

# TiO<sub>2</sub>-assisted photodegradation of dyes: A study of two competitive primary processes in the degradation of RB in an aqueous TiO<sub>2</sub> colloidal solution

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Received 15 April 1997; accepted 24 July 1997

## Abstract

The photocatalytic degradation of rhodamine B (*N,N,N',N'*-tetraethylrhodamine, RB) had been studied in a colloidal TiO<sub>2</sub> solution under both UV and visible light irradiation. Two different photodegradation processes of RB, photobleaching and *N*-deethylation, were examined in detail. The *N*-deethylation of RB was attributed to the oxidation by HOO<sup>·</sup> or OH<sup>·</sup> radicals generated from the dye-photosensitized and/or TiO<sub>2</sub> catalyzed reactions; while the photobleaching of RB was found to occur via dye cationic radical. The aromatic rings of RB cannot be destroyed in the absence of oxygen under visible light irradiation. Various additives, Fe<sup>3+</sup>, EDTA, MV<sup>2+</sup>, different atmosphere (O<sub>2</sub> and N<sub>2</sub>), time-resolved laser flash photolysis and spin trapping electron paramagnetic resonance (ESR) were used to determine the possible mechanisms involved. © 1998 Elsevier Science B.V.

**Keywords:** Photodegradation; Photobleaching; *N*-deethylation; Rhodamine B; Titanium dioxide

## 1. Introduction

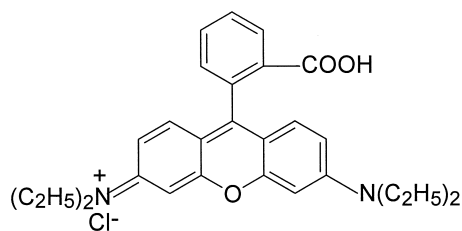
In recent years, semiconductor nanoparticles have been found very efficient in destroying organic compounds [1–7]. Lots of excellent studies have been published on the photocatalytic degradation of toxic organics under UV or visible light irradiation. The eventual photodegradation products of organic compounds and the reaction kinetics have been examined. But the mechanisms of the photodegradation, especially the initial steps, have not been re-

vealed yet. Bandgap excitation of TiO<sub>2</sub> particles can initiate the oxidation and reduction processes of the adsorbed substrate. Alternatively, an adsorbed colored molecule can inject an electron from its excited state into the semiconductor particles and itself become a positively charged radical, which undergoes further transformation to give stable products. The two processes seem to be different. But several studies have shown that the same types of reactive species, such as <sup>·</sup>O<sub>2</sub><sup>-</sup>, OH<sup>·</sup>, OOH<sup>·</sup>, OOH<sup>-</sup>, and H<sub>2</sub>O<sub>2</sub> are formed in both processes. These reactive species play an important role in the TiO<sub>2</sub>-assisted advanced photooxidation of organic compounds.

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The ubiquitous and hazardous nature of dye-containing wastewater requires researchers to find efficient methods to convert highly toxic dye to harmless products. But the study of TiO<sub>2</sub>-assisted photodegradation of dyes under both UV light and visible light irradiation has attracted only limited attention. Fewer publications are found dealing with the initial reaction mechanisms for the dye photodegradation [8]. However, previous studies demonstrate that the idea of the photodegradation of dyes by visible light irradiation may provide a promising prospect for the efficient utilization of sunlight in the treatment of dye-containing wastewaters.

As one important represent of xanthene dyes, rhodamine B is famous for its good stability as dye laser materials. Previously we have reported the TiO<sub>2</sub>-assisted photodegradation of several dyes under visible light irradiation [9]. It was found that RB underwent two different but competitive photochemical processes during the irradiation: photobleaching and high efficient *N*-deethylation. Different conditions and various additives could affect these two processes, especially the presence and absence of oxygen. This character of RB makes it a good material for us to study the difference of the photoreaction initial steps between bandgap excited and sensitizer excited degradation of organic compounds.



Rhodamine B

In the present study, we report the possibility of using dye RB as a probe to study the TiO<sub>2</sub>-assisted photocatalytic reaction of dyes under both UV and visible light irradiation. Various additives were used to illustrate the mechanisms

of RB photoreaction. Laser flash photolysis and spin trapping electron paramagnetic resonance (ESR) are also utilized to find more information about RB photodegradation. Since an aqueous TiO<sub>2</sub> colloid is only stable in acidic media and the process of *N*-deethylation is comparatively faster in acidic media, we chose the acidic media (pH 0.8–1.1) to study the two intended photochemical processes, *N*-deethylation and photobleaching.

## 2. Experimental section

### 2.1. Materials

Rhodamine B, FeCl<sub>3</sub>, disodium ethylenediaminetetraacetate (EDTA), TiCl<sub>4</sub> and methyl viologen (MV<sup>2+</sup>) were of analytical reagent grade and were used without further purification. The TiO<sub>2</sub> particles used in the ESR analysis is P-25 (anatase) catalyst with a surface area of 55 m<sup>2</sup>/g. 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, Sigma) is used in the ESR spin trap. Deionized and doubly distilled water was used throughout this study. Colloidal TiO<sub>2</sub> was synthesized by a simple hydrolysis method: 550 μl (5 mmol) of TiCl<sub>4</sub> was rapidly injected to 1000 ml of highly acidic solution (previously adjusted at pH 1.0 by adding HCl) under vigorous stirring at room temperature. The TiO<sub>2</sub> colloidal solution formed was then stirred for at least 4 h. No stabilizing agents were used. The TiO<sub>2</sub> colloids produced by this technique were stable for about several months at room temperature and no precipitation was observed.

