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Quantum yields of active oxidative species formed on TiO_2 photocatalyst

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Abstract

The quantum yield of hydroxyl radical (•OH) production during TiO_2 photocatalysis was estimated to be 7×10^{-5} in aqueous solution by means of a method using terephthalic acid as a fluorescence probe. This value is much lower than the quantum yield of ordinary photocatalytic reactions ($\sim10^{-2}$). Conversely, the quantum yield of hole generation estimated by iodide ion oxidation was equivalent (5.7×10^{-2}) to that of ordinary photocatalytic reactions. This implies that oxidative reactions on TiO_2 photocatalyst occur mainly via photogenerated holes, not via •OH. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: TiO_2 photocatalysis; OH radical; Photogenerated hole; Fluorescence probe; Quantum yield

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1. Introduction

The photocatalytic degradation of pollutants using TiO_2 is attracting considerable attention for the application to environmental problems [1–9]. We have focused our attention on developing transparent TiO_2 materials with useful self-cleaning, deodorizing and antibacterial functions using low-intensity UV light sources in the indoor environment [10–18]. For mechanistic details of photocatalysis of TiO_2, a number of researchers have reported the observation of several radical species formed on TiO_2 during the photochemical reactions. The process is initiated by the band-gap excitation of the TiO_2 under UV illumination. The electrons and holes thus produced diffuse to the surface and react with surface species. For photogenerated electrons, using the chemiluminescence technique, we have recently shown that the electrons are trapped by adsorbed oxygen molecules with a high quantum yield to generate superoxide, $O_2{}^-$ [19,20]. Conversely, surface adsorbed water reacts with photogenerated holes to produce •OH [21–25]. Evidence supporting the generation of •OH as an active species includes the detection of hydroxylated reaction intermediates [26–28], distribution of the hydroxylation products [29,30] and electron paramagnetic resonance (EPR) detection of •OH using spin traps that scavenge •OH [31–33]. The •OH is often assumed to be the major species responsible for the photocatalytic oxidative reactions. However, several recent studies have questioned whether this mechanism may be reasonable to all TiO_2 photocatalytic oxidation reactions. There also exists a significant body of literature that supports the idea that oxidation may occur directly via the photogenerated holes [34–37]. The detailed mechanism for the photooxidation reactions remains a controversial issue today. In the present work, we have introduced the fluorescence method [38] for the direct measurement of the amounts of •OH production (Fig. 1). Thus, our objective is to elucidate the role of •OH and photogenerated hole in TiO_2 photocatalysis.

2. Experimental

Terephthalic acid, sodium hydroxide (NaOH), iodine and potassium iodide were purchased from Wako Pure Chemicals (high-purity grade). 2-hydroxyterephthalic acid was synthesized by the hydrolysis of 2-bromoterephthalic acid [39]. The structure was confirmed by NMR, IR and UV–VIS absorption spectra. The high-purity water used in this experiment was distilled, deionized and then purified with the Milli-Q system (Nippon Millipore Co., Tokyo).

Terephthalic acid was dissolved in dilute NaOH solution (2×10^{-3} M) and used for the experiments. Starch (1 g) was ground with 10 ml cold water and then was slowly added to 200 ml of hot water. The solution was boiled until it became translucent and was then cooled to room temperature. The

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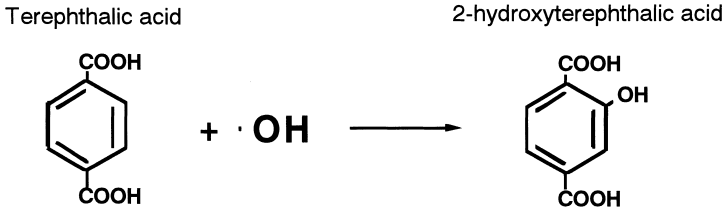


Fig. 1. Formation of 2-hydroxyterephthalic acid as a result of the reaction between terephthalic acid and •OH.

supernatant fraction of the starch solution was used in the experiments.

Fluorescence spectra of 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer. UV–VIS absorption spectra were recorded using a UV–VIS absorption spectrophotometer (Shimadzu, UV-3100PC).

