Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol and Phenolic Compounds in Aqueous Suspension of Pure Titania: Demonstrating the Existence of a Surface-Complex-Mediated Path

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The visible-light-induced degradation reaction of 4-chlorophenol (4-CP) was investigated in aqueous suspension of pure TiO$_2$. Contrary to common expectations, 4-CP could be degraded under visible illumination ($\lambda > 420$ nm), generating chlorides and CO$_2$ concomitantly. The observed visible reactivity was not due to the presence of trace UV light since the visible-light-induced reactions exhibited behaviors distinguished from those of UV-induced reactions. Dichloroacetate could not be degraded under visible light, whereas it degraded with a much faster rate than 4-CP under UV irradiation. The addition of *tert*-butyl alcohol, a common OH radical scavenger, did not affect the visible reactivity of 4-CP, which indicates that OH radicals are not involved. Other phenolic compounds such as phenol and 2,4-dichlorophenol were similarly degraded under visible light. The surface complexation between phenolic compounds and TiO$_2$ appears to be responsible for the visible light reactivity. Diffuse reflectance UV−vis spectra showed that 4-CP adsorbed on TiO$_2$ powder induced visible light absorption. The visible light reactivity among several TiO$_2$ samples was apparently correlated with the surface area of TiO$_2$. The visible-light-induced photocurrents on a TiO$_2$ electrode could be obtained only in the presence of 4-CP. It is proposed that a direct electron transfer from surface-complexed phenol to the conduction band of TiO$_2$ upon absorbing visible light (through ligand-to-metal charge transfer) initiates the oxidative degradation of phenolic compounds. When the surface complex formation was hindered by surface fluorination, surface platinization, and high pH, the visible-light-induced degradation of 4-CP was inhibited. The evidence of visible-light-induced reactions and the experimental conditions affecting the visible reactivity were discussed in detail.

Introduction

Titanium dioxide has been intensively investigated as a photocatalyst and is still the most efficient, most practical, and most studied photocatalyst despite extensive efforts to find photocatalytic materials outperforming TiO$_2$. The photocatalytic reactions on TiO$_2$ are initiated by absorbing UV photons that can excite valence band (VB) electrons to conduction band (CB) in the solid lattice and are completed through the subsequent interfacial electron transfers and thermal reactions occurring on the surface.[1] The photoinduced redox reactions on TiO$_2$ result in the generation of reactive oxygen species such as OH radicals and superoxides, which are mostly responsible for the strong oxidizing power of TiO$_2$.

In general, pure TiO$_2$ with the band gap of 3.0−3.2 eV is inactive under visible light illumination, which limits the practical application of TiO$_2$ photocatalysts. Therefore, pure TiO$_2$ has been modified by various ways such as impurity doping[2−7] and dye sensitization[8−11] to obtain visible light reactivity. Some studies, however, reported that pure unmodified TiO$_2$ showed the visible light photocatalytic reactivity although the substrate alone does not absorb visible light at all. Li et al.[12] observed the visible-light-induced degradation of H$_2$O$_2$ on TiO$_2$ and ascribed the visible light reactivity to the formation of surface complexes of H$_2$O$_2$/TiO$_2$ that absorb visible light.

Cho et al.[13] recently reported that pure TiO$_2$ in aqueous solution of a nonionic surfactant having polyoxyethylene groups (Brij) exhibited visible light activity for the reduction of CCl$_4$ and Cr(VI) and observed a broad absorption band (320−500 nm) in the Brij/TiO$_2$ solution. They proposed that a complex formation between the surfactant functional group and TiO$_2$ surface is responsible for the weak visible light absorption and the subsequent visible-light-induced electron transfer. Agrios et al.[14,15] also observed that 2,4,5-trichlorophenol formed a charge-transfer complex on TiO$_2$ and correlated the charge-transfer surface complex formation with visible light absorption among several chlorophenols. The visible-light-induced transformation of 2,4,5-trichlorophenol on TiO$_2$ produced coupling products only, and no mineralization was achieved. They reported that the charge-transfer complex formation was highly favored with P25 TiO$_2$ that has mixed phases of anatase and rutile and that the complexation on pure-phase anatase or rutile was significantly reduced. The above examples share a similarity in that surface complex formation on pure TiO$_2$ is responsible for the visible-light-induced photocatalytic transformation of substrates that do not absorb visible photons by themselves. Since a majority of TiO$_2$ photocatalytic reactions have been studied under UV irradiation, the potential visible light reactivities of TiO$_2$ due to the surface complex formation mechanism seem to be largely unrecognized. There should be more examples of such surface complexation that has visible light activity.

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In this study, we demonstrated that 4-chlorophenol (4-CP), which is one of the most common substrates that have been used in the studies of photocatalytic degradation, can be actually degraded and mineralized under visible irradiation ($\lambda > 420$ nm). The visible light reactivity of 4-CP was correlated with the surface complex formation that was supported by the diffuse reflectance UV−vis spectra and visible-light-induced photocurrent generation. Other phenolic compounds showed similar visible light reactivity. Various experimental evidence for the visible light reactivity of phenolic compounds was presented and discussed.