### 2.2. Methods and apparatus

UV light irradiation was carried out with a 100 W Hg lamp ( $\lambda > 330$  nm, Toshiba SHLS-1002A). The visible light source was a 500 W halogen lamp (made by Institute of Electric Light Source of Beijing) placed in a cylindrical glass vessel. A glass thimble together with wa-

ter circulation was used to avoid overheating. After carefully comparing the visible light source with and without a cut-off filter (remove wavelength below 470 nm), no difference was found except that the photoreaction of RB with the cut-off filter is slower than without it. So all experiments were carried out without the light filter. In typical experiments, 50 ml of  $\text{TiO}_2$  colloidal solution ( $5 \times 10^{-3}$  M) containing RB ( $2 \times 10^{-5}$  or  $1 \times 10^{-5}$  M) and other additives ( $\text{FeCl}_3$ , EDTA, and  $\text{MV}^{2+}$ ) was transferred into a 70 ml pyrex glass vessel and stirred for at least half an hour before irradiation to ensure the adsorption/deadsorption equilibrium. A 3 ml aliquot was taken at given irradiation time intervals during an experiment. The solution was then analyzed on Shimadzu 1600A spectrophotometer. In the anaerobic study, the solution was de-aerated by bubbling high pure  $\text{N}_2$  gas for half an hour in dark before irradiation and the  $\text{N}_2$  gas purge was continued during the irradiation. Fluorescence spectrum was recorded on a Perkin-Elmer LS-05 fluorimeter. The transient absorption spectrum was determined using a flash photolysis apparatus which consisted of a DCR 2(30)A laser (Quanta-Ray Nd:YAG), a pulse xenon lamp, a multi-channel analyzer. ESR spectrum was obtained using a Bruker Model ESP 300E ESR spectrometer. The excitation source was a Quanta-Ray Nd:YAG laser system. A computer is employed for data acquisition and manipulation.

### 3. Results and discussion

#### 3.1. The degradation of RB under visible light irradiation

According to the oxidation potential of RB and the band edges of  $\text{TiO}_2$  [1,4,10], the excited RB molecules can inject electrons into the conduction band of  $\text{TiO}_2$  particles, and themselves become dye cationic radicals which undergo further transformation to products. The absorption spectra of a RB/ $\text{TiO}_2$  solution under both

air-saturated and  $\text{N}_2$ -saturated conditions recorded at different time intervals during the visible light irradiation are shown in Fig. 1. In the former case, the maximum absorption shifted from 558 to 498 nm with the increased illumination time. It has been shown in earlier studies that the *N*-deethylation of RB causes the blue shift in the maximum absorption of the dye solution [10,11]. The *N*-deethylation products of RB, rhodamine, has a light absorption maximum at 498 nm. It then disappeared rapidly after the *N*-deethylation. From the absorption spectra, no new products or intermediate products with absorption in the near-ultraviolet region were observed (Fig. 1a). Fig. 1b presents the spectral changes of RB as a function of irradiation time under a deaerated condition. No blue shift happened, while with the decrease of the 558 nm absorption, there is a very fast increase in the light absorption at 224 nm, which is the characteristic peak of the aromatic ring. This indicates that the aromatic rings of RB are not broken during the irradiation, only the big conjugated  $\pi$ -system was destroyed. Long time visible light photolysis did not make the 224 nm absorption disappear. The photobleaching product is relatively stable in the deaerated situation. It is also stable in the dark under air-saturated conditions. This is quite different from the photodegradation in  $\text{O}_2$ -saturated solutions. Apparently the presence of oxygen is responsible for the difference.

The extinction coefficient of the blue-shift products of RB did not vary much according to the literature [10] and the data obtained in this study (Fig. 1a). Considered our goal is to study the primary steps of the competitive processes of *N*-deethylation and the disappearance of the color absorption, we simplified the analytical method and calculated the concentration change of the colored intermediate products of RB and RB itself by the extinction coefficient of RB.

In acidic media of pH 1, both RB molecules and the  $\text{TiO}_2$  surface are positively charged [12]. Because of the strong electrostatic repulsion between these similarly charged matters,

