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Photocatalytic Reactivity and Diffusing OH Radicals in the Reaction Medium Containing TiO_2 Particles

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Abstract−The generation of OH radicals on UV-illuminated TiO_2 surface is mainly responsible for the photocatalytic oxidation of pollutants in various contaminated environmental media. Although the reactivity of OH radicals is largely limited within the surface region, the possibility of OH desorption and diffusion into the reaction medium has been often raised. This study provides several examples for the presence of diffusing OH radicals in aqueous solution and polymer matrix containing TiO_2 particles. The photocatalytic degradation rates of $(CH_3)_4N^+$ in TiO_2 suspension were comparable between acidic and alkaline conditions, which could not be explained by a simple electrostatic surface charge model. From the present mechanistic study, it is suggested that the photocatalytic oxidation of $(CH_3)_4N^+$ at acidic pH mainly proceeds through free OH radicals in the solution bulk, not on the surface of TiO_2. The diffusing OH radicals also played the role of main oxidants in the solid phase. The photolysis of TiO_2-embedded PVC composite films generated cavities around the imbedded TiO_2 particles and the development of cavity diameter continued even after the direct contact between the PVC and TiO_2 was prohibited. This implied that active oxygen species that were photogenerated on TiO_2 surface desorbed and diffused across a few micrometers to react with the polymer matrix.

Key words: Photocatalysis, TiO_2, Hydroxyl Radicals, PVC, Tetramethylammonium

INTRODUCTION

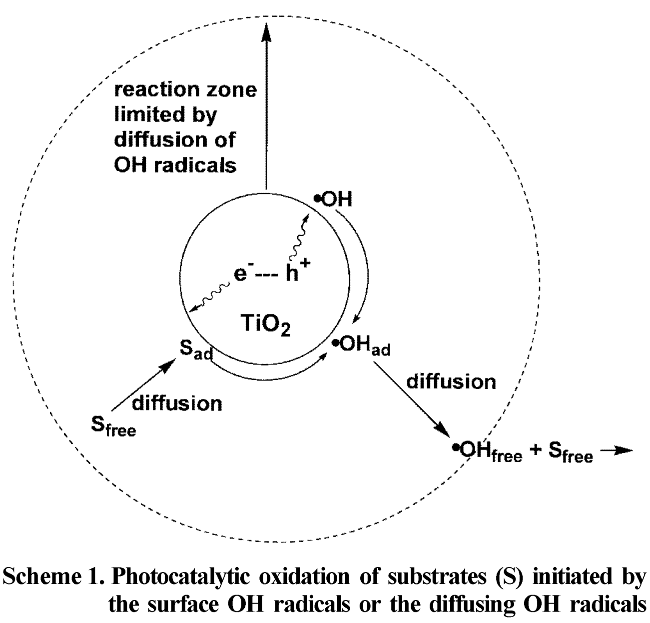
Semiconductor photocatalysis has been extensively studied for its application to the remediation of polluted water and air [Hoffmann et al., 1995]. In particular, TiO_2 has been the most popular and successful photocatalyst for this purpose [Choi et al., 2000, 2001; Cho et al., 2001; Chai et al., 2000]. Titanium dioxide generates a pair of a conduction band (CB) electron and a valence band (VB) hole in the solid oxide lattice upon absorbing a photon with energy greater than 3.2 eV (or shorter wavelength than 388 nm) and the subsequent charge transfers at the interface initiate various kind of redox reactions. The CB electrons and VB holes in TiO_2 are moderate reductants (E_{cb}=−0.5 V_{NHE} at pH 7) and strong oxidants (E_{vb}=+2.7 V_{NHE} at pH 7), respectively. Most of the strong remedial power of TiO_2 photocatalysts is mainly ascribed to the strong oxidation potential of VB. Accordingly, other wide band gap semiconductors with high positive values of E_{vb} such as ZnO, WO_3, and SnO_2 often show comparable oxidative reactivities.

The VB holes react with substrates through either the direct charge transfer or the generation of OH radicals [Fox and Dulay, 1993]. The OH radicals that are very strong oxidants (E^0=2.8 V_{NHE}) are produced on TiO_2 surface by the reaction of VB holes with the surface hydroxyl groups or adsorbed water molecules (reaction 1). Although the surface-generated OH radicals react with adsorbed substrate on the surface in most cases, the possibility that the OH radicals desorb from the surface and diffuse into the bulk medium has been often raised (reaction 2) [Turchi and Ollis, 1990].

$$h^+_{vb} + {>}OH_{surf}\ (\text{or } H_2O_{ad}) \rightarrow \bullet OH_{surf} \tag{1}$$

$$\bullet OH_{surf} \rightarrow \bullet OH_{free} \tag{2}$$

Scheme 1 illustrates the photocatalytic oxidation process through



Scheme 1. Photocatalytic oxidation of substrates (S) initiated by the surface OH radicals or the diffusing OH radicals in the bulk medium.