Experimental Section

Chemicals and Materials. Chemicals used in this study include 4-chlorophenol (4-CP, Sigma), 2,4-dichlorophenol (2,4-DCP, Sigma), 2,4-dichlorophenoxyacetate sodium salt (2,4-D, Aldrich), 4-nitrophenol (4-NP, Aldrich), phenol (PhOH, Junsei), dichloroacetate (DCA: $CHCl_2CO_2Na$, Aldrich), NaF (Samchun, Korea), *tert*-butyl alcohol (TBA, Shinyo), $FeCl_3 \cdot 6H_2O$ (Kanto), and superoxide dismutase (SOD, Sigma, manganese-containing enzyme, lyophilized). All reagents were used as received. Titanium dioxide powder used as a main photocatalyst was Ishihara ST-01 that has the pure anatase phase and the specific Brunauer−Emmett−Teller (BET) surface area of 340 m^2/g. Other commercial TiO_2 samples such as Degussa P25, Junsei, Hombikat UV100, anatase (Aldrich), and rutile (Aldrich) were also tested and compared with ST-01 for their visible light reactivity.

Surface fluorinated TiO_2 (F-TiO_2) was prepared by adding 10 mM NaF to an aqueous TiO_2 suspension.[16−19] Surface platinized TiO_2 (Pt/TiO_2) was obtained using a photodeposition method as described elsewhere.[20−22] Titanium dioxide (0.5 g/L) suspension with 1 M methanol (electron donor) and 0.1 mM chloroplatinic acid (H_2PtCl_6) was irradiated with a 200-W mercury lamp for 30 min. After irradiation, Pt-deposited TiO_2 powder was filtered, washed with distilled water, and dried under air. A typical Pt loading on TiO_2 was estimated to be ca. 3 wt %.

Photocatalytic Reaction and Analysis. TiO_2 powder was dispersed in distilled water (0.5 g/L) by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. An aliquot of the substrate stock solution (1 mM) was subsequently added to the suspension to give a desired substrate concentration, and then the pH of the suspension was adjusted with $HClO_4$ or NaOH standard solution. When the absence of dissolved oxygen was needed, the reactor was purged with nitrogen gas for 30 min prior to the photolysis and sealed from the ambient air during irradiation. The typical background O_2 concentration in the N_2-purged suspension was less than 10 μM (measured by a dissolved oxygen meter) and maintained at this level throughout the photolysis. Photoirradiation employed a 300-W Xe arc lamp (Oriel) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 320$ nm for UV illumination and $\lambda > 420$ nm for visible illumination), and then the filtered light was focused onto a 30-mL Pyrex reactor with a quartz window. When the wavelength-dependent photocatalytic reactivities were investigated, a series of long-pass cutoff filters ($\lambda > 320$, 395, 420, 455, 495, 550, and 645 nm) were used. The reactor was filled with minimized headspace and stirred magnetically. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45-μm poly(tetrafluoroethylene) (PTFE) syringe filter (Millipore). Duplicate or triplicate photocatalytic degradation (PCD) experiments were carried out under each experimental condition to confirm reproducibility.

The degradation of 4-CP (or other phenolic compounds) and the production of intermediates were monitored using a high performance liquid chromatograph (HPLC, Agilent 1100 series) equipped with a diode array detector and a ZORBAX 300SB C18 column (4.6 × 150 mm). The eluent consisted of a binary mixture of water containing 0.1% phosphoric acid and acetonitrile (80:20 by volume). Identification and quantification of ionic intermediates and products were performed by using an ion chromatograph (IC, Dionex DX-120) that was equipped with a Dionex IonPac AS 14 (4 mm × 250 mm) column and a conductivity detector. The eluent solution was 3.5 mM Na_2CO_3/1 mM $NaHCO_3$. The evolution of CO_2 was monitored using a gas chromatograph (GC, Hewlett-Packard 6890) that was equipped with a flame ionization detector (FID), a Porapak column, a CO_2 methanizer (HP G2747A), and a gas-sampling valve. Dissolved organic carbon was measured using a total organic carbon analyzer (TOC-V_{CSH}, Shimadzu).

Characterizations. To investigate the substrate−TiO_2 interaction, diffuse reflectance UV−vis spectroscopy (DRUVS) was employed. TiO_2 samples for DRUVS were prepared as follows. An organic substrate such as 4-CP was added to aqueous TiO_2 suspension in the same concentration ratio as in the case of photocatalytic reaction. When F-TiO_2 was used instead of pure TiO_2 to see if the surface fluorination of TiO_2 influences the substrate−TiO_2 interaction, NaF (10 mM) was added to the TiO_2 suspension and the pH was adjusted at pH 3. The substrate-adsorbed TiO_2 powder was obtained by evaporating the water solvent and drying under air. The obtained powder was diluted with barium sulfate (TiO_2/$BaSO_4$ = 1:19 by weight) and then measured for DRUVS using a UV−vis spectrophotometer (Shimadzu UV-2401PC) equipped with a diffuse reflectance attachment (Shimadzu ISR 2200).