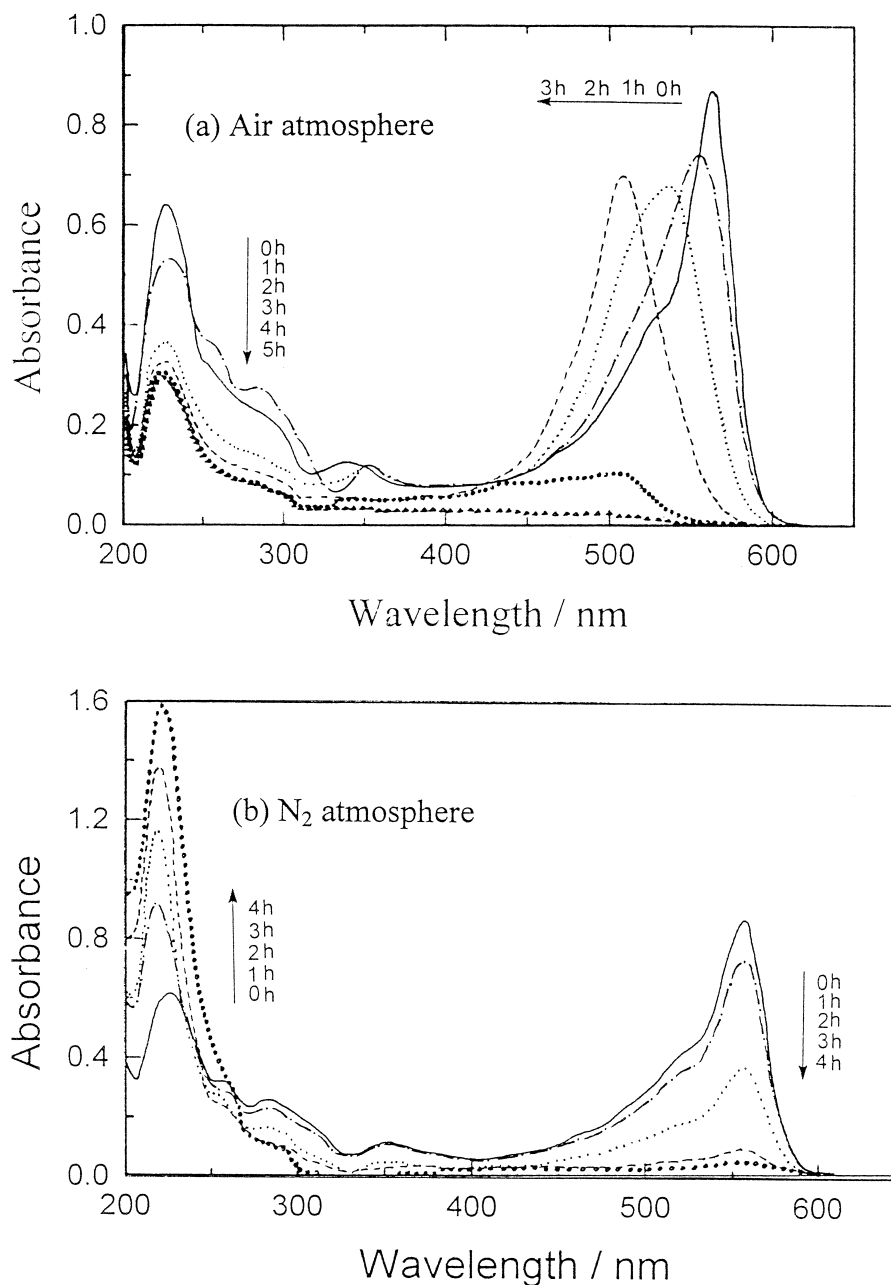


Fig. 1. Absorption spectra of RB in colloidal TiO<sub>2</sub> ( $5 \times 10^{-3}$  M) solution (pH 0.8) in the photocatalytic degradation under visible light irradiation. (a) Air-saturated condition; (b) O<sub>2</sub>-free condition. (—) 0 h; (---) 1 h; (···) 2 h; (-·-) 3 h; (◦ ◦ ◦) 4 h; (△ △ △) 5 h.

RB molecules cannot adsorb easily on the TiO<sub>2</sub> surface. Our experimental results have shown that there is almost no difference in the RB absorption spectra in the presence or absence of

TiO<sub>2</sub>. And only about 16% of RB ( $5 \times 10^{-7}$  M) fluorescence intensity was quenched by TiO<sub>2</sub> ( $5 \times 10^{-3}$  M) from the RB emission spectra analysis. The photodegradation of RB under

visible light illumination under both air-saturated and de-aerated conditions are shown in Fig. 2. In acidic media, RB can react even in the absence of  $\text{TiO}_2$  under the visible light photolysis. But the presence of  $\text{TiO}_2$  accelerates this photoreaction significantly. The presence of

oxygen makes the *N*-deethylation process possible. Experiments show that the pH values can affect the rate of the RB *N*-deethylation process. The higher the pH, the slower the *N*-deethylation. In the condition of pH 10, no *N*-deethylation can be observed according to our

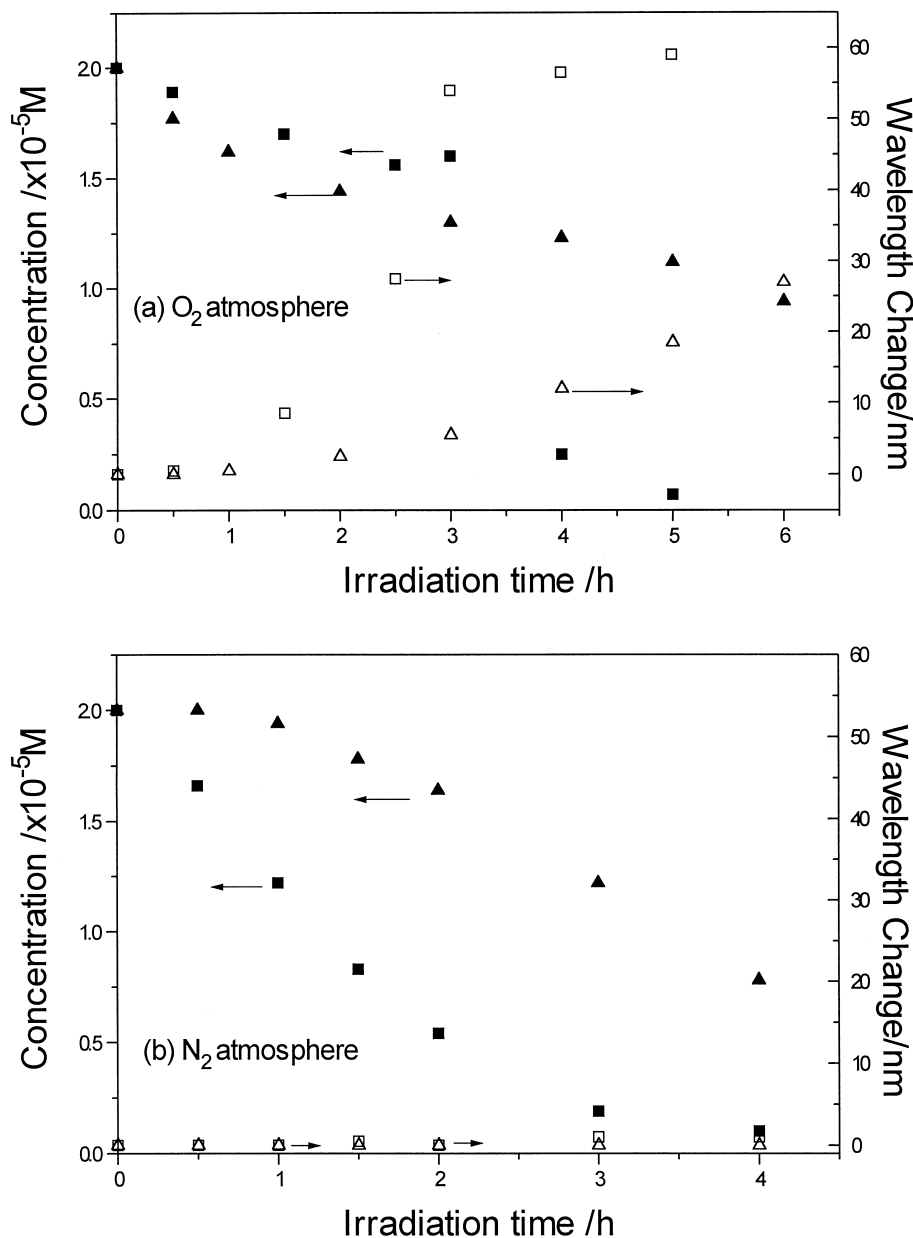
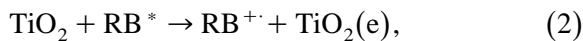
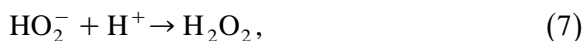
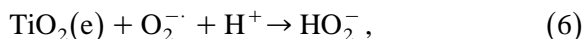
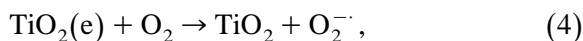
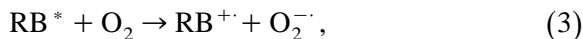