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the surface OH radicals or the diffusing free OH radicals. Whether the free OH radicals are present and how far they diffuse away from the surface have important mechanistic implications in the photocatalytic remediation process. In this study, we provide evidence for diffusing free OH radicals in aqueous TiO_2 suspension and in the solid matrix of TiO_2-containing polymer. Both the photocatalytic degradation of tetramethylammonium (TMA) in TiO_2 suspension and the photocatalytic decomposition of TiO_2-embedded PVC (Polyvinylchloride) films in the ambient air took place not only on the TiO_2 surface but also in the bulk of medium.

EXPERIMENTAL

1. Photocatalytic Degradation of Tetramethylammoniums (TMA) in TiO_2 Suspension

Titanium dioxide (Degussa P25), a mixture of 80% anatase and 20% rutile with an average BET surface area of 50±15 m^2/g, was used as photocatalyst without further activation. Tetramethylammonium hydroxide (TMAH) was purchased from Aldrich. All TiO_2 suspensions were prepared at a concentration of 0.5 g/L and were dispersed by simultaneous sonication and shaking. An aliquot of the TMA stock solution (1 mM) was subsequently added to the suspension to give a desired concentration; then the pH of the suspension was adjusted with HCl or NaOH standard solution. 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 cut-off filter (λ>300 nm); then the filtered light was focused onto a 90-mL Pyrex reactor with a quartz window. The reactor was filled with minimized headspace, sealed with a rubber septum and stirred magnetically. Sample aliquots were withdrawn by a 1-mL syringe and filtered through a 0.45-μm PTFE filter (Millipore). Identification and quantification of ionic intermediates and products were performed by using an ion chromatograph (IC, Dionex DX-120).

The surface concentrations of TMA ions on TiO_2/water interface were directly monitored by using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) [Hug and Sulzberger, 1994; Martin et al., 1996]. Spectra were recorded by using an FTIR spectrometer (Bomem, MB 104) equipped with a deuterated triglycine sulfate detector (DTGS) and an ATR unit (Spectra-Tech, ARK kit) with a horizontal ZnSe crystal. The ZnSe crystal (73 mm×8 mm×3 mm, crystal angle 45°) was bonded in a trough-shaped plate to hold liquid samples. For the preparation of TiO_2 coating layers, 300 μL of suspension containing 0.76 mg of TiO_2 was applied over the one side of the ZnSe crystal plate and allowed to dry under ambient air. The TMA solution was applied on the trough-plate and equilibrated with the TiO_2-coated ZnSe plate. The IR spectra of the TMA on the TiO_2/water interface were taken with varying the solution pH.

2. Photolysis of TiO_2-PVC Composite Films

Powder of PVC [-$(CH_2CHCl)_n$-] was supplied by LG Chemical Co. The TiO_2 photocatalyst was Degussa P25. PVC-TiO_2 composite films were cast as follows. The polymer stock solution was prepared by dissolving 50 g of PVC in 1 L of tetrahydrofuran (THF) under vigorous stirring. In order to minimize the size of TiO_2 aggregates that were embedded in the PVC matrix, the fraction of smaller TiO_2 aggregate was separated by a centrifugal method. In a typical preparation, 75 mg of the centrifuged TiO_2 powder was suspended in 100 mL of PVC stock solution to give 1.5 wt% of TiO_2 content with respect to the total mass of PVC. An aliquot of 3 mL PVC-TiO_2 solution was spread on a slide glass and dried for two days. The thickness of the resulting PVC-TiO_2 composite film was measured to be 25-30 μm by a micrometer. The transmittance of the PVC-TiO_2 composite film was typically around 80% at λ=600 nm. All the films were irradiated through a Pyrex filter under a 200-W mercury lamp. The light flux onto the sample was measured to be 1.5 mW/cm^2 (300<λ<400 nm) with a power-meter. The surface morphological images of the irradiated composite film were taken by using a field emission scanning electron microscope (FE-SEM) with the pre-treatment of Pt deposition.