Photocurrent generation was measured with a TiO_2/ITO electrode immersed in aqueous solution of 4-CP. For preparing the TiO_2/ITO electrode, an ITO plate was coated with TiO_2 film using Carbowax as a binder.[23] Two grams of Carbowax (50 wt % solution in poly(ethylene glycol)) was mixed with 0.2 g of TiO_2 powder, and the resulting paste was cast on an ITO plate using a doctor-blade technique, with tracks of two layers of Scotch Magic Tape, and then dried for 20 min in air and calcined at 450 °C for 30 min to burn off organics and bind the TiO_2 film to the ITO plate. The TiO_2/ITO electrode, a saturated calomel electrode (SCE), and a graphite rod were immersed in the reactor as working (collector), reference, and counter electrodes, respectively. Nitrogen gas was continuously purged through the suspension. Photocurrents were measured in aqueous solution with or without 4-CP as a function of irradiating wavelengths with application of a potential (+0.5 V vs SCE) using a potentiostat (EG&G 263A2) connected to a computer.

Results and Discussion

PCD of 4-CP under Visible Irradiation. Figure 1a shows that 4-CP can be degraded in a visible-light-illuminated suspension of pure TiO_2 (ST-01). The stoichiometric amount of chloride was produced from the PCD of 4-CP. A significant amount of CO_2 was also generated from the PCD of 4-CP under visible irradiation (Figure 1b). Although 4-CP was completely removed within 5 h of visible irradiation, the mineralization occurred much more slowly (as shown from the CO_2 generation profile). The CO_2 generated after 40 h of visible irradiation corresponded to 50% mineralization of the initial 4-CP concentration. Similar TOC reduction was also observed. However, little aromatic intermediates were detected by HPLC analysis. The present observation that 4-CP can be degraded and partially
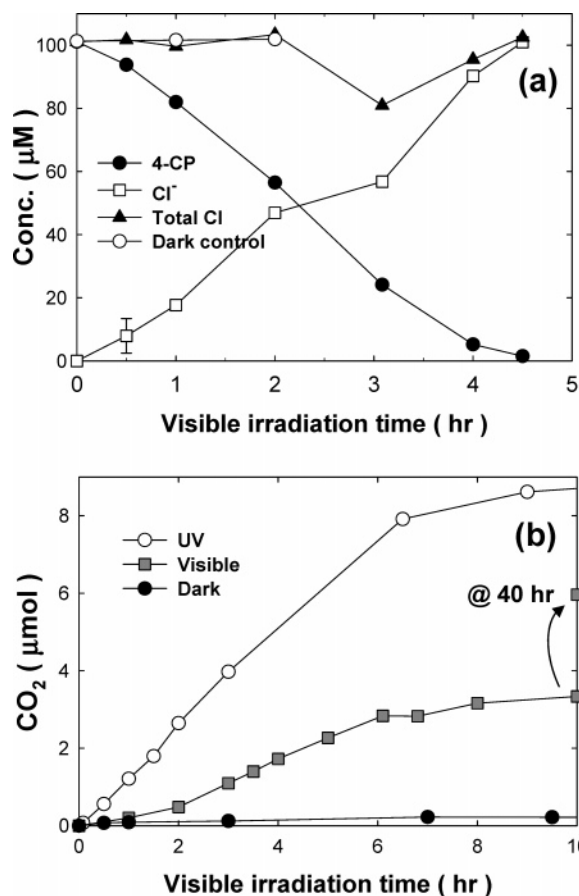
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Figure 1. (a) PCD of 4-CP in aqueous suspension of pure TiO_2 (ST-01) and (b) the concurrent CO_2 generation under visible irradiation (λ > 420 nm).

Figure 2. PCD of 4-CP and DCA under (a) UV and (b) visible irradiation.

mineralized into CO_2 is certainly unexpected. Both pure TiO_2 and 4-CP do not absorb any photons with λ > 420 nm, and 4-CP little adsorbs on a TiO_2 surface in aqueous suspension. However, the visible-light-induced degradation of 4-CP with pure TiO_2 has been reported previously. Lettmann et al.[24] reported that 6% and 15% of 4-CP was removed after 100 min of visible irradiation (λ > 400 nm) with Degussa P25 and Hombikat UV 100, respectively, but they ascribed this visible light reactivity to traces of UV light leaking into a reactor. However, this does not seem to be simply due to leaking UV. Figure 2 compares the PCDs of 4-CP and DCA under UV and visible light irradiation. Note that their relative PCD rates are very different between UV and visible light systems. Under UV light, DCA was degraded with a much faster rate than 4-CP whereas the degradation of DCA was negligible under visible light. If leaking UV light were responsible for the degradation of 4-CP, the degradation of DCA should be still faster than that of 4-CP in Figure 2b. Therefore, 4-CP degradation on pure TiO_2 under visible irradiation cannot be attributed to the leaking UV light. The mechanism of 4-CP degradation under visible irradiation should be different from that under UV irradiation.