Fig. 2. Photocatalytic degradation of RB in acidic aqueous (pH 0.8)  $\text{TiO}_2$  colloidal solution (■) and neat acidic water (pH 0.8) solution (▲) under visible light irradiation. (a)  $\text{O}_2$ -free; (b)  $\text{O}_2$  present. The open symbols are the results of wavelength change.

previous study in the P-25 TiO<sub>2</sub> suspension [13]. Because the photosensitization reaction possibly includes the following [1,4,5,14]:



or

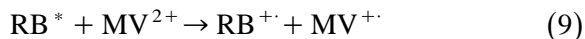


Eqs. (3)–(8) cannot happen if there was no oxygen. High H<sup>+</sup> concentration is favored for Eqs. (3)–(8) because the pK<sub>a</sub> of the OOH<sup>·</sup> radical and H<sub>2</sub>O<sub>2</sub> are 4.8 and 1.6, respectively. Only the OOH<sup>·</sup> and H<sub>2</sub>O<sub>2</sub>, not their conjugated bases, can exist in the media of pH 1. Note that RB<sup>\*</sup> means the RB<sup>\*</sup> singlet state because the φ<sub>ST</sub> of RB<sup>\*</sup> is very small in water (only 0.04) when compared to the large fluorescence quantum yield of 0.46. The influence of <sup>3</sup>RB<sup>\*</sup> is negligible [15]. Also, the possibility that <sup>1</sup>O<sub>2</sub> takes part in the reaction had already been eliminated by results reported in Ref. [11]. Eq. (3) elucidated the fact that the RB degradation can also happen in the absence of TiO<sub>2</sub>, because the excited RB<sup>\*</sup> can reduce O<sub>2</sub> to O<sub>2</sub><sup>·-</sup>, leading to the formation of other oxidant species according to Eqs. (5)–(8) [16,17]. Since the presence of TiO<sub>2</sub> greatly enhanced the photodegradation of RB, it is reasonable to assume that Eq. (2) is much faster than Eq. (3). That the blue shift occurs only in the presence of O<sub>2</sub> as shown in Fig. 1 indicates that the O<sub>2</sub><sup>·-</sup>, OOH<sup>·</sup>, HO<sub>2</sub><sup>·-</sup>, H<sub>2</sub>O<sub>2</sub>, or OH<sup>·</sup> are responsible for the *N*-deethylation and photodegradation. The pH-dependence of RB *N*-deethylation provides the evidence that more attention should be paid to OOH<sup>·</sup>, H<sub>2</sub>O<sub>2</sub> and OH<sup>·</sup> [1,4,18]. After adding H<sub>2</sub>O<sub>2</sub> to the RB aqueous solution and RB/TiO<sub>2</sub>

solution, almost no reaction was observed under visible light irradiation and in the dark, respectively. This result eliminated the possibility of H<sub>2</sub>O<sub>2</sub> as a main reaction agent. The importance of OOH<sup>·</sup> and OH<sup>·</sup> in this reaction is obvious.

### 3.2. The effect of electron acceptor

An electron acceptor methyl viologen (MV<sup>2+</sup>) was added to the system to circumvent the formation of OOH<sup>·</sup> and OH<sup>·</sup> in the absence of TiO<sub>2</sub>. The reduced form of MV<sup>2+</sup> is chemically inert [19]. The MV<sup>2+</sup> concentration (5 × 10<sup>-4</sup> M) is large enough to make the influence of O<sub>2</sub> negligible. Under such a condition, the bleaching happened very fast, the solution discolored completely after 1 h of irradiation and no *N*-deethylation was observed even in the presence of O<sub>2</sub>. Since RB<sup>\*</sup> can be formed via Eq. (1), the excited RB<sup>\*</sup> can further reduce MV<sup>2+</sup>.



Then the formed RB<sup>·+</sup> leads to the fast photobleaching. (Note that electron transfer from TiO<sub>2</sub> to MV<sup>2+</sup> is impossible [5] at pH 1. Experiments carried out under both TiO<sub>2</sub>-containing and TiO<sub>2</sub>-free conditions confirmed this fact.) The presence of the electron acceptor is not the complete condition for the RB photodegradation (*N*-deethylation and photobleaching). That is, the electron acceptor cannot take the place of O<sub>2</sub> in the visible light induced RB degradation. More evidences from this point of view are given below.

From the above discussion, it is expected that adding an electron acceptor like Fe<sup>3+</sup> will to some extent inhibit Eqs. (3) and (4) under the visible light irradiation because the electron acceptor competes with oxygen for the electrons. The formation of OOH<sup>·</sup> and OH<sup>·</sup> is then much slower than that in the Fe<sup>3+</sup>-free case. The experimental results as shown in Fig. 3 are in agreement with this expectation. The role of Fe<sup>3+</sup> in this case is the same as which is