Soda-lime glass coated with silica thin film (ca. 100 nm), were dip-coated using titanium isopropoxide solution (Type NDH-520C, Nippon Soda). A withdrawal rate of 20 cm min^{-1} was used for all plates. Coated titanium isopropoxide was wiped off from one side of the plate using ethyl acetate and the plates were dried in a furnace for 30 min at 120°C. They were subsequently calcined at 500°C for 1 h. The above dip-coating procedure was repeated four times to produce TiO_2 film with anatase crystal structure on one side of the plates.

A 9 mm×9 mm TiO_2 film plate was placed at the side of the bottom half of a 1 cm×1 cm fused silica standard spectrophotometric cell with 1 ml of terephthalic acid or iodine solution. The TiO_2 film plate in the solution was illuminated with a 200 W high pressure mercury lamp (Yamashita Denso, HYPERCURE 200) through a UV filter (Toshiba, UV-D36B). The excitation light intensity was measured using a UV radiometer (UVR-36, TOPCON) at the sample position.

3. Results and discussion

A TiO_2 film was illuminated in terephthalic acid solution (5×10^{-4} M) with UV light with an intensity of 1 mW cm^{-2}. The fluorescence emission spectrum (excitation at 315 nm) of the solution was measured every 5 min during illumination. As shown in Fig. 2, gradual increase in the fluorescence intensity at ca. 425 nm was observed with increasing illumination time. The generated spectrum has the identical shape and maximum wavelength with that of 2-hydroxyterephthalic acid. This implies that fluorescent products formed during TiO_2 photocatalysis are due to the specific reaction between •OH and terephthalic acid. Based on the reports in radiation chemistry and sonochemistry [39–44], it is reasonable to assume that photogenerated O_2^-, $HO_2^\bullet$ and H_2O_2 do not interfere with the reaction between •OH and terephthalic acid.

In order to determine the amount of •OH formed by photocatalysis, there should exist enough probe molecules, i.e. terephthalic acid, on the TiO_2 surface to trap all of the generated •OH. This can be checked by studying the influence of solution stirring at different initial concentrations of terephthalic acid. Below a concentration of $\sim10^{-5}$ M, induction of the fluorescence peak at 425 nm was increased by stirring the solution during illumination. This indicates that there were insufficient terephthalic acid molecules on the TiO_2 film to trap generated •OH. However, at a concentration of ca. 4×10^{-4} M, no change in the florescence intensity was observed even when the solution was stirred. Thus, above this concentration, it is considered that there exist enough terephthalic acid molecules to trap •OH produced on TiO_2.

To determine the absolute number of •OH from the increased fluorescence intensity, the trapping efficiency of •OH by the probe molecule should be elucidated. The trapping efficiency is a chemical yield based on the terephthalic acid converted to the hydroxy-product. It can be determined using a system in which a known amount of •OH is generated. Absolute quantum yields for the formation of •OH in the laser photolysis of aqueous solutions of H_2O_2 have been determined to be 0.98 (308 nm) and 0.96 (351 nm) [45]. In this case, a scavenging technique involving the reaction between •OH and SCN^- ions and the time resolved detection by visible absorption of the $(SCN)_2^-$ radical ion was used. Using these quantum yields, the trapping efficiency of •OH by terephthalic acid can be estimated as follows. A mixture of 100 ml of 30% H_2O_2 and 900 ml of terephthalic acid solution was illuminated with light of 325 nm using a He–Cd laser. The absorption spectra of terephthalic acid and H_2O_2 are such that the 325 nm laser light is absorbed by H_2O_2 to degrade forming •OH. The absorption efficiency of the

