalocyanine could act as a cocatalyst in the TiO_2-

SCHEME 1: Preparation of $Fe^{III}Pc/TiO_2$ Photocatalyst by the Sol−Gel Method
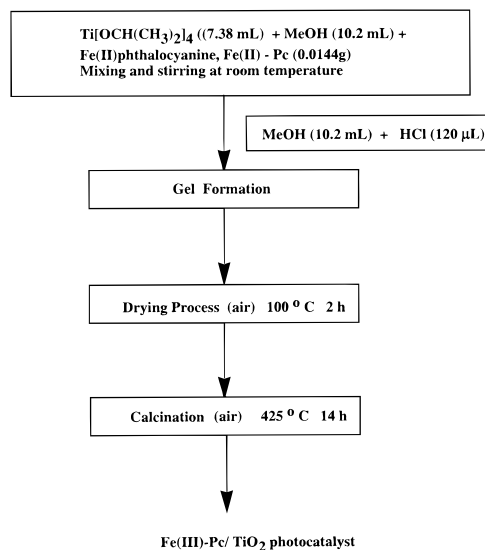
stimulated photodegradation of pollutants. That is, light-induced production of H_2O_2 by the TiO_2 excitation (via the dimerization of $^\bullet OH$) yields the reactant for the iron(III) phthalocyanine-catalyzed oxidation of the organic pollutant. (iii) Axial ligation of the pollutant to the metal ion of iron(III) phthalocyanine concentrates the pollutant at the catalyst.

Here, we wish to report on the preparation of a novel iron-(III) phthalocyanine/TiO_2 photocatalyst. The photocatalyst reveals enhanced photocatalytic activities as compared to nonmodified TiO_2 for the degradation of a series of organic pollutants. The iron(III) phthalocyanine is incorporated into a TiO_2 gel that is further calcined to yield the active photocatalyst.

Experimental Section

The nonmodified TiO_2 and the iron(III) phthalocyanine-modified TiO_2 catalyst were prepared as described in Scheme 1. A sol of titanium(IV) isopropoxide, 7.38 mL in 10 mL methanol, was prepared. After 15 min, a solution that contained 10 mL of methanol and concentrated aqueous HCl, 120 μL, was added slowly to the sol and the mixture was allowed to gel for 60 min. The resulting gel was dried at 100 °C for 2 h. The resulting powder was calcined by heating to 425 °C for 14 h in air. The iron(III) phthalocyanine-modified TiO_2 catalyst was prepared by the sol−gel method as described above, except that iron(II) phthalocyanine was dissolved in the sol prior to the formation of the gel. The gel obtained was calcined to the anatase form in an identical manner as described for the nonmodified TiO_2 catalyst.

The X-ray diffractograms of the calcined samples were recorded on a Philips PW 1050 powder diffractometer. The diffraction patterns were recorded at room temperature by using Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å) of the samples. A scanning speed of 2 deg/min and a chart speed of 13 mm/deg were generally employed.

The surface area of the iron(III) phthalocyanine-modified TiO_2 and the nonmodified TiO_2 catalyst were measured by nitrogen adsorption at −196 °C by the dynamic BET method[58] using a Micromeritics II 2370 surface area analyzer. The transmission electron micrographs of the samples were recorded with a JEOL, JEM-100 CX, electron microscope operating at an accelerating voltage of 80 kV.

The EPR spectra were recorded at 25 °C, using a Bruker 200D spectrometer operating in the X-band, interfaced with a Stelar

software to a PC−IBM computer for data aquisition and handling. The temperature was controlled by using a Bruker ST 100/700 variable-temperature assembly. Magnetic parameters were measured by field calibration with the DPPH radical ($g = 2.0036$). The accuracy of the reported magnetic parameters are $A_{ii} = \pm 1.0 \times 10^{-4}$ cm^{-1} and $g_{ii} = \pm 0.001$.