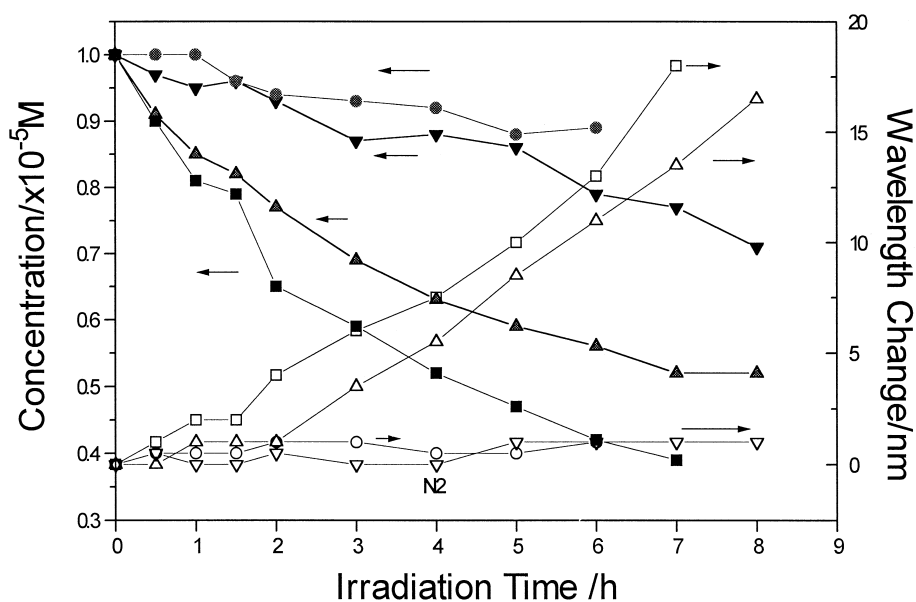


Fig. 3. Photocatalytic degradation of RB under visible light irradiation in pH 1.1 aqueous media. (■)  $\text{TiO}_2/\text{O}_2$ ; (▲)  $\text{Fe}^{3+}/\text{TiO}_2/\text{O}_2$ ; (▼)  $\text{TiO}_2/\text{N}_2$ ; (●)  $\text{Fe}^{3+}/\text{TiO}_2/\text{N}_2$ . The  $\text{Fe}^{3+}$  concentration is  $1 \times 10^{-3}$  M,  $\text{TiO}_2$  is  $5 \times 10^{-3}$  M. The open symbols are the results of wavelength change.

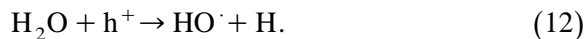
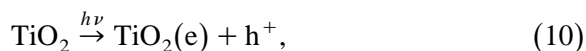
reported in Ref. [20]. The  $\text{HOO}^\cdot$  and/or  $\text{OH}^\cdot$  generated from  $\text{TiO}_2$  particles conduction band electrons and oxygen are necessary for the photodegradation of RB under visible light irradiation.

Because the ethyl (or methyl) groups of xanthene dyes play the role of stabilizing the dye molecules, the deethylated dye molecules are much easier to be decomposed than RB according to the dye chemistry. That is, the *N*-deethylation process of RB is the rate limited step in the degradation of RB. The experimental results obtained above show that without oxygen, visible light induced photocatalytic degradation of RB cannot be fulfilled even after adding electron traps. The only reaction products of the oxygen-free case are the bleached products with maximum absorption at 224 nm, the characteristic absorption of the aromatic rings of RB.

### 3.3. The degradation of RB under ultraviolet light irradiation

The photodegradation of RB under UV light irradiation is shown in Fig. 4. There are similar

characteristics between UV-light irradiation and visible light photolysis according to the light absorption measurements. But unlike visible light irradiation, RB cannot react in the absence of air under UV light irradiation, even the photobleaching reaction. UV-light induced  $\text{TiO}_2$  photocatalytic reaction mechanisms are well demonstrated by several famous research groups [1,4]. The following reactions are involved:



Eqs. (4)–(8) can also happen here.

In the absence of oxygen as an electron acceptor, the electron-hole recombination is so fast that the formation of  $\text{RB}^{+\cdot}$  is inhibited. As discussed above,  $\text{RB}^{+\cdot}$  is the intermediate in the photobleaching process. The lack of  $\text{RB}^{+\cdot}$  depresses this process. Both holes in the valence band of semiconductors and hydroxyl radicals, generated from the reaction of the adsorbed  $\text{H}_2\text{O}$  or  $\text{OH}^-$  with the holes under UV light irradiation, are involved in the photooxidation

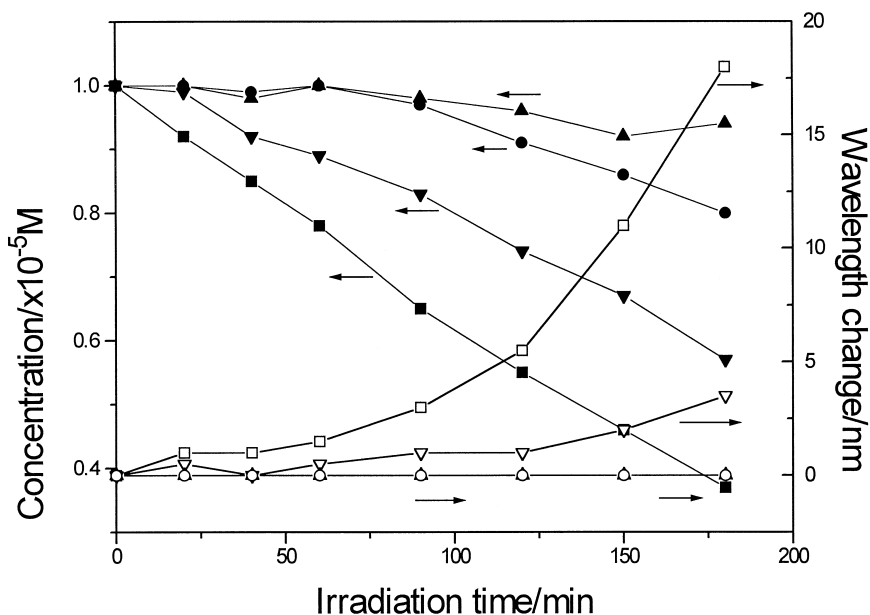


Fig. 4. Photocatalytic degradation of RB under UV light irradiation in acidic media (pH 1.1) under different conditions: (■)  $\text{TiO}_2$  and  $\text{O}_2$  present; (▼) only  $\text{O}_2$  present; (●) only  $\text{TiO}_2$  present; (▲)  $\text{TiO}_2$  and  $\text{O}_2$  absent. The open symbols are the relative wavelength change.

on the  $\text{TiO}_2$  surface [21]. According to previous reports [22], the tightly bound electron donors such as formate, acetate, and glyoxylate at the semiconductor surface can be oxidized by va-

lence hole directly. In the system studied, RB can only slightly be adsorbed on the  $\text{TiO}_2$  surface, so it cannot act as the main scavenger and become  $\text{RB}^+$ . Hence RB cannot undergo the

