FULL PAPER

Efficient Photoinduced Conversion of an Azo Dye on Hexachloroplatinate(IV)-Modified TiO₂ Surfaces under Visible Light Irradiation—A Photosensitization Pathway

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Abstract: The titanium dioxide photocatalyst is employed to examine the influence of chemisorbed hexachloroplatinate(IV) anions ($PtCl_6^{2-}$) on the surface of P-25 TiO₂ particles on the photoinduced conversion of the azo dye Ethyl Orange (EO) in visible light-illuminated Pt^{IV}/TiO_2 dispersions. Spin-trap electron spin resonance (ESR) spectral results, measurement of quantities of organoperoxides formed, total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) assays, together with XPS evidence show that the self-sensitized transformation dynamics of the EO dye mediated by Pt^{IV}/TiO_2 are much faster than those occurring on naked TiO₂ under otherwise identic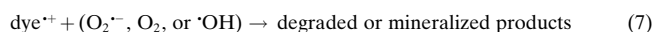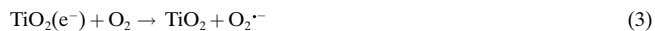al conditions of visible light irradiation. X-ray photoelectron spectral data also show that under the experimental conditions used, no Pt^0 formed on the titania particles during visible light irradiation. We propose a reaction mechanism in which the more rapid conversion of EO in the presence of $PtCl_6^{2-}$ is caused principally by photoexcitation of the dye and not by localized excitation of the tetrachloroplatinate(IV)/TiO₂ particles.

Keywords: dyes · photochemistry · photosensitization · platinum · titanium

Introduction

Colloidal and powdered titania specimens have been proven to be excellent photocatalytic materials on which many organic compounds are photocatalytically and oxidatively (in some cases reductively) degraded under UV irradiation.[1–4] The large body of data suggests a possible and effective approach towards the degradation and mineralization of a wide variety of harmful/toxic organic pollutants in wastewater and towards the purification of drinking water.[5, 6] The photocatalyst TiO₂ is a semiconductor with a bandgap of 3.2 eV for the anatase form, which limits its photoresponse to the ultraviolet region (i.e., to a region below 385 nm). Unfortunately, sunlight consists of only approximately 3–5% UV, and artificial UV light sources tend to be rather expensive and consume large quantities of electrical power.

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Dyes have become major environmental contaminants in many countries.[7] In previous studies[8–12] visible light was utilized efficiently to degrade these dyes in the presence of TiO₂ particulates. The mechanistic details of dye degradation have also been the subject of several studies. In these systems, dyes rather than TiO₂ particles were excited by visible light to appropriate singlet and triplet states, processes which were followed by electron injection into the TiO₂ conduction band. This pathway [Eq. (1)–(7)] is different from the pathway implicated during UV light irradiation.[1–4]

$$\text{dye} + h^+ \rightarrow \text{dye*} \tag{1}$$

$$\text{dye*} + TiO_2 \rightarrow \text{dye}^{\cdot+} + TiO_2(e^-) \tag{2}$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{\cdot-} \tag{3}$$

$$O_2^{\cdot-} + TiO_2(e^-) + 2H^+ \rightarrow H_2O_2 + TiO_2 \tag{4}$$

$$2O_2^{\cdot-} + 2H^+ \rightarrow O_2 + H_2O_2 \tag{5}$$

$$H_2O_2 + TiO_2(e^-) \rightarrow {}^{\cdot}OH + OH^- + TiO_2 \tag{6}$$

$$\text{dye}^{\cdot+} + (O_2^{\cdot-}, O_2, \text{ or } {}^{\cdot}OH) \rightarrow \text{degraded or mineralized products} \tag{7}$$

The fate of the injected electrons depends on the interfacial charge transfer processes, which appear to play an important role under both UV and visible irradiation. The above processes also depend greatly on the surface characteristics of the TiO₂ particles and on the charge carrier mobility and longevity.[13] Accordingly, many reported studies have focused

on the volume and surface modification of TiO_2 in the treatment of pollutants. As reported earlier, coupling TiO_2 with a chelating group,[14] and doping with transitional metal ions[15, 16] or adsorption of cations and anions[17] has a large influence on such processes.

In several interesting and germane papers, Kisch et al.[18–23] have recently reported that small molecular organic compounds such as 4-chlorophenol can be photodegraded efficiently in the presence of an amorphous/microporous titania volume doped with platinum(IV) chloride ($Pt^{IV}/AMM-TiO_2$) and TiO_2 surfaces modified with platinum(IV) chloride or chloroplatinum(IV) complexes. Apparently, local excitation of the platinum(IV) halide under visible light irradiation yields a ligand-to-metal charge-transfer state which undergoes homolytic Pt−X bond cleavage to yield Pt^{III} and a halogen atom. The Pt^{III} intermediate then rapidly transfers an electron to the conduction band of titania, whereas the chlorine atom abstracts an electron from the aromatic phenol, thereby reforming the sensitizer and inducing the degradation of the phenol in the presence of TiO_2 (Scheme 1 A).[21]

In general, all of the cases mentioned above focused principally on the photocatalytic process, namely excitation of photocatalysts by UV or visible radiation. Only a few reports[24, 25] have appeared concerning the effect of transition metal or metal ions on the self-sensitized degradation of dyes under visible light irradiation. We found that copper(II) and iron(III) have a strong suppressing effect on the photoinduced transformation of dyes under visible light irradiation in dye/TiO_2 systems. Doping the TiO_2 photocatalyst with small quantities of metallic platinum (0.2 wt%) significantly accelerated the visible light-induced photodegradation of the sulforhodamine B (SRB) dye.