The fact that the UV- and visible-light-induced PCDs of 4-CP are carried out via different mechanistic pathways is also supported from the following data. Effects of *tert*-butyl alcohol (TBA) addition, surface platinum deposition, and surface fluorination on PCD of 4-CP are compared between UV and visible light systems in Figure 3. First, the addition of TBA as an OH radical scavenger moderately reduced the PCD rate of 4-CP under UV irradiation but it little affected the PCD of 4-CP under visible irradiation. Since OH radicals cannot be generated on visible-light-illuminated TiO_2, the visible PCD process should
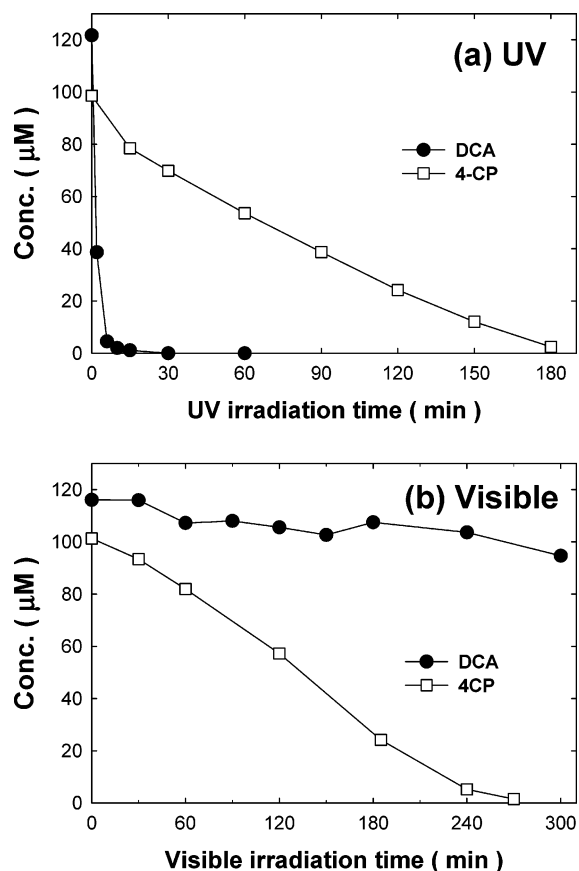
not be mediated by OH radicals. Second, surface platinization and fluorination of TiO_2 highly enhanced the PCD of 4-CP under UV irradiation (Figure 3a) but both of them strongly inhibited the degradation of 4-CP under visible light (Figure 3b). In general, Pt deposits on TiO_2 trap photogenerated CB electrons, subsequently retards the charge pair recombination, and enhances the overall PCD rates as shown in Figure 3a.[10,25,26] Surface fluorination of TiO_2 increases the mobile OH radical generation and enhances the OH-radical-mediated PCD rate.[16−19] The fact that the visible-light-induced degradation of 4-CP was almost completely inhibited when the TiO_2 surface was modified implies that the surface interaction of 4-CP on TiO_2 plays a critical role somehow in the visible PCD mechanism. The pH dependence of visible PCD of 4-CP shown in Figure 4 also indicates that the 4-CP/TiO_2 interaction is important. The visible PCD of 4-CP monotonically decreased with increasing pH and was negligible above pH 10, whereas the UV PCD of 4-CP did not show such a strong dependence on pH.[27,28] Increasing pH gradually changes the surface charge of TiO_2 from positive to negative (pH_{zpc} ∼ 6 for TiO_2),[29] and 4-CP takes the form of phenolate anion above pH 10 (pK_a = 9.41 for 4-CP).[30] The negligible visible PCD of 4-CP above pH 10 appears to be due to the electrostatic repulsion between the negatively charged TiO_2 surface and the 4-CP anion hindering the 4-CP/TiO_2 interaction.