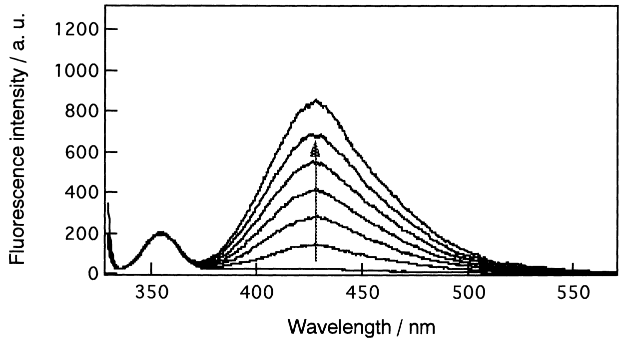
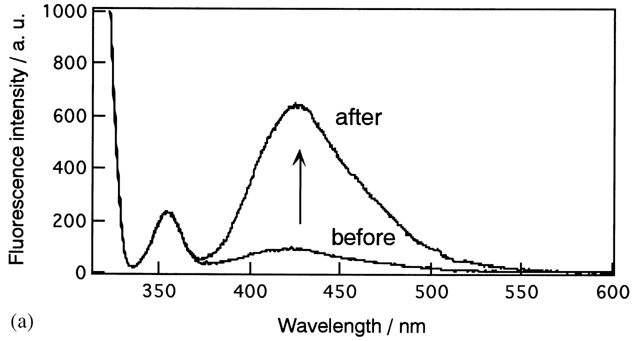
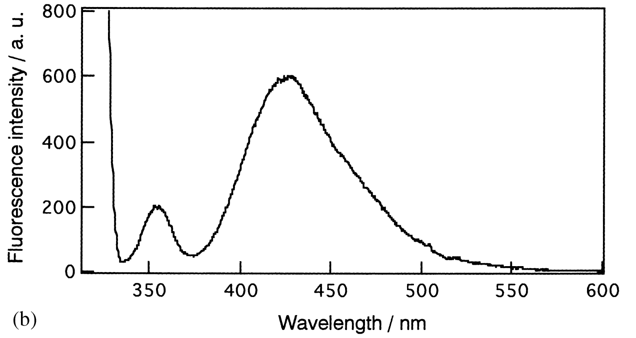


Fig. 2. Fluorescence spectral changes observed during illumination of TiO_2 film in terephthalic acid solution (4×10^{-4} M, excitation at 315 nm). Fluorescence spectra were recorded every 5 min during UV illumination.



(a)



(b)

Fig. 3. (a) Fluorescence spectral changes observed after the illumination of terephthalic acid and H_2O_2 solution (excitation at 315 nm) and (b) fluorescence spectrum of 5×10^{-8} M 2-hydroxyterephthalic acid in 5×10^{-4} M terephthalic acid solution.

laser light was estimated by the UV–VIS absorption spectrum of the H_2O_2 solution. The continuous irradiation of the solution led to the detection of a growing fluorescence signal at 426 nm in a manner similar to that observed with the TiO_2 system (Fig. 3(a)). This signal can be assigned to 2-hydroxyterephthalic acid resulting from the reaction between •OH and terephthalic acid. Induction of the fluorescence gives the trapping efficiency of •OH by terephthalic acid, which was estimated to be ca. 80 % (i.e. ca. 80% of the trapped •OH give rise to hydroxy products).

As mentioned above, when a TiO_2 film was illuminated in terephthalic acid solution, the fluorescence intensity at ca. 426 nm increased gradually. Since the initial concentration of terephthalic acid was 4×10^{-4} M, all of the generated •OH are involved in the reaction with a trapping efficiency of ca. 80%. Therefore, a comparison of the induction of the fluorescence intensity with the fluorescence intensity of a 2-hydroxyterephthalic acid solution (e.g. fluorescence spectrum of 5×10^{-8} M 2-hydroxyterephthalic acid (Fig. 3(b)) provides the quantum yield for •OH). A UV–VIS absorption spectrum of the TiO_2 film gives the absorption efficiency of the excitation UV light to be about 60%. Taking into consideration this value, under a UV illumination intensity of 1 mW cm^{-2}, the quantum yield for •OH production was calculated to be ca. 7×10^{-5}.