In the present study, we examined the effect of a platinum(IV) chloride species ($PtCl_6^{2-}$) chemisorbed onto the TiO_2 surface on the photodegradation of dyes under visible light irradiation. The test target substrate was the azo dye Ethyl Orange (EO). EO is an important representative of the azo dyes and is famous for its relatively stable features as a dye laser material. Addition of small quantities of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) to the aqueous EO/TiO_2 dispersions significantly enhanced the degradation of the EO dye. Results also showed that $PtCl_6^{2-}$ was strongly adsorbed on the TiO_2 surface. In contrast, photodegradation appeared to be rather less efficient when carried out in the presence of TiO_2 alone. To investigate some of the mechanistic details, the irreversible degradation process was monitored by UV/Vis spectroscopy, DMPO spin-trapping electron paramagnetic resonance (ESR) methodologies (DMPO = 5,5-dimethyl-L-pyrroline-N-oxide, and total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) measurements. Photoelectron (XPS) and UV/Vis diffuse reflectance spectral methods were also employed to elucidate the nature of the photocatalyst specimen(s). The experimental results imply that although the degradation of the dye is significantly accelerated in the presence of the Pt^{IV}/TiO_2 specimens, no further photoinduced transformation of the EO dye occurs once the dye is bleached. The self-photosensitized degradation of the dye is the determinant process in the presence of Pt^{IV}/TiO_2.

Results and Discussion

Photoinduced transformation of EO under visible light irradiation: The photoinduced conversion of EO was carried out under visible light illumination at wavelengths greater than 420 nm in aqueous Pt^{IV}/TiO_2 dispersions. The data displayed in Figure 1 A clearly indicate that under otherwise
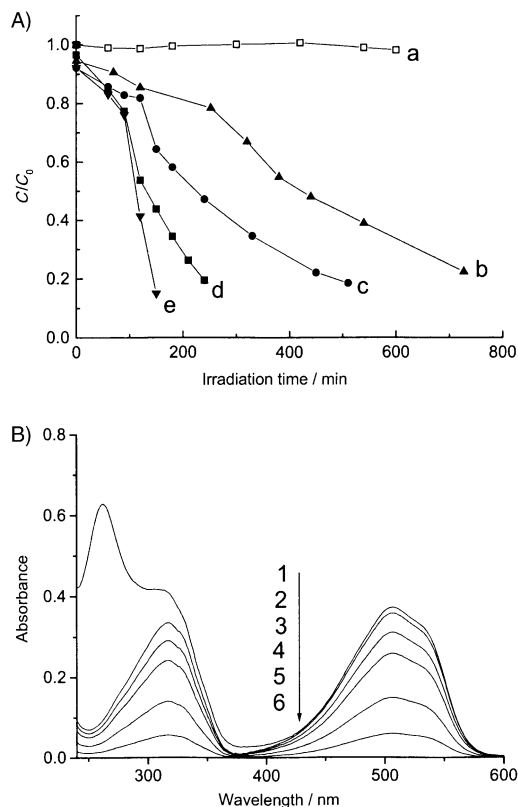

Figure 1. A) Temporal course of the photodegradation of the azo dye Ethyl Orange (EO; 2.0×10^{-5} M; 50 mL) in aqueous dispersions at pH 2.5 and containing 50 mg of catalytic material under visible light irradiation: a) EO + $PtCl_6^{2-}$ + light; b) EO/TiO_2; c) EO/Pt^{IV}/TiO_2 (0.4 wt% in platinum); d) EO/Pt^{IV}/TiO_2 (1.0 wt% in platinum); e) EO/Pt^{IV}/TiO_2 (0.8 wt% in platinum). B) Changes in absorption spectra during the photodegradation of EO (2×10^{-5} M; 50 mL) in aqueous Pt^{IV}/TiO_2 dispersions. Spectrum 1 is before addition of TiO_2 and spectra 2–6 are after visible irradiation for 0, 1, 1.5, 2, and 2.5 h in the presence of TiO_2.

identical conditions Pt^{IV}/TiO_2 exhibits a much greater activity than TiO_2 alone (compare curve b with curves c–e). An aqueous solution of $PtCl_6^{2-}$ and EO induced no degradation of the dye under visible light irradiation (curve a). Results also showed that the 0.8 wt% Pt^{IV}/TiO_2 system (curve e) appeared to be the most efficient; greater concentrations of $PtCl_6^{2-}$ seemed to have a negative effect. At a dye concentration of 2×10^{-5} M, the extent of adsorption of the EO dye on TiO_2 (50 mg) particles was approximately 5% (curve b); the amount of $PtCl_6^{2-}$ has little effect on the absorption of the dye. The UV/Vis absorption spectral changes taking place during the photooxidation of EO in aqueous Pt^{IV}/TiO_2 dispersions are displayed in Figure 1 B. It is clear that $PtCl_6^{2-}$ is adsorbed completely onto the TiO_2 particles when 50 mg TiO_2 is added to the solution (50 mL) and it is stirred in the

dark for 30 min (compare spectra 1 and 2 in Figure 1 B), and no $PtCl_6^{2-}$ was found in the bulk solution during the degradation process. To better scrutinize the adsorption modes and the photooxidative pathway(s), all the experiments were carried out at pH 2.5 and 0.8 wt % Pt^{IV} loading (unless noted otherwise), at which the rate of conversion was the fastest.