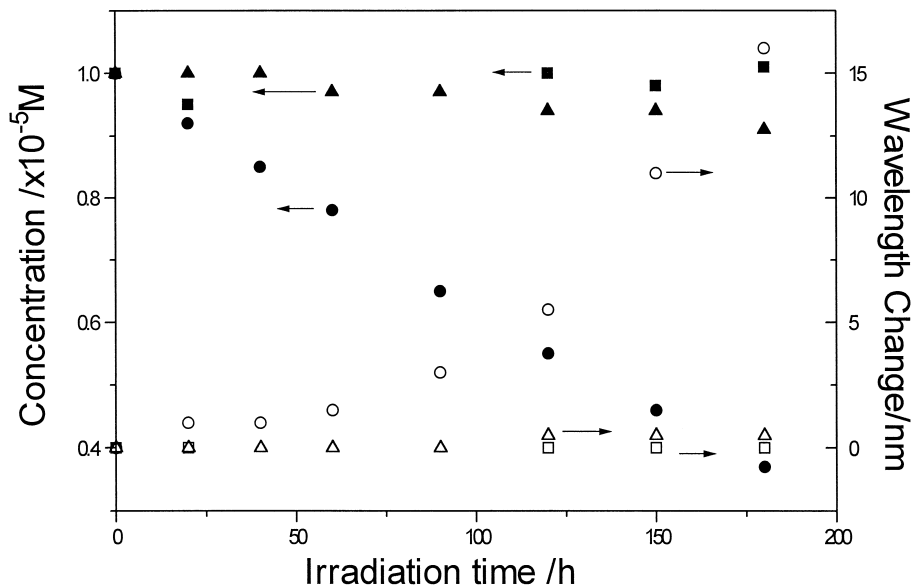


Fig. 5. Photocatalytic degradation of RB (initial  $1 \times 10^{-5} \text{ M}$ ) in pH 1.1 aqueous media under UV light irradiation. (■) EDTA/ $\text{TiO}_2$ / $\text{O}_2$ ; (▲) EDTA/ $\text{TiO}_2$ / $\text{N}_2$ ; (●)  $\text{TiO}_2$ / $\text{O}_2$ . The open symbols are the relative wavelength change. EDTA concentration  $4 \times 10^{-3} \text{ M}$ ;  $\text{TiO}_2$  concentration  $5 \times 10^{-3} \text{ M}$ .



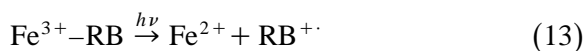
photobleaching reaction without  $O_2$ , as shown in Fig. 4.

### 3.4. The effect of EDTA as hole scavenger

In order to further study the role of hole and hydroxyl radicals in this process, disodium ethylenediaminetetraacetate (EDTA) was used as hole scavenger. The oxidized EDTA undergoes a facile, irreversible decomposition to produce glyoxylic acid and ethylenediamine *N,N'*-diacetic acid [23]. The results in Fig. 5 show that EDTA successfully inhibited the reaction of RB even in the air-saturated case. The concentration of EDTA ( $4 \times 10^{-3}$  M) used is much larger than that of the dye ( $1 \times 10^{-5}$  M). The holes generated upon irradiation are almost completely trapped by EDTA. The lack of  $h^+$  under such a condition not only makes hydroxyl radicals formation impossible, but also inhibits the  $RB^{+\cdot}$  formation by Eq. (11). Consequently, almost no photodegradation of RB was measured.

### 3.5. The effect of $Fe^{3+}$ in the UV light irradiation

It is expected that after adding the electron acceptor,  $TiO_2$  holes can have a relatively longer lifetime to ensure Eqs. (11) and (12) take place. The  $OH^\cdot$  can be formed even in the absence of  $O_2$  under UV light irradiation. Thus, the *N*-deethylation process of RB can be initiated by UV light irradiation in the presence of the electron trap even under oxygen-free conditions. Fig. 6 shows the absorption spectra of RB in the UV light-induced photoreaction after the addition of  $Fe^{3+}$  ( $1 \times 10^{-3}$  M) at different irradiation times. Under such a condition, the photobleaching process is favored in the earlier stages of the reaction, because the reaction



occurs in acidic aqueous media under UV light irradiation [24]. The formation of  $RB^{+\cdot}$  leads to the fast photobleaching. But the holes generated

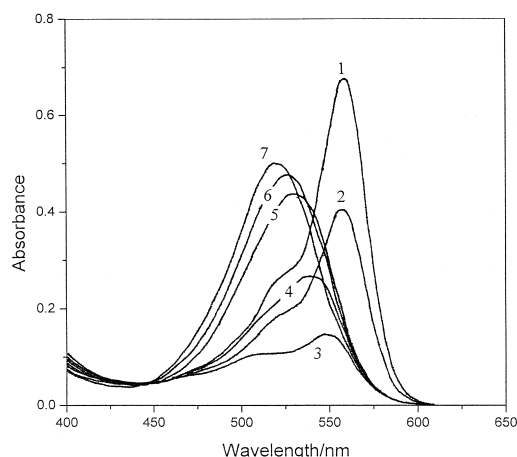


Fig. 6. Absorption spectra of RB ( $1 \times 10^{-5}$  M) in colloidal  $TiO_2$  aqueous solution ( $5 \times 10^{-3}$  M, pH 1.1) under UV light irradiation in  $N_2$ -atmosphere in the presence of  $Fe^{3+}$  ( $1 \times 10^{-3}$  M) with increasing irradiation time: (1) 0 min; (2) 20 min; (3) 40 min; (4) 60 min; (5) 90 min; (6) 120 min; (7) 150 min.

from excited  $TiO_2$  can form  $OH^\cdot$  by Eq. (12). Then the *N*-deethylation reaction happens as shown in Fig. 6. The blue shift of the maximum absorption indicates the *N*-deethylation of RB. The photobleaching process dominates the photoreaction in the initial stage of the photodegradation. It is interesting that the discolored materials gain color again as the *N*-deethylation processed during the later stage of the photoreaction. This means the conjugated structure of the dye was recovered during the *N*-deethylation of RB, thus leading to the color absorption. The phenomenon observed here further demonstrated that although the photobleaching products are quite stable as described earlier in dark or in the absence of oxygen under UV–visible light, the photobleaching of RB is not a complete decomposition. The conjugated  $\pi$ -system of the dye molecules can be recovered again when suitable conditions exists.