RESULTS AND DISCUSSION

1. TiO_2-Water Interface

The photocatalytic degradations of $(CH_3)_4N^+$ (TMA) at various pH were successfully described by the first-order kinetics. Although the molecular charge of TMA was not affected by pH, its degradation rates showed a strong pH-dependence as shown in Fig. 1. The "V"-shaped pH dependence could not be explained in terms of a simple surface-charge model of TiO_2 since the photocatalytic de-

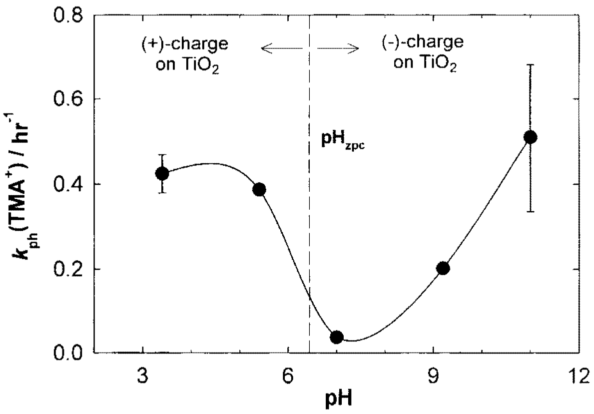

Fig. 1. First-order rate constants, k_{ph}, for the photocatalytic degradation of $(CH_3)_4N^+$ (TMA) as a function of pH. $[TMA]_0$= 100 μM, $[TiO_2]$=0.5 g/L.

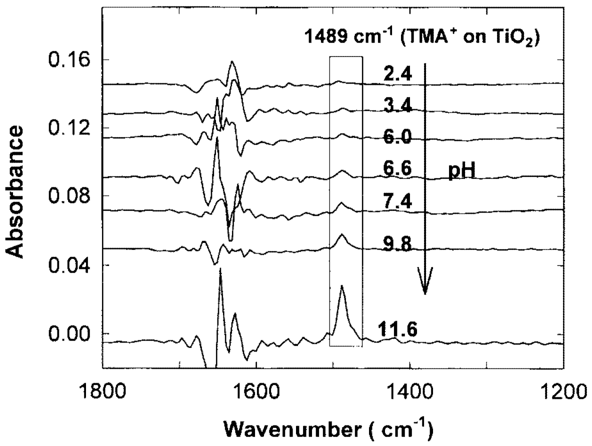

Fig. 2. The pH-dependent ATR-FTIR spectra of TMA at the TiO_2/ water interface.

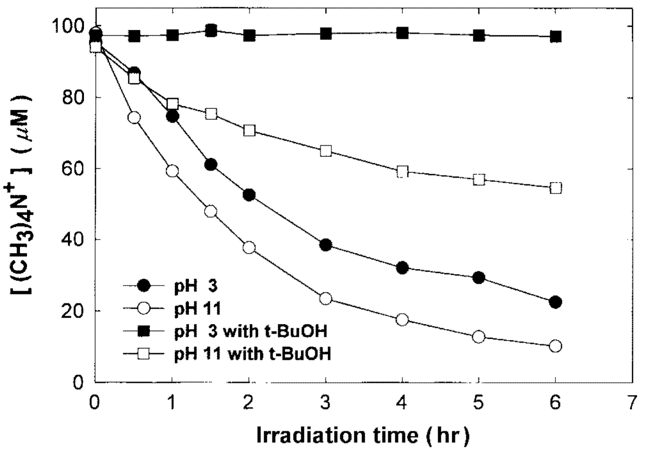

Fig. 3. Effects of OH radical scavenger, *t*-BuOH (10^{-2} M), on the photocatalytic degradation of TMA at pH 3 and pH 11.

gradation rate of cations should be minimal at pH<pH_{zpc} due to the electrostatic repulsion between the cationic substrate and the positively-charged surface [Kormann et al., 1991]. Fig. 2 shows the pH-dependent adsorption behavior of TMA (5 mM) on TiO_2 film, which was monitored by ATR-FTIR method. The IR absorption peak at 1,489 cm^{-1} is assigned to the ν_{15} antisymmetric CH_3 deformation of $(CH_3)_4N^+$ [Berg, 1978]. As predicted from the electrostatic model, TMA was repelled from the TiO_2 surface at acidic pH and strongly attracted with increasing pH above pH_{zpc}, which was also consistent with the previous observations [Connor et al., 1999; Dobson et al., 1997]. Therefore, if the photocatalytic degradation of TMA was initiated by surface-bound OH radicals, it should be very quickly degraded in alkaline solutions, which was not observed. This implies that the photocatalytic degradation of TMA should proceed through not only OH radicals on the surface but also free OH radicals in the solution.