The optical absorption spectra of Pt^{IV}/TiO_2 and P-25 TiO_2 were measured for comparison. The results show that both samples have strong light absorption at wavelengths below 400 nm which is attributed to transitions of electrons from the valence band to the conduction band of TiO_2. With $PtCl_6^{2-}$ species chemisorbed on the TiO_2 specimens, the spectra showed a long and broad absorption tail that extended into the visible region as compared to the naked P-25 titania. Accordingly, this absorption feature of Pt^{IV}/TiO_2 suggests that the photocatalyst can, in principle, be activated throughout the visible wavelengths where light absorption occurs. This feature is probably the ligand-to-metal charge-transfer band or the ligand field band inferred earlier by Kisch et al.[18–23]

The mechanistic steps of dye degradation given earlier [Eq. (1) – (7)], in which the photoinduced dye conversion is mediated by the semiconductor TiO_2 nanoparticles in the dye/TiO_2 system under visible light irradiation, indicate that photodegradation of the dye(s) should generate H_2O_2 as a possible intermediate species.[8–12] However, no formation of H_2O_2 was detected in the present systems. Only organoperoxides were detected during the degradation of the azo dye EO in both Pt^{IV}/TiO_2 and TiO_2 systems, a feature not seen in earlier studies. The temporal formation of organoperoxide(s) during the photoconversion process is displayed in Figure 2. In the presence of $PtCl_6^{2-}$ (curve a), the concentration of the organoperoxide generated increased initially,
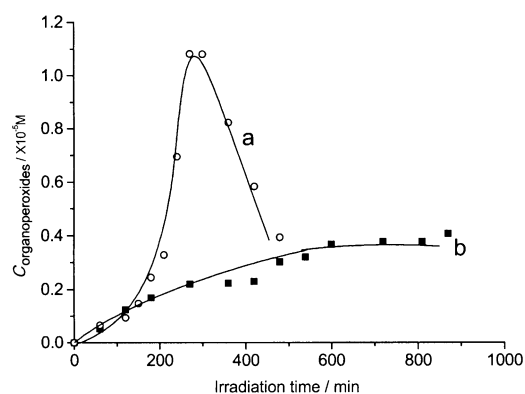

Figure 2. Plots summarizing the formation of organoperoxides during the EO degradation process: a) in the EO/0.8 wt % Pt^{IV}/TiO_2 system; b) in the EO/TiO_2 system.

reaching a maximal concentration of approximately 1.1×10^{-5} M at the exact point (≈ 210 min) at which the dispersion became discolored. Subsequently, the quantity of organoperoxide(s) decreased at longer irradiation times. In the absence of $PtCl_6^{2-}$ (curve b), however, the quantities of organoperoxide(s) increased slowly with the irradiation time to accumulate to a maximal concentration of approximately 3.3×10^{-6} M until the dispersion became discolored. As

evidenced by the results of Figure 2, the Pt^{IV}/TiO_2 photocatalyst appears more active than the naked TiO_2 (compare curve a with curve b).

Our research group has observed the formation of peroxide and its decomposition in aqueous dye/TiO_2 dispersions under visible light irradiation.[9] These observations demonstrate that fast degradation of the dyes is a prerequisite for generation and detection of peroxide. That less organoperoxide formed during the degradation of EO in the absence of $PtCl_6^{2-}$ is likely due to the slow degradation of the dye. The large amount of organoperoxide produced is a result of the rapid degradation of the dye in the presence of $PtCl_6^{2-}$. The fast decomposition of organoperoxide formed in the $PtCl_6^{2-}/TiO_2$ dispersion was observed possibly because of more adsorption of peroxide after the dye molecules were decomposed rapidly.

To test whether organoperoxides are the only peroxide species produced during the degradative process of EO, other azo dyes (e.g., Orange II, Mordant Yellow, Mordant Orange, and Alizarin Yellow GG) were also examined in TiO_2 dispersions under visible light irradiation. Similar to the results from the EO degradation, no H_2O_2 was detected in the appropriate degradative processes; only organoperoxides were formed. It is possible that some special feature(s) of the azo dye structures may be the cause(s) for the generation of the organoperoxides—a notion that needs further exploration.

We employed the ESR spin-trap technique (with DMPO), a useful method to monitor intermediate radicals, to probe the nature of the reactive oxygen species generated during the visible irradiation of these systems. It has been reported[12] that superoxide radical anions are produced first and remain stable in an organic solvent medium (at least in methanol). When the fraction of H_2O increases in the CH_3OH/H_2O mixed solvent system, the superoxide radical anion becomes unstable, leading to difficulty in detection by ESR, especially in H_2O alone. The ESR spectra of the DMPO – $O_2^{\bullet-}$ spin adducts were recorded in both EO/Pt^{IV}/TiO_2 and EO/TiO_2 dispersions in methanolic media at different illumination times; the irradiation source was a Nd:YAG laser (532 nm). The temporal changes in the signal intensity of the $O_2^{\bullet-}$ radical anions in the two systems are illustrated in Figure 3 A.