Photochemical degradations of organic substrates *p*-aminobenzoic acid (**1**), *p*-nitrobenzoic acid (**2**), *p*-chlorophenoxyacetic acid (**3**), salicylic acid (**4**), and aniline (**5**) were examined.
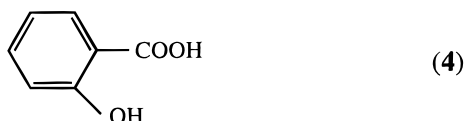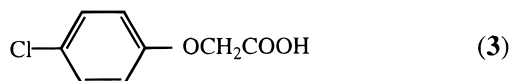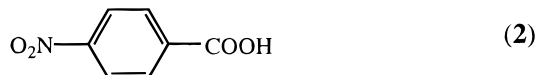
Aqueous solutions of the respective pollutant, 9.6×10^{-5} to 4.2×10^{-4} M, and 2.0−2.5 mg of the respective photocatalyst were placed in a quartz cuvette. The suspension was irradiated with a 200 W Xe (Hg) lamp (Oriel). The cuvette was purged with oxygen during irradiation. After irradiation, the suspension was filtered and the solution was analyzed spectroscopically (Uvikon-860, Kontron spectrophotometer). Although the surface areas of the iron(III) phthalocyanine modified TiO$_2$ and the bare, nonmodified TiO$_2$ are almost identical, we normalized the degradation yields of **1**−**5** according to the respective surface areas.

Adsorption of the organic substrate onto the modified and the nonmodified TiO$_2$ was examined by stirring 100 mg of the catalyst in 2 mL of appropriate concentrations of the substrates in the dark. After equilibration for 1 h, the catalyst was filtered, and the concentration of the organic substrate in the aqueous solution was determined spectroscopically. The adsorption isotherm was analyzed in terms of the Langmuir theory.

DOC Analyses. The analysis of DOC (dissolved organic carbon) was carried out by using an Dohrmann DC-190 TOC (total organic carbon) analyzer ($T = 680$ °C) from Rosemount Analytical. The organic components were oxidized in an oxygen atmosphere at a platinum/alumina contact. The amount of carbon dioxide formed was measured by using a nondispersive IR detector. The (TOC) total organic carbon content was analyzed in this manner and the inorganic carbon content was subtracted from this value. The latter is obtained by treating the samples with concentrated phosphoric acid. The calibration was performed by using salicylic acid, oxalic acid, and potassium hydrophthalate (KHP). All calibration samples could be fitted with a linear calibration curve. The samples were injected three consecutive times (injection volume, 50 μL) and the average values are reported.

GC-MS/FTIR Analysis. For the qualitative and quantitative analysis of the reaction products generated during the photolysis experiments, the samples (2 μL) were injected into a GC (HP 5971A MSD, mass selective detector), coupled with a HP 5965B ID (infrared detector). An HP−INNOWAX capillary column (cross-linked poly(ethylene glycol)) was employed. All reaction products were identified by a combination of MS and FTIR spectroscopy in comparison with analytical databases. Furthermore, the calibration curves for the compounds investigated were also investigated. In all cases, linear dependence of both MS and FTIR areas were obtained.

Results and Discussion

The iron(III) phthalocyanine-modified TiO$_2$ and the non-modified TiO$_2$ were prepared by the method outlined in Scheme 1. Hydrolysis of titanium(IV) isopropoxide in the presence of iron(II)phthalocyanine, Fe^{II}Pc, yields a gel.[59,60] After drying and calcination, a yellow powder that corresponds to the Fe^{III}-Pc/TiO$_2$ photocatalyst was obtained. From the amount of titanium(IV) isopropoxide and iron(II) phthalocyanine employed in the preparation of the sol, the molar ratio of Ti(IV):Fe(III) is ca. 850. The surface area of the iron(III) phthalocyanine-modified TiO$_2$ and the nonmodified TiO$_2$ are 75.4 and 78.1 m^2/g, respectively. The TEM pictures indicate the particle sizes to be in the range 40−60 nm for the iron(III) phthalocyanine-modified TiO$_2$ and 40−80 nm for the nonmodified TiO$_2$, respectively.