Effects of Substrate Structure and the Kind of TiO_2 on Visible PCD. The visible PCD activity is strongly affected by the kind of substrates. Figure 5 compares the visible PCD of various substrates on pure TiO_2 (ST-01). Phenolic compounds such as 4-CP, 2,4-DCP, and phenol could be degraded under visible irradiation, whereas the PCD of DCA was negligible. Though very slow, the visible PCD of 4-NP and 2,4-D was not
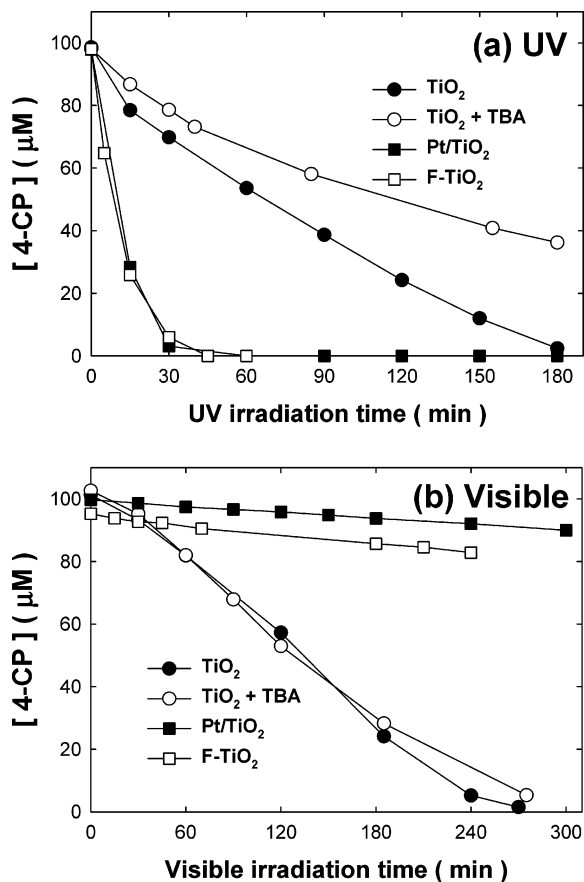
Figure 3. Effects of *tert*-butyl alcohol (TBA, 10 mM) addition, Pt deposition, and surface fluorination on the PCD of 4-CP under (a) UV and (b) visible irradiation.
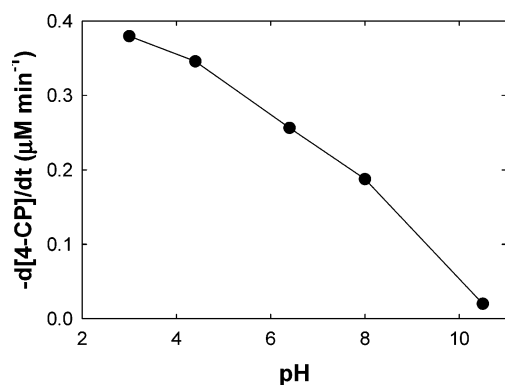

Figure 4. pH dependence of PCD of 4-CP under visible irradiation.

Figure 5. PCDs of several organic substrates in visible-irradiated suspension of pure TiO$_2$ (ST-01).

that the surface area is more important than the crystalline phase of TiO$_2$. The visible PCD reactivity was higher with higher BET surface area of TiO$_2$ samples as shown in Figure 6b, which reconfirms that the substrate−surface interaction is a critical factor in determining the visible PCD activity. However, the difference in visible PCD activity among various TiO$_2$ samples cannot be ascribed to the surface area alone. Many other surface-related parameters (e.g., OH group density and acidity, surface defect states, surface charge density) should contribute to the overall reactivity. Also, the rate ratios (r_{vis}/r_{uv}) of the visible PCD to the UV PCD were markedly different depending on the kind of TiO$_2$ sample. As for ST-01, the visible and UV PCD rates of 4-CP were 0.38 and 0.56 μM/min, respectively (i.e., $r_{vis}/r_{uv} = 0.68$), whereas those for P25 were 0.11 and 2.84 μM/min (i.e., $r_{vis}/r_{uv} = 0.039$). Although P25 is much more active than ST-01 under UV illumination, P25 is less active than ST-01 under visible light. Because the visible PCD mechanism is different from the UV PCD mechanism, the visible PCD activity cannot be correlated with the UV PCD activity.

Visible Light PCD Mechanism. The spectroscopic evidence of surface complex formation on TiO$_2$ was obtained using DRUVS. DRUV spectra of pure TiO$_2$ (ST-01) and TiO$_2$/ substrate powders are compared in Figure 7a. Since the TiO$_2$/ substrate powder was prepared by evaporating water from the suspension and not by filtering TiO$_2$ particles equilibrated with the substrate adsorption, more substrates were forced to adsorb on the TiO$_2$ surface in the powder sample and consequently the substrate−surface interaction should be far more enhanced from that in the suspension. The TiO$_2$/DCA spectrum is identical to that of pure TiO$_2$, but the TiO$_2$/phenolic compounds significantly absorb in the region of $\lambda > 400$ nm. This is consistent with the fact that DCA was not degraded at all but

negligible. It is interesting to note that the visible PCDs of 4-CP and 4-NP are very different, which seems to be related to different acidity constants (pK_a = 9.41 and 7.15 for 4-CP and 4-NP, respectively).[30] In the dark aqueous suspension, the adsorption of all phenolic compounds on TiO$_2$ was negligible or very minor. Nevertheless, a very small fraction of them seem to form surface complexes that are responsible for visible PCD.