The ESR temporal spectra of the DMPO – $O_2^{\bullet-}$ species in the EO/Pt^{IV}/TiO_2 system are illustrated in Figure 3 B. Six characteristic peaks were observed (the two middle signals were not resolved under our conditions); these increased in intensity with irradiation time. No such signals were detected in the dark; that is, generation of $O_2^{\bullet-}$ anions in the two systems inherently implicates irradiation. From Figure 3 A, it is evident that in the EO/Pt^{IV}/TiO_2 system, the intensity of the DMPO – $O_2^{\bullet-}$ signal increased sharply after irradiation began and then decreased after reaching a maximal value after approximately 40 s (curve a). In contrast, the signals for DMPO – $O_2^{\bullet-}$ produced in the EO/TiO_2 system were less intense and remained unchanged after laser irradiation for nearly 240 s (curve b). The results of the ESR spectra of the DMPO – $O_2^{\bullet-}$ spin adducts are consistent with the formation of organoperoxide species. Note that detection of the $O_2^{\bullet-}$ radicals necessitated increasing the EO concentration fivefold
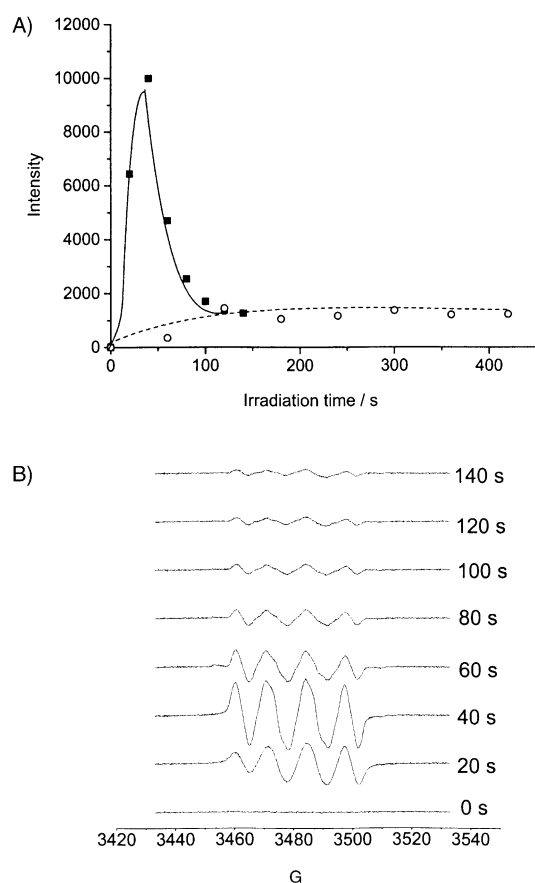
Figure 3. A) Plots of ESR signal intensity changes of the DMPO–$O_2^{\cdot-}$ adducts with increasing irradiation time: a) in the EO (1.0×10^{-4} M)/ 0.8 wt % Pt^{IV}/TiO_2 (1 g L^{-1}) dispersion; b) in the EO (1.0×10^{-4} M)/TiO$_2$ (1 g L^{-1}) dispersion. B) ESR spectral changes of the DMPO–$O_2^{\cdot-}$ adducts with irradiation time in the EO/0.8 wt % Pt^{IV}/TiO_2 system.

displayed in Figure 4. Upon visible light irradiation of these dispersions, the TOC of the bulk solution decreased gradually in all cases to remain unchanged, ultimately as a result of the photodegradation of the dye and/or of any intermediate
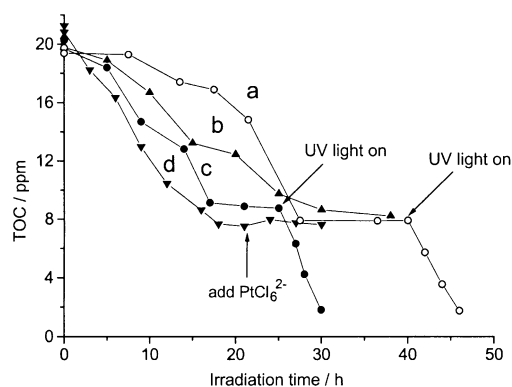

Figure 4. Temporal changes in total organic carbon (TOC) in the degraded bulk solution during the photodegradation of EO (5×10^{-5} M, pH 2.5; aqueous media): a) EO/TiO$_2$ alone; b) EO/0.4 wt % Pt^{IV}/TiO_2; c) EO/ 0.8 wt % Pt^{IV}/TiO_2; d) EO/1.0 wt % Pt^{IV}/TiO_2.

compared to the concentration used to detect formation of organoperoxides by other techniques. Accordingly, the intensity of the DMPO–$O_2^{\cdot-}$ signals should not be correlated with the quantities of organoperoxides. Our goal was to verify that the trends were in reasonably good accord. We conclude from Figure 3 that $O_2^{\cdot-}$ radicals are formed much more efficiently in the presence of $PtCl_6^{2-}$ in titania dispersions than in naked TiO$_2$ dispersions alone.

DMPO spin-trapping ESR experiments were also carried out to probe whether DMPO–$\cdot$OH adducts also formed in illuminated dispersions containing the EO dye. The relevant ESR spectra revealed no signature (1:2:2:1 signals) of the DMPO–$\cdot$OH radical adducts during the degradation processes, contrary to the case of xanthene dyes (e.g., the SRB dye), which do produce the $\cdot$OH species when irradiated in the presence of TiO$_2$.[9, 10] This result is consistent with the findings that except for organoperoxide species, no H$_2$O$_2$ formed in the degradation of EO.