The X-ray diffractograms of the iron(III) phthalocyanine-modified TiO$_2$ reveal the presence of only the anatase phase, whereas in the case of the nonmodified TiO$_2$, the anatase phase is the major constituent of the photocatalyst (ca. 80%) accompanied by a rutile phase (ca. 20%).

EPR measurements indicate the presence of iron(III) phthalocyanine in the resulting iron(III) phthalocyanine-modified TiO$_2$ photocatalyst.

The Fe^{III}Pc/TiO$_2$ photocatalyst was used to study the photodegradation of a series of organic aromatic compounds in aqueous solutions, e.g., *p*-aminobenzoic acid (**1**), *p*-nitrobenzoic acid (**2**), *p*-chlorophenoxyacetic acid (**3**), salicylic acid (**4**), and aniline (**5**). The effectiveness of the degradation of these substrates by the Fe^{III}Pc/TiO$_2$ photocatalyst was compared to the photodegradation yields of these substrates by nonmodified TiO$_2$. Figure 1A shows the absorbance spectra of *p*-aminobenzoic acid (**1**) solution at time intervals of irradiation with the nonmodified photocatalyst. After ca. 15 min of irradiation, the absorbance band of **1** decreases. At longer irradiation times (30 and 60 min) the absorbance of the solution decreases further and the maxima are shifted to $\lambda = 260$ nm. This behavior of the solution absorptivity is consistent with a photoinduced degradation of **1** that generates intermediates. Figure 1B shows the degradation of **1** in the presence of Fe^{III}Pc/TiO$_2$ photocatalyst. The substrate **1** is degraded at an impressive rate in the presence of iron(III) phthalocyanine-modified TiO$_2$ catalyst as compared to the nonmodified TiO$_2$ catalyst. For example, after 60 min of irradiation, only 50% of **1** is degraded by the nonmodified TiO$_2$ catalyst, whereas complete mineralization is achieved by the iron(III) phthalocyanine-modified TiO$_2$ catalyst.
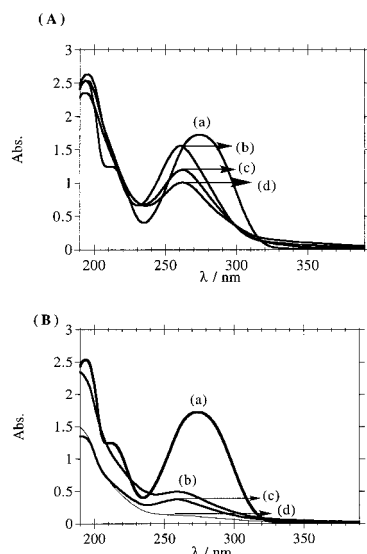
(A)

(B)

Figure 1. (A) Absorption spectra of an aqueous *p*-aminobenzoic acid (**1**) solution (9.6×10^{-5} M) (a) before irradiation, (b) after 15 min of irradiation, (c) after 30 min of irradiation, and (d) after 60 min of irradiation in the presence of nonmodified TiO$_2$ photocatalyst (2.4 mg in 2.5 mL of solution). (B) Absorption spectra of an aqueous *p*-aminobenzoic acid (**1**) solution (9.6×10^{-5} M) (a) before irradiation, (b) after 15 min of irradiation, (c) after 30 min of irradiation, and (d) after 60 min of irradiation in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst (2.5 mg in 2.5 mL of solution).

TABLE 1: GC-MS Analysis of the Photoirradiated Solutions at Different Time Intervals of Illumination

catalyst	irradiation time, min	*p*-aminobenzoic acid (**1**),[a] ppm	salicylic acid (**4**),[a] ppm	aniline (**5**),[a] ppm
			substrate	
Fe^{III}Pc/TiO$_2$	0	14.2 (12.5)	33.9 (34.5)	40.8 (42.0)
	15	8.5 (10.5)	ND	28.7 (37.5)
	30	3.4 (8.0)	12.5 (24.5)	21.5 (32.5)
	60	0 (5.0)	0 (10.5)	5.2 (24.5)
TiO$_2$	0	14.2 (12.5)	33.9 (34.5)	40.8 (42.0)
	15	11.3 (13.0)	30.8 (35.0)	ND
	30	8.6 (11.0)	25.5 (32.5)	34.5 (40.0)
	60	5.4 (10.5)	17.4 (26.0)	29.4 (37.0)

[a] Determined by GC-MS analyses, in bracket DOC values. ND = not determined.