Figure 6a shows that the visible PCD of 4-CP is strongly influenced by the kind of TiO$_2$ photocatalysts. Among various commercial TiO$_2$ samples, Ishihara ST-01 and Hombikat UV 100 that have the highest surface area show the highest visible PCD activity for 4-CP. Both samples are pure anatase. Although Agrios et al.[15] claimed that P25 is better than Aldrich anatase in surface complexation and visible reactivity of chlorophenols because of the mixed crystallinity of the former, our case shows higher visible reactivity with pure anatase than P25. It seems
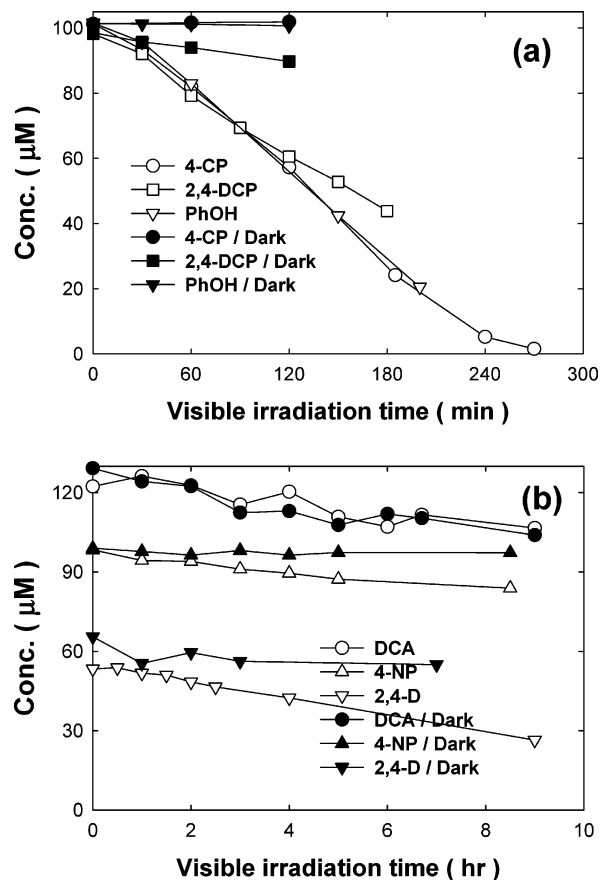
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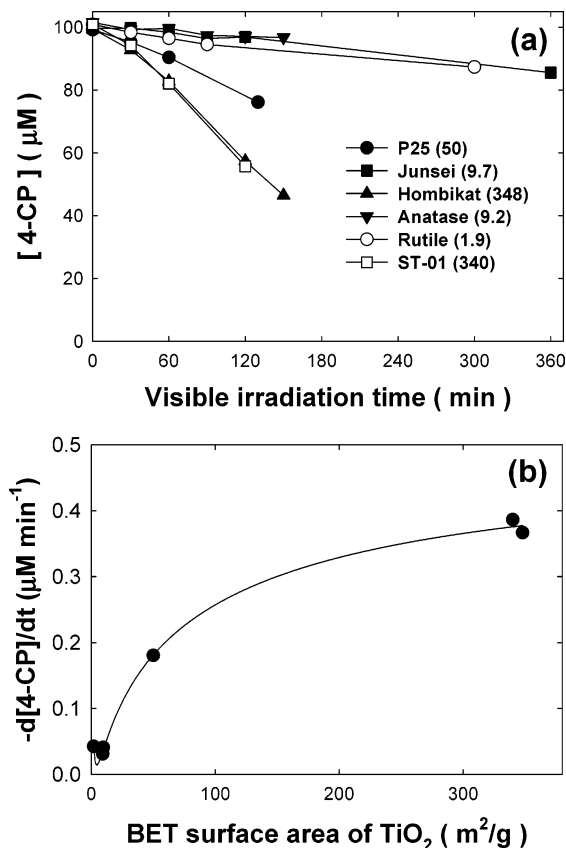*J. Phys. Chem. B, Vol. 109, No. 11, 2005* **5147**

Figure 6. (a) Visible-light-induced PCD of 4-CP with various commercial TiO_2 samples. The numbers in parentheses by the label are BET surface area in m^2/g. (b) The observed rates of 4-CP degradation (from panel a) as a function of the BET surface area of TiO_2 samples.

phenolic compounds could be removed under visible light. The visible light absorption by the TiO_2/phenolic compound powders indicates that surface complexes form between TiO_2 and phenolic compounds. The most probable structure is that the substrate is attached to the surface through a phenolate linkage (reaction 1).