### 3.6. Time-resolved laser flash photolysis and ESR study

To further study the characteristic of RB photolysis, a time-resolved laser flash photoly-

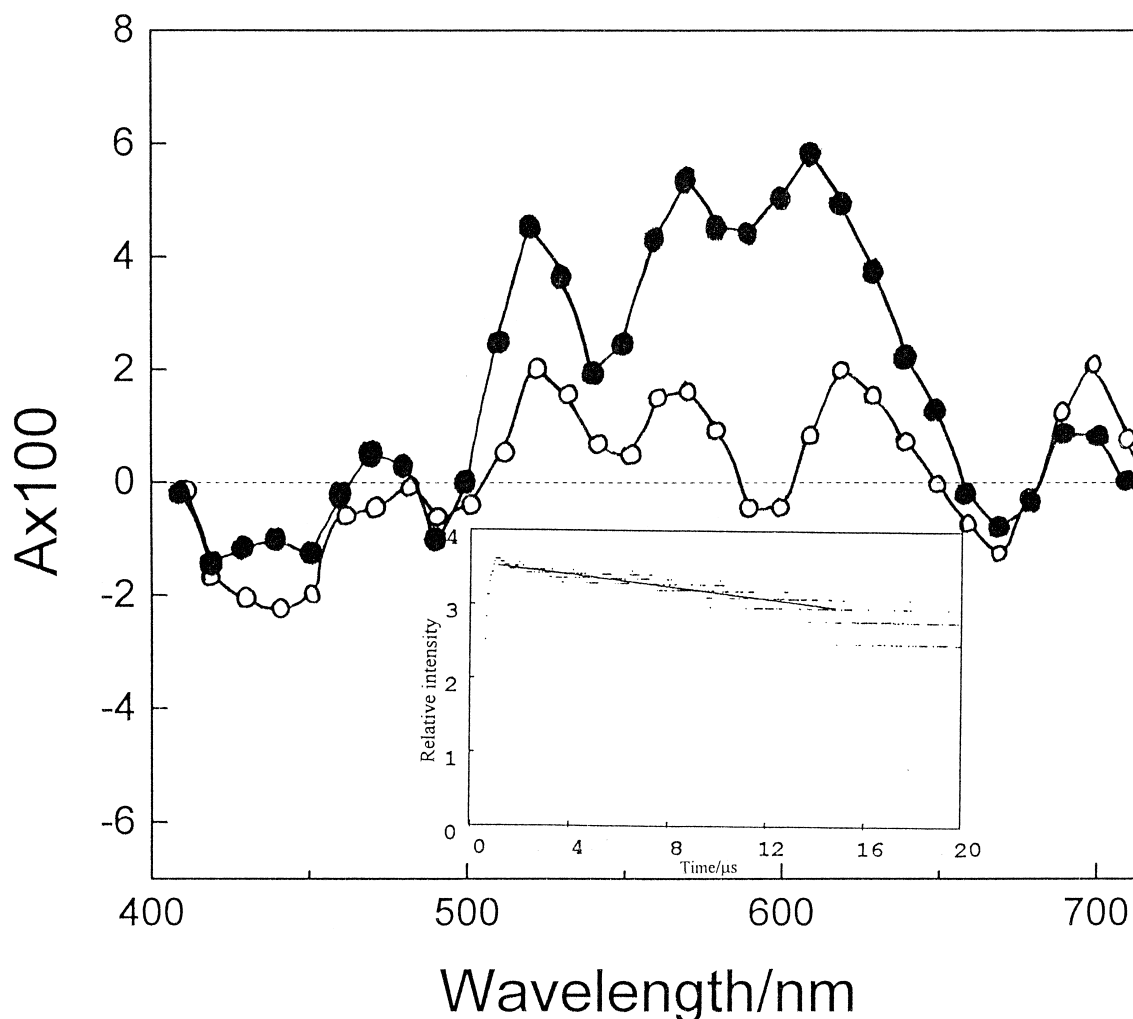


Fig. 7. Transient absorption spectra recorded at (●) 2  $\mu$ s and (○) 19  $\mu$ s following the 532 nm laser excitation of RB/TiO<sub>2</sub> aqueous solution (RB  $1 \times 10^{-5}$  M, TiO<sub>2</sub>  $5 \times 10^{-3}$  M, pH 1.1) in N<sub>2</sub>-saturated condition. The inset shows the formation of RB<sup>+</sup> at 610 nm.

sis study was carried out. The absorption spectra of the RB/TiO<sub>2</sub>/N<sub>2</sub> system after 532 nm laser excitation are shown in Fig. 7. The decay of the 610 nm transient absorption is shown as inset.

The spectra show maximum absorption at 520 and  $\sim$  610 nm. The transient absorption at these wavelengths decays quickly and a bleaching of the absorption in the 450 nm region is seen in longer time scales. The transient absorption at 610 nm is attributed to the formation of the cationic radical RB<sup>+</sup> which has a lifetime

of  $\sim$  10.7  $\mu$ s [25]. The bleaching observed in longer time scales showed that the photobleaching product is quite stable and the process is irrecoverable even in the absence of oxygen. In the mean time, experimental results show that in the cases of RB/TiO<sub>2</sub> in O<sub>2</sub>-atmosphere and neat RB in N<sub>2</sub>-atmosphere, no obvious signal can be observed. The reason for the former is that RB<sup>+</sup> is not stable in the presence of oxygen as described above. Thus, its signal is not detectable in the present setup in the case of RB/TiO<sub>2</sub> in O<sub>2</sub>-atmosphere. No signal for RB<sup>+</sup>

was observed in the absence of  $\text{TiO}_2$  in  $\text{N}_2$ -atmosphere. This further points out the importance of  $\text{TiO}_2$  in the photoreaction.