The concentrations of the solution were also monitored by GC-MS analyses. An excellent correlation was observed between the results obtained from UV−vis spectra and GC-MS studies. Table 1 shows the results obtained from GC-MS studies for the degradation of *p*-aminobenzoic acid (**1**). It is observed that after 60 min of irradiation, complete mineralization is achieved by the iron(III) phthalocyanine-modified TiO$_2$ catalyst, whereas in the presence of nonmodified TiO$_2$ catalyst, the concentration of **1** after 60 min of irradiation is 5.4 ppm, indicating that only ca. 60% is degraded.

The enhanced photodegradation of organic substrates by the Fe^{III}Pc/TiO$_2$ photocatalyst was also observed for the other organic substrates **2**−**5**. Photoirradiation of *p*-nitrobenzoic acid (**2**) with the Fe^{III}Pc/TiO$_2$ catalyst for 60 min leads to ca. 83% degradation of the substrate, whereas the nonmodified TiO$_2$ effects only 32% of the degradation. Similarly, the photodegradation of *p*-chlorophenoxyacetic acid (**3**) and salicylic acid (**4**) is substantially faster in the presence of the modified catalyst. Figure 2 shows the absorption spectra of the aqueous solution of *p*-chlorophenoxyacetic acid (**3**) upon irradiation in the presence of Fe^{III}Pc/TiO$_2$ and the nonmodified TiO$_2$ catalyst. After 60 min of irradiation in the presence of Fe^{III}Pc/TiO$_2$, ca.
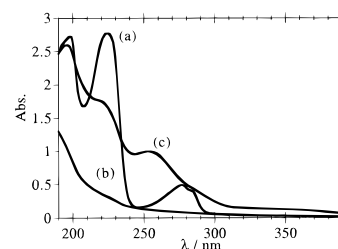

Figure 2. Absorption spectra of an aqueous solution of *p*-chlorophenoxyacetic acid (**3**) (3.0×10^{-4} M) (a) before irradiation, (b) after 60 min of irradiation in the presence of Fe(III)phthalocyanine-modified-TiO$_2$ photocatalyst, Fe^{III}Pc/TiO$_2$, and (c) after 60 min of irradiation in the presence of the nonmodified TiO$_2$ photocatalyst. In all experiments 2.2−2.5 mg of the respective catalyst in 2.5 mL of solution were used.

Figure 3. Absorption spectra of an aqueous solution of aniline (**5**) (4.2×10^{-4} M) (a) before irradiation, (b) after 60 min of irradiation in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst, and (c) after 60 min of irradiation in the presence of nonmodified TiO$_2$ photocatalyst. In all experiments 2.2−2.5 mg of the respective catalyst in 2.5 mL of solution were used.
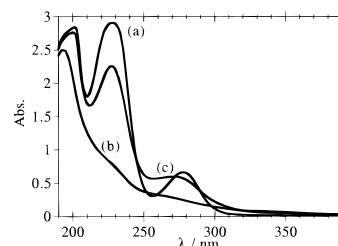
88% of **3** is completely mineralized as evidenced by the almost complete depletion of the aromatic absorbance band (Figure 2, curve b). With the nonmodified TiO$_2$, a tailing absorbance in the region 280−400 nm is observed (curve c), indicative of the formation of new aromatic intermediates. The activity of the Fe^{III}Pc/TiO$_2$ is preserved. After photodegradation of **3** with the photocatalyst, in the first run, the Fe^{III}Pc/TiO$_2$ was centrifuged and used for a second run. No noticeable degradation in the photocatalytic activity was observed. Similarly, the degradation of **4** is enhanced in the presence of the Fe^{III}Pc/TiO$_2$ as compared with the TiO$_2$ catalyst. After 60 min of irradiation, complete mineralization of **4** is achieved, whereas only ca. 50% of **4** is degraded after 60 min of irradiation with the nonmodified TiO$_2$ photocatalyst.