$$\equiv Ti-OH + HO-Ph \rightarrow \equiv Ti-O-Ph + H_2O \qquad (1)$$
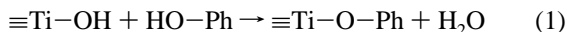
This kind of surface complexation enables the visible light absorption through ligand-to-metal charge transfer (LMCT) between the substrate (ligand) and the Ti(IV) site on the surface.[31,32] Recently, Seo et al.[33] demonstrated that the LMCT-mediated visible light absorption is enabled not only by the covalent bonding (inner-sphere complexation) like reaction 1 but also by the physical adsorption (outer-sphere complexation) of polyaromatic hydrocarbons on TiO_2. Stafford et al.[34] also reported that 4-CP adsorbed on dry TiO_2 powder changed the color of TiO_2 from white to yellow and suggested the phenolate linkage formation on the basis of the measurement of diffuse reflectance FTIR spectroscopy. Agrios et al.[15] recently showed that a series of chlorophenols did form CT complexes on TiO_2 surfaces by measuring the DRUV spectra. Although they reported that the surface complexation was weaker with lesser-chlorinated phenols and that the visible light absorption by TiO_2/phenol and TiO_2/4-CP was negligible, this study using TiO_2 with higher surface area (ST-01), however, shows that 4-CP and phenol indeed form visible-light-absorbing LMCT complexes on pure titania. In addition, the visible light absorption by the TiO_2/4-CP complex was higher than that by TiO_2/2,4-DCP (Figure 7a).
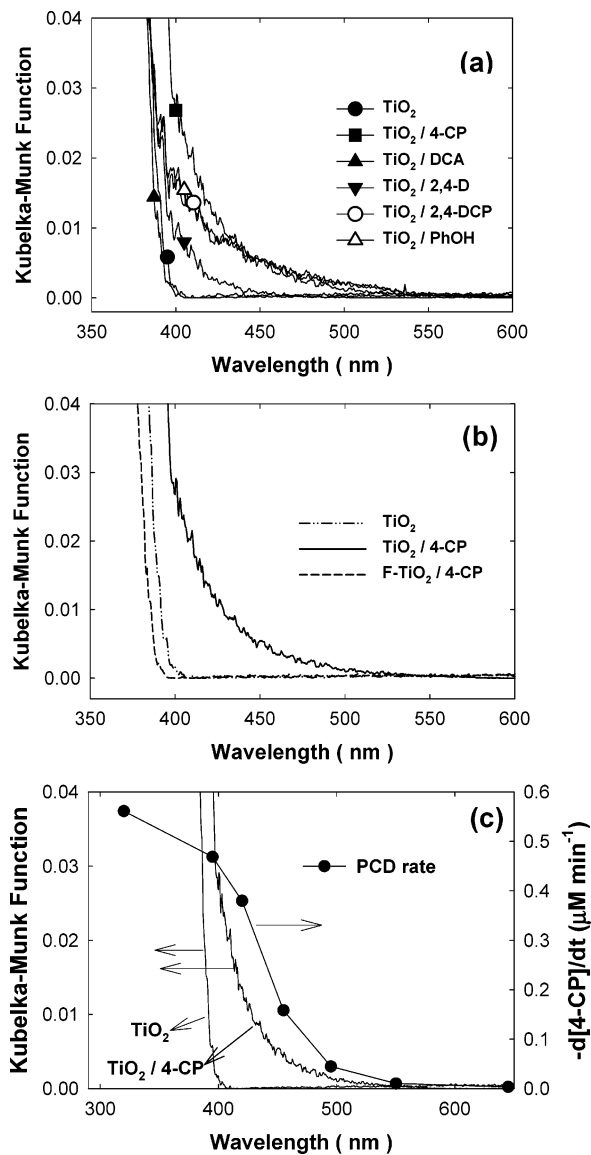
Figure 7. Diffuse reflectance UV/vis spectra of substrate-adsorbed TiO_2 powder. Effects of (a) the kind of substrates and (b) surface fluorination. (c) The wavelength-dependent PCD of 4-CP is compared along with the reflectance spectra.

The surface complexation of the reaction 1 type is essentially a condensation reaction between a surface hydroxyl group and a substrate hydroxyl group. But aliphatic alcohols do not seem to form such complexes in aqueous TiO_2 suspension judging from the fact the addition of excess TBA did not inhibit the visible-light-induced degradation of 4-CP at all (Figure 3b). If TBA competed for the surface hydroxyl groups with 4-CP, the visible-light-induced degradation of 4-CP should be hindered in the presence of TBA. Much higher acidity of phenolic compounds than aliphatic alcohols seems to be responsible for reaction 1. On the other hand, the presence of surface hydroxyl groups is certainly essential for the CT complex formation. Figure 7b shows that the surface complex formation between TiO_2 and 4-CP (i.e., visible absorption) is completely prohibited upon fluorinating the TiO_2 surface, which is in accord with the inhibited visible PCD of 4-CP with F-TiO_2 (Figure 3b). The surface fluorination replaces the surface hydroxyl groups ($\equiv Ti-OH$) with the fluorides ($\equiv Ti-F$)[16-19] and should inhibit reaction 1. Therefore, the observed fluorination effects indicate that the surface complexation of 4-CP should be associated with the surface hydroxyl groups on TiO_2. When the surface hydroxyl

Figure 8. (a) Visible-light-induced current (I_{ph}) generation on a TiO$_2$/ITO electrode in water with or without 4-CP. (b) I_{ph} and PCD rate are compared as a function of the wavelength. The wavelength in the abscissa refers to the cutoff λ of the long-pass filter (i.e., irradiation wavelengths > λ_{cutoff}).

groups are depleted, the surface complexation of 4-CP that is responsible for visible light activation should be hindered. In a similar sense, Pt deposition on TiO$_2$ seems to inhibit the surface complex formation of 4-CP and subsequently reduces the visible light activity as shown in Figure 3b. How the presence of Pt deposits inhibits the surface complexation on TiO$_2$ is not quite clear. It is speculated either that Pt deposits cover the surface OH sites or that the presence of Pt deposits changes the acidity of surface hydroxyl groups to influence reaction 1. Increasing pH deprotonates the hydroxyl groups ($\equiv$Ti$-$OH $\rightarrow$ $\equiv$Ti$-$O$^-$ + H$^+$), which makes the surface complexation of 4-CP (reaction 1) unfavored and consequently decreases the visible activity (Figure 4). In Figure 7c, the DRUV spectrum of TiO$_2$/4-CP powder is compared with the wavelength-dependent PCD rate of 4-CP. The wavelength-dependent profiles of visible light absorption by TiO$_2$/4-CP and PCD rate of 4-CP are qualitatively very similar, which confirms that the visible PCD of 4-CP is directly related to the TiO$_2$/4-CP complex formation.