Total organic carbon (TOC) values reflect the general measure of organics in the solution bulk. Thus, changes in TOC mirror the degree to which an organic substrate degrades or mineralizes during the irradiation period. TOC values measured during the photodegradative conversion of EO in EO/TiO$_2$ and EO/Pt^{IV}/TiO$_2$ systems under various conditions and after removal of the catalyst particles are

formed. Different quantities of $PtCl_6^{2-}$ added to the systems resulted in different mineralization kinetics. The naked TiO$_2$ system (curve a) appeared to be the slowest, and remain unchanged after approximately 27 h of irradiation. The processes occurring in the Pt^{IV}/TiO$_2$ systems (curves b–d), however, were relatively more rapid. Given the measurement errors, there was little difference in the extent of mineralization (ca. 40 % of TOC remaining) among all the systems examined under visible light irradiation. The unchanged TOCs refer to complete discoloration of the dispersions subsequent to which any remaining organic fragment was no longer decomposed upon further irradiation by visible light.

To investigate whether the remaining fragments could be degraded further by involvement of the $PtCl_6^{2-}$ anionic species under visible light irradiation, 4×10^{-5} M $PtCl_6^{2-}$ was added to the discolored dispersions and visible light irradiation was continued. Results showed that the TOC remained unchanged (curve d), indicating that addition of $PtCl_6^{2-}$ to the EO/TiO$_2$ system had no further effect on the mineralization of intermediate products. However, further irradiation of the discolored dispersion with UV light led to a rapid decrease of TOCs (curves a and c), demonstrating that further mineralization of oxidized dye fragments occurred. It is relevant to re-emphasize that dyes photodegrade in UV light by a pathway that is totally distinct from the pathway that prevails under visible light radiation. In the former, TiO$_2$ is excited by the UV actinic light to produce the two charge carriers h$^+$ and e$^-$. The former degrades organic compounds through involvement of $\cdot$OH radicals produced by oxidation of surface hydroxyl groups of water molecules.

Earlier we reported a comparative study between photocatalysis with UV irradiation (in which photocatalytic material was photoactivated) and self-sensitized catalysis under visible irradiation (in which titania was made photoinactive) in the degradation of dyes in aqueous TiO$_2$ dispersions.[26] In photocatalysis the intermediate products were further decom-

posed and both the TOC and COD of the dispersion were diminished by nearly 100%. In contrast, in self-sensitized catalysis only partial TOC and COD were diminished, with both TOC and COD remaining unchanged after the dispersions became discolored.

The fact that additional $PtCl_6^{2-}$ had no effect on the mineralization of intermediate products after discoloration of the dispersions adds further credence to the inference that degradation of EO occurs mainly through a self-photosensitization process (excitation of the dye) and not through a photocatalytic process (excitation of the catalytic material). For comparison, changes in TOC with visible light irradiation time were also examined in both dispersions with sulforhodamine B (SRB) as the target substrate. The TOC changes displayed the same situation as that reported here for EO; that is, the TOC remaining in the solution bulk was no longer affected by irradiation once the dispersions were discolored. Clearly, Pt^{IV}/TiO_2 had no further effect on the mineralization of the dyes. Accordingly, any degradation of the dye on Pt^{IV}/TiO_2 is due to a photosensitization process.

Changes in chemical oxygen demand (COD_{Cr}) of the dispersions reflect the degree to which the substrate is degraded or mineralized in the entire dispersion (i.e., both in the bulk solution and on the surface of the catalyst, as the measurements are done on the whole dispersion) during irradiation. Table 1 summarizes the results of COD_{Cr} values for the two systems before visible light irradiation and after a longer period of irradiation when the dispersions had been discolored.

Table 1. COD_{Cr} changes of EO (50 mL, 5×10^{-5} M) dispersions ([$PtCl_6^{2-}$] = 1×10^{-4} M, pH 2.5, TiO_2 loading 100 mg).

Samples	Original COD_{Cr} [$mg O_2 L^{-1}$]	Final COD_{Cr} [$mg O_2 L^{-1}$]	Mineralization extent [%]
EO/TiO$_2$	35.8	17.6	51
EO/Pt^{IV}/TiO$_2$	36.2	17.0	53

COD_{Cr} values for the irradiated EO/Pt^{IV}/TiO_2 suspensions decreased with increasing illumination time from an initial value of 36.2 $mg O_2 L^{-1}$ (before illumination) to 17.0 $mg O_2 L^{-1}$ after 18 h of irradiation (about 53% COD removed), whereas it required 30 h of visible irradiation to achieve the removal of approximately 51% of the total COD in the EO/TiO_2 system. In keeping with the results of TOC measurements, the final mineralization yield for the EO/Pt^{IV}/TiO_2 system is nearly identical to that of the EO/TiO_2 dispersion once the dispersions were discolored.

Results of cyclic experiments with the Pt^{IV}/TiO_2 photocatalyst specimens are shown in Figure 5. After four degradation cycles, the activity did decrease to some extent. We tentatively attribute this deactivation to adsorption of somewhat refractory degraded intermediate species.