The photodegradation of aniline (**5**) was also examined in the presence of the Fe^{III}Pc/TiO$_2$ and the nonmodified TiO$_2$ catalyst. Figure 3 shows the absorption spectra of aqueous aniline solutions in the presence of the two photocatalysts. Irradiation of the aniline solution for 60 min in the presence of Fe^{III}Pc/TiO$_2$ photocatalyst, Figure 3, curve b, leads to almost complete mineralization, and from the absorbance spectra we conclude that >85% of the substrate is degraded. In contrast, irradiation of the aniline solution with the nonmodified TiO$_2$ photocatalyst reveals the formation of a photoproduct with an absorbance maximum at $\lambda = 270$ nm and the solution exhibits a tailing absorbance in the region $\lambda = 300−400$ nm. In fact, photodegradation of aniline (**5**) by TiO$_2$ is accompanied by yellow coloration of the solution, whereas the photodegradation of **5** by Fe^{III}Pc/TiO$_2$ yields a clear noncolored solution. The yellowish coloration of the solution is attributed to the formation of trace amounts of diazo dyes. The formation of a photoproduct that absorbs at $\lambda = 270$ nm upon irradiation of the solution with nonmodified TiO$_2$ is indicative of a new aromatic product, presumably phenol.

TABLE 2. GC-MS Analysis of the Photoirradiated Solutions at Different Time Intervals of Illumination

catalyst	irradiation time, min	substrate	
		p-nitrobenzoic acid (**2**),[a] ppm	p-chlorophenoxyacetic acid (**3**),[a] ppm
Fe^{III}Pc/TiO$_2$	0	42.7 (42.5)	55.4 (55.5)
	30	24.1 (35.0)	21.4 (36.7)
	45	17.7 (31.5)	ND
	60	13.5 (28.5)	0 (28.4)
TiO$_2$	0	42.7 (42.5)	55.4 (55.5)
	30	34.4 (43.5)	45.2 (52.5)
	45	30.9 (36.5)	ND
	60	29.1 (35.5)	40.0 (45.0)

[a] Determined by GC-MS analyses, in bracket DOC values. ND = not determined.

The discussion has emphasized the superior photocatalytic activity of the Fe^{III}Pc/TiO$_2$ photocatalyst in the light-stimulated degradation of the substrates **1**−**5**. A precise analysis of the photoirradiated solutions was obtained by GC-MS assaying of samples of the solution at different time intervals of illumination. Tables 1 and 2 summarize the concentrations at time intervals of illumination.

The GC-MS results clearly reveal the superior photocatalytic activity of the Fe^{III}Pc/TiO$_2$ photocatalyst. For example, from Table 1, we can see that after 30 min of irradiation, the concentration of salicylic acid (**4**) is 12.5 ppm with the modified catalyst, whereas it is 25.5 ppm with the nonmodified catalyst. After 60 min of irradiation, complete mineralization is achieved by the Fe^{III}Pc/TiO$_2$ photocatalyst, whereas only ca. 50% of **4** is degraded by the nonmodified catalyst.

From Table 2, the enhanced activity of Fe^{III}Pc/TiO$_2$ photocatalyst is clearly evident. After 60 min of irradiation, complete mineralization of p-chlorophenoxyacetic acid (**3**) is achieved with the Fe^{III}Pc/TiO$_2$ catalyst, whereas the concentration of **3** is 40.0 ppm after 60 min of irradiation, indicating that only ca. 28% of **3** is degraded by the nonmodified catalyst. Similarly, the photodegradation of p-nitrobenzoic acid (**2**) is substantially faster in the presence of the modified catalyst. Further, Table 1 shows that the photodegradation of aniline (**5**) is substantially faster in the presence of the modified catalyst. After 60 min of irradiation, the concentration of aniline is 5.2 ppm and we conclude that >85% of substrate is degraded. In contrast, on irradiation of an aqueous solution of aniline, with the nonmodified TiO$_2$ photocatalyst, the concentration of aniline is 29.4 ppm after 60 min of irradiation.