Fig. 8 shows the ESR spectra of spin-trapped  $\text{OH}^\cdot$  radicals after 532 nm laser excitation for 30 s of a  $\sim 3$  mm diameter quartz tube cell filled with  $\text{TiO}_2/\text{RB}/\text{DMPO}$  slurry. The slurry was made from  $\sim 100$  mg P-25  $\text{TiO}_2$ , 0.5 ml RB solution ( $1.5 \times 10^{-4}$  M, pH 1), and  $\sim 0.05$  ml of 0.45 M DMPO aqueous solution under air-equilibrated condition. Since it is impossible to detect  $\text{OH}^\cdot$  radicals under steady state ESR measurement owing to their high reaction activity and short lifetime, DMPO was commonly used as  $\text{OH}^\cdot$  trap to form relatively stable nitroxides [26,27]. Because in aqueous  $\text{TiO}_2$  colloidal solution ( $5 \times 10^{-3}$  M), the  $\text{TiO}_2$  concentration is too low, the number of  $\text{OH}^\cdot$  radicals formed by photosensitization of  $\text{TiO}_2$  colloids is too small to be detectable by the present facil-

ity. No DMPO-OH radicals were detected. Taking the place of  $\text{TiO}_2$  colloids with an aqueous dispersion of P-25 particles makes the radicals formed easy to detect. The characteristic 1:2:2:1 signals of DMPO-OH in the  $\text{TiO}_2$  (P-25) dispersion system are shown in Fig. 8. Longer time excitation weakened the signals. About 10 min after the photolysis only much weaker 1:2:2:1 signals could be detected. Because DMPO-OOH has a much shorter half-life time ( $< 100$  s) than DMPO-OH ( $> 1$  h) in water [26], the present study can only demonstrate that  $\text{OH}^\cdot$  radicals can be formed during the visible light photolysis of RB/ $\text{TiO}_2$  slurry. But the results obtained at least show that (i)  $\text{OH}^\cdot$  or  $\text{OOH}^\cdot$  radicals can be formed by the method of photosensitization of  $\text{TiO}_2$  by dyes; and (ii) the *N*-deethylation photoprocess of RB under air-equilibration and visible light irradiation can be attributed to the reaction with  $\text{OH}^\cdot$  and/or  $\text{OOH}^\cdot$ .

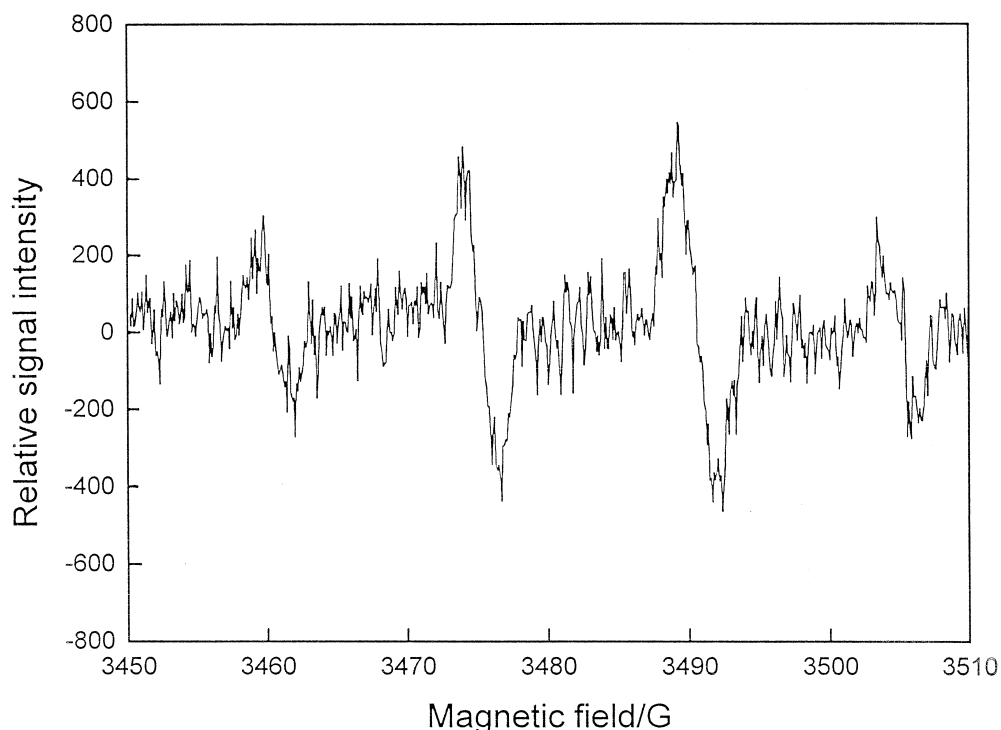


Fig. 8. ESR spectra of the RB/ $\text{TiO}_2$ /DMPO slurry after 30 s excitation by 532 nm laser under air-equilibrated condition (the slurry is composed of 0.5 ml  $1.5 \times 10^{-4}$  M RB (pH 1),  $\sim 100$  mg P-25  $\text{TiO}_2$ , and 0.05 ml 0.45 M DMPO).

#### 4. Conclusion

RB can undergo rapid photocatalytic degradation on the air-saturated TiO<sub>2</sub> colloidal solution under the irradiation of both visible and UV light. Two different photoprocesses, photobleaching and *N*-deethylation, compete with each other in the primary steps of the photo-reaction. The formation of RB<sup>+</sup> is a prerequisite for photobleaching, while OOH<sup>·</sup> and/or OH<sup>·</sup> is responsible for the *N*-deethylation. The experiments with the addition of various electron acceptors such as Fe<sup>3+</sup>, MV<sup>2+</sup>, EDTA and in different atmospheres (O<sub>2</sub> or N<sub>2</sub>) demonstrates that both photodegradation pathways of RB, photobleaching and *N*-deethylation, exist in the air-saturated TiO<sub>2</sub> solution.

#### Acknowledgements

Financial support from the National Natural Science Foundation of China, the Committee of Science and Technology of China, the Foundation of Chinese Academy of Sciences, is gratefully acknowledged. Thanks to Dr. Y. Zuo (Florida International University, USA) for his kind comments and English-correction. We also thank professors J. Chen and W. Wang for their help in ESR and laser flash photolysis measurements. The work in Tokyo is sponsored by the Grand-in-aid for scientific research from Ministry of Education (No. 066400759) and the environmental protection project from the Japan Environment Agency.

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