Mechanism discussion: The novel photocatalyst reported by Kisch et al. did afford degradation of 4-chlorophenol (4-CP) under visible light irradiation; a similar visible light-induced photodegradation of 4-CP also occurs with a coke-containing titanium dioxide photocatalyst.[27] The relevant mechanistic
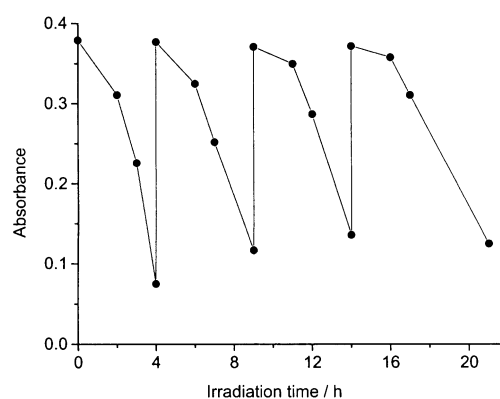

Figure 5. Profiles of cyclic tests of a Pt^{IV}/TiO_2 specimen in the degradation of the azo dye EO.

step was described as arising from visible light excitation of the platinum(IV) chloride affording a Pt^{III} species and a weakly surface-bound chlorine atom, Cl(0). It is the latter strongly oxidizing radical that was postulated to lead to the degradation of the chlorophenol on the surface or in the solution bulk (Scheme 1 A).[21] It is relevant to note that the 4-CP is not excited by visible light and consequently cannot produce electrons. In contrast, the azo dye system examined here is easily excited by visible light to produce excited states, for example ^{1,3}dye*, which under suitable circumstances are poised to inject electrons into the conduction band of the TiO_2 semiconductor, with the dye being converted to a radical cation (dye$^{\cdot+}$).

Characterization of the Pt^{IV}/TiO_2 photocatalyst during the degradation process was accomplished by using X-ray photoelectron spectroscopic (XPS) methodologies. Figure 6 shows
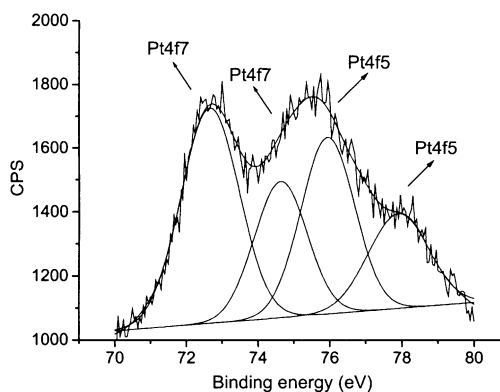

Figure 6. X-ray photoelectron spectrum of the chemisorbed Cl_nPt^{IV} species after the visible light-induced self-photosensitized degradation of the dye Ethyl Orange in EO/Pt^{IV}/TiO_2 air-equilibrated aqueous dispersions. Note that a similar spectrum is obtained prior to the degradation of the dye.

the peak for the Pt^{IV}/TiO_2 sample at the end of degradation under visible light irradiation. The XPS spectral features show the presence of Pt^{IV} and Pt^{II}; no elemental platinum(0) was found (of which the binding energy is 70.9 eV). Clearly, platinum(IV) was not reduced to elemental Pt^0 by the electrons produced on excitation of the dye by visible light radiation, in contrast to the cases in which Pt^{IV} species are reduced to Pt^0 in the presence of reducing agents and TiO_2 under UV

irradiation in anaerobic media.[28] Note that XPS spectra taken prior to the degradation of the EO dye also showed the presence of Pt[II] species at a concentration equivalent to that observed after the degradation of EO. It is likely that the Pt[II] species were produced during the work-up of the XPS sample. A control experiment in which the platinum(II) species (PtCl$_4^{2-}$) was added to the EO/TiO$_2$ dispersion showed that Pt[II] had a negative effect on the degradation of the EO dye. Accordingly, we concluded that Pt[II] species were not produced during the degradation of EO in EO/Pt[IV]/TiO$_2$ dispersions.

On the basis of the experimental evidence and the above discussion, a likely mechanism for the Pt[IV]/TiO$_2$-assisted catalysis of the photoinduced conversion of Ethyl Orange (and by extrapolation other azo dyes) is depicted in Scheme 1 B. We propose that the injected electrons can easily be trapped by the adsorbed tetrachloroplatinate(IV) surface complex, which is formed by chemisorption during the dark equilibrium period, to produce a transient Pt[III] species by an efficient electron transfer between the TiO$_2$ conduction band and Pt[IV], thereby obviating the homolytic Pt−Cl bond cleavage under irradiation. The platinum(III) intermediate subsequently reacts rapidly with pre-adsorbed O$_2$ on the TiO$_2$ surface to produce the superoxide O$_2^{\bullet-}$ radical anions, followed by formation of organoperoxides, as evidenced by ESR spectroscopy, through the reaction depicted in Scheme 1 B. This electron transfer leads to efficient charge separation and effectively suppresses the recombination event through back electron transfer between the EO$^{+\bullet}$ and the injected electrons. In the absence of Pt[IV], recombination of the electrons in the conduction band (or surface defects) of TiO$_2$ with the EO$^{\bullet+}$ cation radicals adsorbed on the surface of TiO$_2$ can compete effectively with molecular O$_2$, so that the extent

of scavenging of electrons by O$_2$ is somewhat lessened. In contrast, the efficient electron transfer from the conduction band to the adsorbed Pt(IV) increases the amount of O$_2^{\bullet-}$ formed on the surface of TiO$_2$. Accordingly, the ESR difference observed in the quantity of O$_2^{\bullet-}$ radicals produced between the Pt[IV]/TiO$_2$ and TiO$_2$ dispersions is understandable.