It can be realized that the spectroscopic assay of the degradation rates of the substrates **1**−**5** coincides with the results obtained by GC-MS analysis of the respective irradiated samples. For example, Figure 4A shows the rate of photodegradation of **1** by Fe^{III}Pc/TiO$_2$ catalyst as assayed by spectroscopic analysis (curve a) and GC-MS (curve b) and the rates of light-induced degradation of **1** by the nonmodified TiO$_2$ catalyst by the same analytical methods, curves c and d, respectively. Similarly, Figure 4B shows the rate of photodegradation of **2** by the Fe^{III}Pc/TiO$_2$ heterogeneous photocatalyst analyzed by the absorption spectra and GC-MS, curves a and b, respectively, and the respective mineralization rates of **2** using the nonmodified TiO$_2$ photocatalyst, curves c and d, respectively.

The elucidation of the mechanism leading to the enhanced photocatalytic activity of Fe^{III}Pc/TiO$_2$ as compared to that of nonmodified TiO$_2$ catalyst is quite complex and might originate from several complementary routes. We have performed a series of experiments that allow us to exclude several mechanisms and to formulate a possible pathway for the enhanced
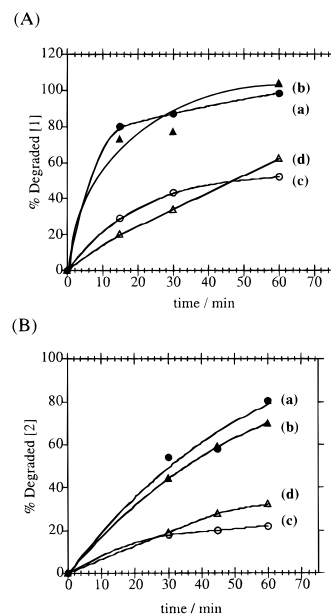

Figure 4. (A) Amount of photodegraded (% degraded) p-aminobenzoic acid (**1**) in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst: (a) assayed spectroscopically, (b) analyzed by GC-MS analysis and in the presence of nonmodified TiO$_2$ photocatalyst, (c) assayed spectroscopically, and (d) analyzed by GC-MS analysis. In all experiments 2.2−2.5 mg of the respective catalyst in 2.5 mL of solution were used. (B) Amount of photodegraded (% degraded) p-nitrobenzoic acid (**2**) in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst: (a) assayed spectroscopically, (b) analyzed by GC-MS analysis and in the presence of nonmodified TiO$_2$ photocatalyst, (c) assayed spectroscopically, and (d) analyzed by GC-MS analysis. In all experiments 2.2−2.5 mg of the respective catalyst in 2.5 mL of solution were used.

photocatalytic features of Fe^{III}Pc/TiO$_2$. The crystalline phase of the TiO$_2$ catalyst is important in controlling its photocatalytic activity, and previous reports indicated that the rutile phase is less active[61,62] and in some cases inactive[63,64] in the photodegradation of organic compounds. While the modified photocatalyst Fe^{III}Pc/TiO$_2$ exists entirely in the anatase phase, the nonmodified TiO$_2$ photocatalyst includes a rutile phase (ca. 20%). The significant differences in the photocatalytic activities of the two heterogeneous photocatalysts cannot be attributed to the structural composition of the two systems. The surface areas of the heterogeneous photocatalysts could further influence the photodegradation yields. Nevertheless, we find that the two photocatalysts, Fe^{III}Pc/TiO$_2$ and the nonmodified TiO$_2$, exhibit similar surface areas, 75.4 and 78.1 m^2/g. Thus, the surface areas of the two photocatalysts are essentially identical. A further factor controlling the photocatalytic property of the heterogeneous system could involve the adsorption affinities of the substrates to the photocatalyst surface. We have examined the adsorption properties of **3** onto the Fe^{III}Pc/TiO$_2$ and the nonmodified TiO$_2$ photocatalysts. The adsorption constants for **3** onto the nonmodified TiO$_2$ catalyst and the iron-(III) phthalocyanine-modified catalyst were determined to be 4.5×10^2 and 5.4×10^2 M^{-1}, respectively. This excludes the possibility of enhanced binding of **3** to the Fe^{III}Pc/TiO$_2$ photocatalyst as a result of increased hydrophobicity or π-stacking to the Fe^{III}Pc/TiO$_2$ photocatalyst.