Let us now estimate the quantum yield for the oxidation reaction of I^- resulting from TiO_2 photocatalysis. It is known that I^- is oxidized by photoexcited TiO_2, producing I_2. Therefore, the quantum yield of this reaction can be determined by observing the I_2 produced. The experiments were performed under the same conditions as those used for the fluorescence method. A 9 mm×9 mm TiO_2 film was placed at the side of the bottom half of the cell with 1 ml of 10^{-2} M KI aqueous solution. The TiO_2 film was illuminated with UV light at 1 mW cm^{-2}. During UV light illumination, the solution was stirred magnetically. The amount of I_2 formed in the reaction was determined by the iodo-starch reaction method. When a 100 ml aliquot of starch solution was added to the solution after UV light illumination for 30 min, the solution turned blue as a result of the iodo-starch reaction. The absorption at ca. 580 nm increased, as shown in Fig. 4. The amount of I_2 formed in the solution was calibrated from an iodine-KI solution of known concentration, i.e. a calibration curve of absorbance for the iodine-KI solution versus I_2 concentration was drawn. From the absorbance of the spectra in Fig. 4, the concentration of iodine formed in 1 ml of 10^{-2} M KI aqueous solution was found to be 8.2×10^{-5} M. Therefore, the quantum yield of photogenerated holes was calculated to be ca. 5.7×10^{-2}. This value is much higher than the quantum yield for •OH production (7×10^{-5}). If we believe that •OH is the only reactive species, the photocatalytic oxidation of I^- is not understandable.

In fact, the quantum yields for ordinary photocatalytic oxidative reactions are usually much higher than the one estimated for •OH formation estimated here. For example, the quantum yields for the oxidation of 1-propanol [46], bleaching of methylene blue [47] and the oxidation of toluene [29] are reported to be 0.2, 5.6×10^{-2} and 3×10^{-3}, respectively. The present low value is not consistent with the assumption that the photodegradation of pollutants with TiO_2 is primarily proceeded by •OH [21–25,48].

The •OH is often regarded as a major active species involved in photocatalytic oxidative reactions [21–25,48]. Besides •OH, a great deal of discussion has been centered on the role and importance of positive hole oxidation. Equally convincing evidence in support of direct hole oxidation as a main step in photooxidation process has been presented. EPR and laser flash photolysis studies have revealed that

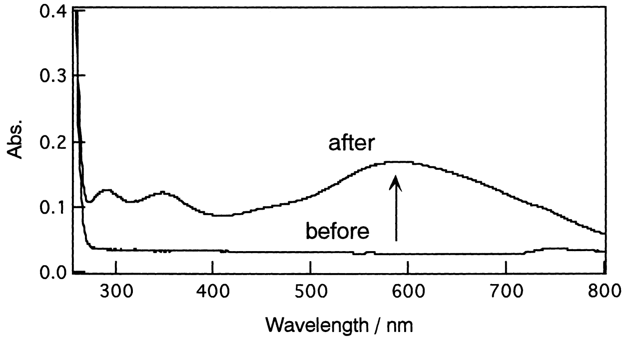


Fig. 4. UV–VIS absorption spectra of iodine (formed from the photocatalytic oxidation of I^-) solution before and after the addition of starch solution.

a paramagnetic species forms upon the band-gap illumination of TiO_2 that can be assigned to surface trapped holes [49–51]. The identity of the trapped hole is an oxygen anion radical ($O^{\bullet -}$) covalently bound to titanium atoms at or below the surface, e.g. Ti^{IV} O Ti^{IV} $O^{\bullet}$, which has been identified with EPR [50,51]. In fact, it is known that these EPR signals disappear upon the addition of hole scavengers that are strongly bound to the surface, for example, KI. Taking all of these results into consideration, we conclude that photogenerated holes play a major role in the oxidation processes associated with TiO_2 photocatalysis.

4. Conclusion

In this study, we have adopted the use of terephthalic acid as a fluorescence probe for the quantitative measurement of $^{\bullet}OH$ production in TiO_2 photocatalysis. It was found that the quantum yield for $^{\bullet}OH$ production is much lower (7×10^{-5}) than those for ordinary photocatalytic reactions ($\sim10^{-2}$). Conversely, the quantitative analysis of I^- oxidation indicates that photogenerated holes play a major role in TiO_2 photocatalysis. In TiO_2 photocatalysis, it has been suggested that active species may diffuse from the photocatalyst surface and participate in oxidative reactions in the bulk solution [52–54]. However, the results obtained in the present study indicate that reactions occur mainly at the surface of the photocatalyst via photogenerated holes rather than by free diffusion into the homogeneous phase.

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