In summary, the primary step in the rapid degradation of the azo dye EO in the presence of PtCl$_6^{2-}$ is essentially photoexcitation of the dye and not excitation of adsorbed PtCl$_6^{2-}$, although the catalyst specimen does exhibit a definite light absorption throughout a portion of the visible wavelengths. As evidenced from the TOC and COD results, no intrinsic differences were observed between Pt[IV]/TiO$_2$ and TiO$_2$ dispersions in the mineralization of EO. We emphasize that the existence of PtCl$_6^{2-}$ had a negligible effect on the mineralization of the substrate when the dispersion had been discolored. The discolored dispersions contain small molecular intermediates, which have no absorption features in the visible region and thus cannot be excited by visible light. Accordingly, if localized excitation of PtCl$_6^{2-}$ were the primary step in the overall pathway it should have led to the complete degradation (i.e., mineralization) of the azo dye. The results of the experiments presented here suggest otherwise (Scheme 1 B).

To obtain further insights into the mechanism, we also examined the degradation of sodium benzensulfonate, N,N-diethylaniline, and 2,4-dichlorophenol (2,4-DCP) in Pt[IV]/TiO$_2$ dispersions under visible light irradiation. These substrates have no light absorption characteristics in the visible spectral region (wavelengths longer than 400 nm). Neither sodium benzensulfonate nor N,N-diethylaniline were photodegraded in Pt[IV]/TiO$_2$ dispersions, except for some loss of the substrates through adsorption on titania. The 2,4-DCP was degraded gradually under conditions similar to those reported by Macyk and Kisch.[21] These additional control experiments lend further credence to the idea that the self-photosensitized degradation of EO is the determinant process in the present system. Even if localized excitation of PtCl$_6^{2-}$ does cause other organic compounds to degrade under otherwise identical conditions as used here, such degradation was negligible in our system of azo dyes. Notwithstanding this, work is proceeding on other substrates of different structures to ascertain the general degradative process of substances that otherwise compete effectively with the surface platinum(IV) complex for the actinic photons in the visible spectral region.

Conclusion

Small quantities of hexachloroplatinate(IV) anions chemisorbed on the surface of TiO$_2$ (P-25) have a strong acceleratory effect on the photodegradation of the azo dye EO under visible light irradiation. The improved activity is ascribed to efficient electron transfer between the TiO$_2$ conduction band and the chemisorbed Pt[IV] species, which leads to efficient charge separation and assists in producing greater quantities of O$_2^{\bullet-}$ radical anions and organoperoxides than is otherwise the case on naked TiO$_2$ surfaces. No photoreductive conversion of the surface Pt[IV] species to elemental Pt[0] was
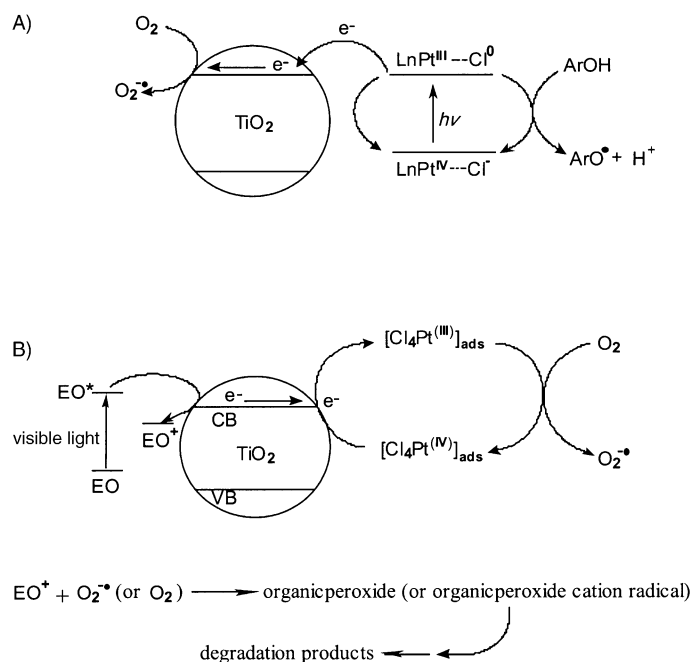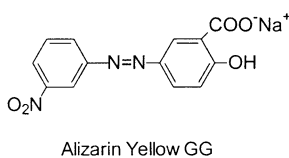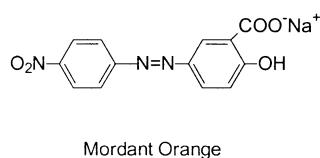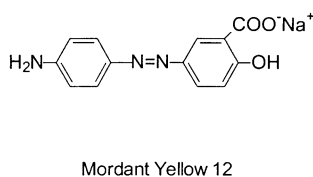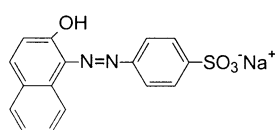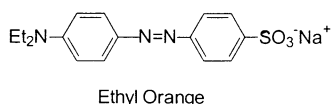

Scheme 1. A) Postulated mechanism for the visible light-induced oxidative degradation of 4-chlorophenol in aerobic aqueous media (from ref. [21]). B) Proposed mechanism for the photodegradation of EO on Pt[IV]/TiO$_2$ surfaces under irradiation with visible light wavelengths.

observed under the experimental conditions used; this is a well-known reaction that results in the deposit of metallic platinum on the surface of TiO$_2$ by UV irradiation in the presence of a reducing agent in anaerobic aqueous media.