Further attempts to elucidate the enhanced photodegradation of the organic substrates by the Fe^{III}Pc/TiO$_2$ catalysts involve the possible participation of Fe^{III}Pc in the photochemical process. The substrate p-aminobenzoic acid (**1**) was irradiated with the Fe^{III}Pc/TiO$_2$ photocatalyst using a cutoff filter of $\lambda \geq 455$ nm. Under these conditions, the TiO$_2$ semiconductor cannot be
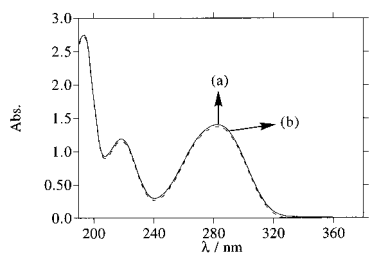
Figure 5. Absorption spectra of an aqueous *p*-aminobenzoic acid (**1**) solution (7.7×10^{-5} M) (a) before irradiation and (b) after 30 min of irradiation in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst (2.4 mg in 2.5 mL of solution) with a cutoff filter $\lambda \geq$ 455 nm.
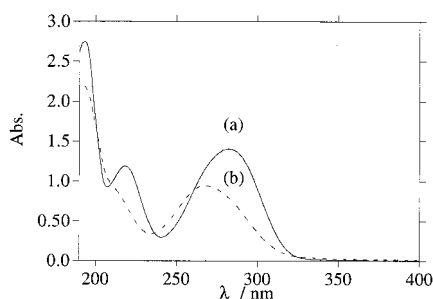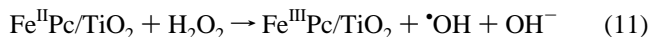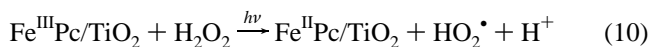

Figure 6. Absorption spectra of an aqueous *p*-aminobenzoic acid (**1**) solution (7.7×10^{-5} M) (a) before irradiation and (b) after 30 min of irradiation in the presence of iron(III) phthalocyanine-modified TiO$_2$ photocatalyst (2.4 mg in 2.5 mL of solution) and 5×10^{-4} M H$_2$O$_2$ with a cutoff filter $\lambda \geq$ 455 nm.

excited since direct band-gap excitation of the TiO$_2$ requires photons of $\lambda \leq$ 400 nm, and only the iron(III) phthalocyanine is excited. Figure 5 shows the absorbance spectra of a solution of **1** upon irradiation with the Fe^{III}Pc/TiO$_2$ photocatalyst for 30 min with the filtered light, $\lambda \geq$ 455 nm. Clearly, the absorbance spectrum of **1** is unaltered, indicating that it is not degraded. Thus, direct photodecomposition of **1** by the iron(III) phthalocyanine does not occur. Also, the lack of degradation of **1** upon irradiation, $\lambda \geq$ 455 nm, with Fe^{III}Pc/TiO$_2$ rules out the possible photosensitization of the TiO$_2$ by the excitation of iron(III) phthalocyanine as a route for enhancing the photocatalytic activity of TiO$_2$. That is, the semiconductor is not activated by the excitation of the metal phthalocyanine. No degradation of **1** was observed in the presence of Fe^{III}Pc alone (i.e., in the absence of TiO$_2$) at $\lambda \geq$ 455 nm.