In order to verify the role of free OH radicals, the photocatalytic degradation of $(CH_3)_4N^+$ at pH 3 and 11 were compared in the absence and presence of *tert*-butyl alcohol (*t*-BuOH) as shown in Fig. 3. Since diffusing free OH radicals, if any, would be scavenged by excess *t*-BuOH in the solution (reaction 3),

$$(CH_3)_3COH+\bullet OH_{free} \rightarrow \bullet CH_2C(CH_3)_2OH+H_2O \qquad (3)$$

its inhibitory effect on the photocatalytic degradation could be taken as an evidence of the solution-phase mechanism [Richard and Lemaire, 1990]. The complete inhibition of TMA degradation by *t*-BuOH was observed at pH 3, while the inhibition at pH 11 was only partial. With the present experimental conditions and the literature rate constants [k(*t*-BuOH+•OH)=6×10^8 $M^{-1}s^{-1}$, k(TMA+•OH)=7×10^6 $M^{-1}s^{-1}$ [Bobrowski, 1980]; [*t*-BuOH]=10^{-2} M, [TMA]=10^{-4} M], we calculate that 100% of free OH radicals should be scavenged by *t*-BuOH. The complete inhibition at pH 3 supports the free OH radical action in solution while the partial inhibition at pH 11 suggests a dual surface-solution mechanism.

Whether the initial oxidation occurs on the surface of the photocatalyst or in the solution bulk has been often disputed. While the supporting evidence for the surface oxidation is dominant, the solution-phase mechanism has been often reported. Sun and Pignatello reported that free OH radicals were involved in the photocatalytic oxidation of 2,4-dichlorophenoxyacetic acids depending on pH [Sun and Pignatello, 1995]. Minero et al. argued that the photocatalytic oxidation of phenol on fluorinated TiO_2 proceeded almost entirely via free OH radicals [Minero et al., 2000a, b]. This study adds another example of homogeneous OH radical oxidation in the TiO_2/UV system.

2. TiO_2-PVC Interface

We have recently reported a detailed study on the photocatalytic degradation and characterization of the irradiated PVC-TiO_2 composite films under ambient air [Cho and Choi, 2001]. The surface morphology of the irradiated polymer films was analyzed by SEM. Fig. 4a-e show the surface images of the PVC-TiO_2 composite films that were irradiated for 0, 25, 50, 100, and 200 hrs under air, respectively. The SEM images reveal that the degradation of the PVC matrix started from the PVC-TiO_2 interface and led to the formation of cavities around TiO_2 particle aggregates. The individual cavity became highly inter-connected with irradiation, and then coalesced to a size of ~10 μm. Further irradiation led to smoothing out the cavities. This is similar to the previous observation [Horikoshi et al., 1998], which reported the formation of holes in an illuminated TiO_2-blended PVC film in water. The PVC-TiO_2 film that was irradiated under nitrogen atmosphere showed little sign of degradation, which confirmed the necessity of oxygen for photocatalytic reaction in the solid phase. The SEM images also imply that the active oxygen species generated on TiO_2 surface desorbed and diffused through a finite distance to etch out the polymer matrix. Otherwise, the photocatalytic degradation would have stopped at an earlier stage (e.g., Fig. 4b) where the crevice developed between the TiO_2 surface and the polymer matrix inhibited the oxidizing species on TiO_2 from directly contacting the polymer. As for PVC whose glass transition temperature (81 °C) is well above room temperature [Lide, 1997], the mobility of the polymer chains is restricted. The enlarged view (Fig. 4f) of a cavity around TiO_2 particles clearly shows that the cavity boundary was well separated by 1-2 μm from the particle boundary. This supports that the oxidizing radicals desorbed from the TiO_2 surface in this solid-solid interface region. This argument is also consistent with recent reports [Tatsuma et al., 1999, 2001], which observed that the active oxygen species (most likely OH radicals) generated on illuminated TiO_2 diffused away from the surface into the gas phase.

CONCLUSIONS

In order to investigate whether OH radicals diffuse out from the photocatalyst surface, we have carried out both the photocatalytic degradation of TMA in aqueous TiO_2 suspension and the photocatalytic decomposition of TiO_2-embedded PVC films in the ambient air. In both cases of the TiO_2/water and TiO_2/PVC interface, the active oxidizing species, most likely OH radicals, desorbed from the TiO_2 surface and diffused into the reaction medium to initiate the degradation reaction in the bulk. While the adsorbed OH radicals strictly limit the reaction sites on the photocatalyst surface, the diffusing OH radicals could expand the reaction zone up to much larger volume (Scheme 1). The behavior of diffusing free OH radicals is also important in understanding other advanced oxidation processes [Kang et al., 2001]. In general, the free OH radicals desorbed from TiO_2 surface seem to take part in the photocatalytic ox-