Experimental Section

Materials: P-25 TiO$_2$ (ca. 80% anatase, 20% rutile; BET area ca. 50 m^{2}g^{-1}) was kindly supplied by Degussa Co. The Ethyl Orange dye (EO) was of laser-grade quality (Across Co.). All other dyes (see structures below) and chemicals were of laboratory reagent-grade quality and were used without further purification. Deionized and doubly distilled water was used throughout this study.

Et$_2$N—⟨ ⟩—N=N—⟨ ⟩—SO$_3^-$Na$^+$

Ethyl Orange

Orange II (Acid Orange 7)

Mordant Yellow 12

Mordant Orange

Alizarin Yellow GG

Photoreactor and light source: The visible light source was a 500-W halogen lamp (Institute of Electric Light Source, Beijing) positioned inside a cylindrical Pyrex vessel and surrounded by a circulating water jacket (Pyrex) to cool the lamp, to maintain the ambient temperature at 298 K, and to block unwanted infrared radiation. An appropriate cutoff filter was also placed outside the Pyrex jacket to ensure complete removal of radiation below 420 nm, and to ensure that irradiation of the dispersion was achieved only by visible light wavelengths.

Procedure and analyses: An aqueous suspension of EO (typically 50 mL, 2×10^{-5} M; an initial pH of 2.5 adjusted with HClO$_4$), H$_2$PtCl$_6 \cdot$ 6H$_2$O (at the desired concentrations), and TiO$_2$ (50 mg) in a 50-mL Pyrex glass vessel was magnetically stirred in the dark for approximately 30 min prior to irradiation to permit an adsorption/desorption equilibrium to be reached. At given irradiation time intervals, 3-mL aliquots were collected, centrifuged, and subsequently filtered through a Millipore filter (pore size 0.22 μm) to remove the catalyst particulates. The filtrates were analyzed by recording the UV/Vis spectrum of EO at 507 nm with a Lambda Bio 20 spectrophotometer (Perkin–Elmer). When PtCl$_6^{2-}$ was added to the EO solution acidified with HClO$_4$ to pH 2.5, a strong characteristic absorption band of PtCl$_6^{2-}$ appeared at 259 nm. However, after TiO$_2$ was added and the suspensions were stirred in the dark for 30 min, the absorption peak at 259 nm was no longer observable. In all the experiments in which the Pt^{IV} content changed from 0.4 wt% to 2 wt%, no PtCl$_6^{2-}$ was found in the bulk solution during the degradation process. From this we inferred that PtCl$_6^{2-}$ had been chemisorbed completely on the surface of the TiO$_2$ specimens. The specimens so modified were relatively stable. Evidently, chemisorption occurred during the 30 min stirring period, most likely through formation of Ti−O−Pt bonds.

The concentration of organoperoxides formed during irradiation of a 50-mL solution of EO containing 50 mg of TiO$_2$ or Pt^{IV}/TiO$_2$ was assayed immediately by the DPD method[29] after removal of catalyst particles by centrifugation and filtration at various time intervals; this is a photometric

method in which the DPD (*N,N*-dimethyl-*p*-phenylenediamine) reagent is oxidized by organoperoxides based on the peroxidase-catalyzed reaction. To discriminate between the formation of H$_2$O$_2$ and organoperoxides, catalase was added to the degraded solution before utilization of the DPD method because the catalase enzyme eliminates H$_2$O$_2$ (but not organoperoxide species) from a mixture that might contain both H$_2$O$_2$ and organoperoxides.[30] Total organic carbon (TOC) was assayed in the EO degradation process by using an Apollo 9000 TOC analyzer (Terkmar Dohrmann Co.); the assays were carried out after removal of catalyst particulates. The COD$_{Cr}$ data were obtained by direct measurements without removal of the catalyst particulates by using the potassium dichromate titration method.[31] ESR signals of the radicals spin-trapped by DMPO were examined with a Bruker ESP 300E spectrometer; the relevant irradiation source was a Quanta–Ray Nd:YAG pulsed laser system ($\lambda =$ 532 nm; frequency = 10 Hz). To minimize measurement errors, the same quartz capillary tube was used throughout the ESR measurements. The UV/Vis diffuse reflectance spectra of the photocatalyst specimens were recorded with an Hitachi U-3010 spectrophotometer (Japan) equipped with an integrating sphere attachment ($\Phi = 160$ nm). The analyzed spectral range was 200–800 nm, and BaSO$_4$ was the reflectance standard. X-ray photoelectron spectroscopic (XPS) examinations of the samples were carried out on the 220I-XL multifunctional spectrometer (VG Scientific, England) by using Al Kα radiation. The samples for XPS measurements were prepared through evaporation under reduced pressure (below 323 K; Table 2).

Table 2. Quantification table for experiment XPS.

Peaks	Center	SF	Peak area	FWHM	Tx. Function	Norm area	[AT] [%]
Pt4f5	77.90	6.81	619.855	1.964	6364.4	0.00018	18.333
Pt4f5	75.94	6.81	1025.042	1.749	6360.1	0.00031	30.312
Pt4f7	74.63	8.65	779.866	1.732	6357.3	0.00018	18.154
Pt4f7	72.66	8.65	1426.466	1.909	6353.1	0.00033	33.201

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