A further possibility that was examined includes the possible participation of the iron(III) phthalocyanine in a photo-Fenton type reaction. For this purpose, we irradiated the aqueous solution of **1** in the presence of a low concentration of H$_2$O$_2$, 5×10^{-4} M, in the presence of filtered light. Figure 6 shows the absorbance spectrum of the solution after 30 min of irradiation, curve b. Clearly, ca. 30% of substrate **1** is decomposed. The dark oxidation of **1** by Fe^{III}Pc/TiO$_2$ with added H$_2$O$_2$, 5×10^{-4} M, is slow, and only <5% of the substrate is oxidized during 30 min of reaction. These experiments suggest a potential cooperative activity of the Fe^{III}Pc and TiO$_2$ components in the enhanced photodegradation of **1−5**. Our results show that the Fe^{III}Pc component is photocatalytically active in the degradation of **1** only in the presence of added H$_2$O$_2$. The direct TiO$_2$-induced degradation of the organic substrates is stimulated by ·OH. Our results indicate that the photochemical excitation of the Fe^{III}Pc component, $\lambda \geq$ 455 nm, can generate from H$_2$O$_2$ reactive species for the degradation of the organic pollutants. A possible route for the generation of reactive radical species for the degradation of the organic substance is outlined below in eqs 10 and 11. Photoinduced oxidation of H$_2$O$_2$ by the iron-

(III) phthalocyanine yields HO$_2$$^\bullet$, whereas the reduced metal phthalocyanine Fe^{II}Pc is oxidized by H$_2$O$_2$ via a dark process to generate $^\bullet$OH.

$$Fe^{III}Pc/TiO_2 + H_2O_2 \xrightarrow{h\nu} Fe^{II}Pc/TiO_2 + HO_2{}^\bullet + H^+ \quad (10)$$

$$Fe^{II}Pc/TiO_2 + H_2O_2 \rightarrow Fe^{III}Pc/TiO_2 + {}^\bullet OH + OH^- \quad (11)$$

Thus, the only aspect that needs to be addressed relates to the source of H$_2$O$_2$ in the aqueous system that includes the heterogeneous photocatalyst Fe^{III}Pc/TiO$_2$ and the organic pollutant. The photodegradation of the organic pollutants by the TiO$_2$ semiconductor involves the generation of ·OH species by the direct band-gap excitation of the semiconductor, eqs 1−4. Dimerization of the $^\bullet$OH radicals yields H$_2$O$_2$, eq 3. This latter process depletes the reactive intermediates that are active in the degradation of the pollutants. Furthermore, H$_2$O$_2$ can be formed by the direct two-electron reduction of O$_2$ by conduction-band electrons, a process competing with the direct formation of $^\bullet$OH. The Fe^{III}Pc component acts as a photoactive element for the regeneration of the radicals and therefore for the enhancement in the photocatalytic transformations.[65]

In conclusion, we have reported on a novel photocatalyst for the degradation of organic aromatic substrates based on the functionalization of TiO$_2$ with iron(III) phthalocyanine. We suggest that the enhanced photocatalytic activity of Fe^{III}Pc/TiO$_2$ originates, at least in part, from the complementary functions of the two components in generating $^\bullet$OH, the active species in the light-induced degradation of the aromatic substrates. The direct photoexcitation of TiO$_2$ provides a source for $^\bullet$OH and the semiconductor-stimulated degradation of the substances. Formation of $^\bullet$OH results in dimerization and formation of H$_2$O$_2$, and the latter product acts as substrate for the light-induced formation of $^\bullet$OH by Fe^{III}Pc. The effective formation of $^\bullet$OH at the catalytic interface prevents the diffusion of intermediate degradation products to the bulk aqueous solution. We thus observe the complete mineralization of the aromatic substrates in the presence of Fe^{III}Pc/TiO$_2$.

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(65) A further possibility suggested by a reviewer for the enhanced activity of the Fe^{III}Pc/TiO$_2$ photocatalyst involves the spatial separation of the charge carriers in the modified catalyst. That is, Fe^{III}Pc could provide a shallower electron traps and, hence, indirectly accelerate oxygen reduction relative to the nonmodified TiO$_2$ photocatalyst. This possibility cannot be overruled and we thank the reviewer for this suggestion.