To investigate the role of the TiO$_2$/4-CP complex in the visible light activation, we monitored the photocurrent generation from a TiO$_2$/ITO electrode immersed in aqueous 4-CP solution. As illustrated in Figure 8a, the TiO$_2$/4-CP surface complex is excited by absorbing visible light and subsequently transfers an electron into the electrode to generate visible-light-induced current (I_{ph}). The time profiles of photocurrents generated under λ > 455 nm irradiation are shown in Figure 8a. Figure 8b compares the photocurrent generated in the presence of 4-CP with that obtained in the absence of 4-CP as a function of irradiation wavelength. The visible-light-induced current is generated only in the presence of 4-CP, and the wavelength-dependent variations of I_{ph} and PCD rate are concurrent in the visible region (λ > 400 nm).

Since DRUVS, I_{ph}, and PCD rate all are similarly varied as a function of λ in the visible region, the mechanism of visible

SCHEME 1: Surface-Complex-Mediated Photodegradation of 4-CP on Pure TiO$_2$ under Visible Irradiation

PCD of 4-CP is now quite clear. The TiO$_2$/4-CP surface complex is excited by visible light through LMCT with direct transfer of an electron from 4-CP to TiO$_2$ CB, which is subsequently followed by a series of degradation reactions of 4-CP. The key mechanism is schematically illustrated in Scheme 1. The visible-light-induced electron transfer from 4-CP to CB in Scheme 1 is a direct transition without involving the excited state of 4-CP. Once an electron is injected into CB, it should be transferred to suitable electron acceptors. Otherwise it recombines with the surface complex to make a null cycle. Figure 9a shows the effect of electron acceptors on the visible PCD of 4-CP. As expected, 4-CP was not degraded at all under N$_2$-saturated conditions (i.e., in the absence of an electron acceptor). However, when ferric ions were present as an alternative electron acceptor in the anoxic suspension, 4-CP could be degraded as fast as in the presence of O$_2$. On the other hand, in the presence of O$_2$,

Figure 9. Effects of (a) electron acceptor and (b) superoxide dismutase (SOD, 15 mg/L) on visible-light-induced PCD of 4-CP.

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superoxides should be generated as a result of electron transfer to O_2 (see Scheme 1) and they may react with 4-CP and contribute to the degradation of 4-CP. To check whether superoxides play a role or not, the visible PCD of 4-CP was carried out in the presence of superoxide dismutase (SOD)[35,36] (Figure 9b). The addition of SOD did not affect the visible PCD rate, which indicates that the role of superoxide in 4-CP degradation is insignificant.

Conclusions

It is taken for granted that pure titania cannot be activated by visible light. The band gap of about 3 eV is simply too large to absorb visible photons directly unless some defect sites are populated in the band gap. Therefore, any visible-light-induced reactions on pure titania should be initiated by indirect ways. The most common example of visible-light-induced reactions on pure TiO_2 is the sensitized degradation of dyes.[37,38] On the other hand, visible-light-induced degradation of colorless substrates on pure TiO_2 should be mediated by substrate−surface complexation that enables the visible light absorption through LMCT. While some examples of visible-light-absorbing TiO_2/substrate complexation have been reported,[12−15,31−33] phenol and 4-CP were not considered to be of this kind. Phenol and 4-CP do not absorb visible light by themselves and hardly adsorb on the TiO_2 surface in aqueous suspension. Therefore, the absence of their visible light reactivity has been assumed without any doubt and any sign of visible light reactivity has been overlooked. This study clearly demonstrates that phenolic compounds can be degraded on pure TiO_2 under visible light through the surface complexation mechanism on the basis of reactivity, DRUVS, and photocurrent measurements although the fraction of surface-complexed phenolic compounds in aqueous TiO_2 suspension is very small. The visible-light-induced reactions exhibited behaviors that were distinguished from those of UV-induced reactions. The surface complexes between TiO_2 and 4-CP (or other phenolic compounds) absorb visible light, and the subsequent interfacial electron transfer initiates PCD reaction of 4-CP. The visible light reactivity was apparently proportional to the surface area of TiO_2. When the surface complex formation was hindered by surface fluorination, surface platinization, and high pH, the visible-light-induced PCD was inhibited as well.

Considering the fact that simple phenolic compounds such as phenol and 4-CP have been widely employed as test substrates in measuring PCD activity of visible-light-active photocatalytic materials, their inherent visible light reactivity with pure TiO_2 should certainly be recognized and taken into account when interpreting reactivity data. Some positive signs of visible light reactivity obtained from PCD of phenolic compounds could result from the enhanced surface complexation, not necessarily from the redox power of electron−hole pairs generated by the band gap excitation under visible light.

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