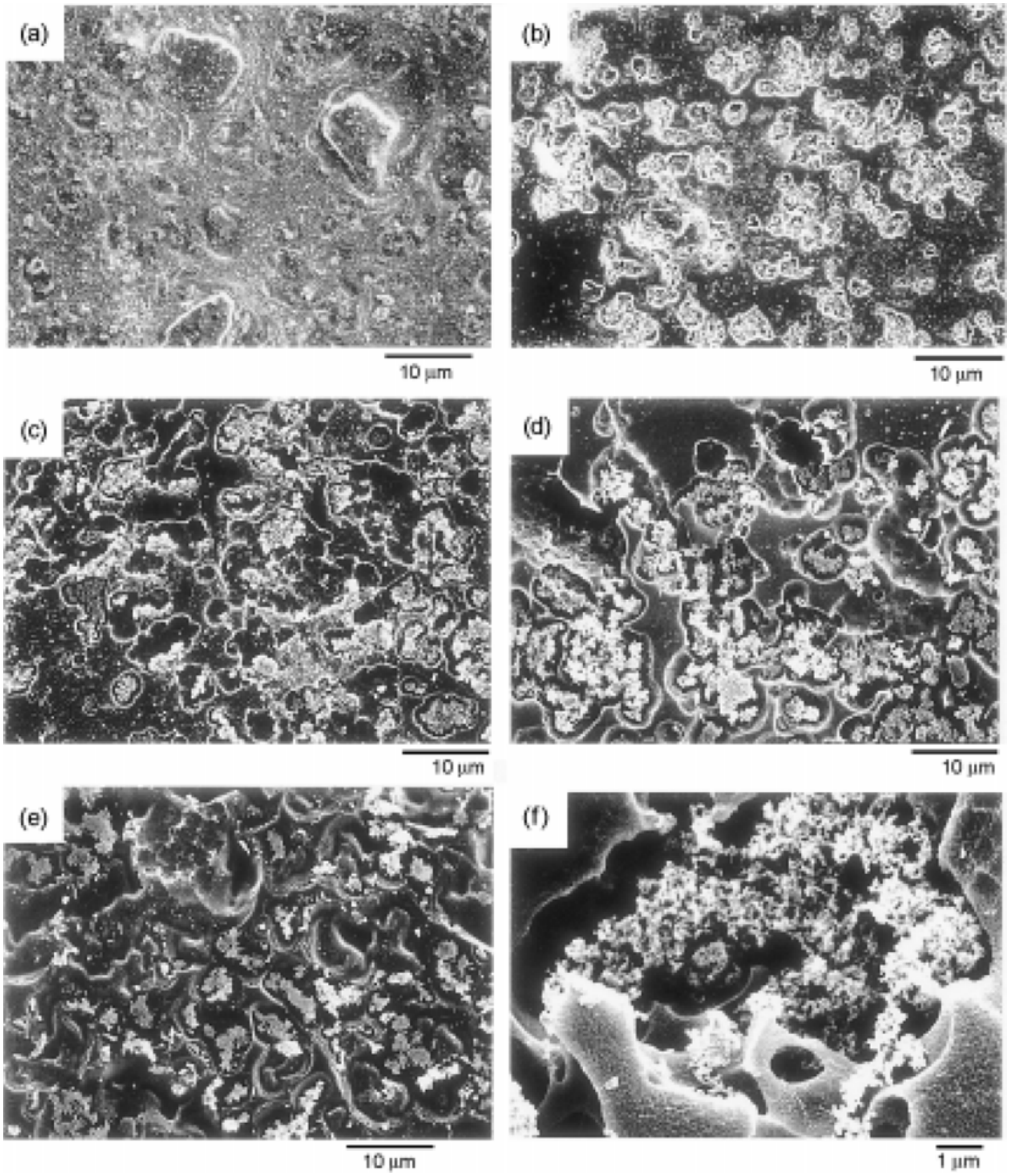

Fig. 4. SEM images of the PVC-TiO_2 (1.5 wt%) composite film surface. (a) before irradiation; (b) 25 hrs irradiated; (c) 50 hrs irradiated; (d) 100 hrs irradiated; (e) 200 hrs irradiated; (f) 100 hrs irradiated (enlarged view).

idation reactions to some extent. However, remaining to be answered are the specific experimental conditions or parameters that drive the OH radical desorption and how far the desorbed OH radicals diffuse out.

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