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Photocatalytic transformation of rhodamine B and its effect on hydrogen evolution over Pt/TiO_2 in the presence of electron donors

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Abstract

In the presence of electron donors, oxalic acid, ethanol and disodium ethylene-diamine tetraacetate (EDTA), the photocatalytic transformation of rhodamine B (Rh B) and its effect on photocatalytic hydrogen evolution over Pt/TiO_2 have been examined. UV–Vis and fast atom bombardment mass spectrometry (FABMS) evidences demonstrate that two reductive reaction paths (photocatalytic hydrogenation and additive combination of Rh B with ethanol radical) take place over Pt/TiO_2 in the reaction system. The adsorption behavior of Rh B on Pt/TiO_2 with coexisting electron donors is a key factor for the transformation. As a result of the hydrogenation and the addition of ethanol radical, the rates of photocatalytic hydrogen generation by the donors decrease notably. A possible reaction mechanism is discussed.

Keywords: Photocatalytic hydrogen evolution; Rhodamine B; Hydrogenation; Ethanol radical addition; Pt/TiO_2

1. Introduction

Since Fujishima and Honda [1] reported the photoelectrochemical water-splitting by a TiO_2 electrode, photocatalytic production of hydrogen by water-splitting has been thought to be the best promising approach. However, in the absence of electron donor, the efficiency of photocatalytic hydrogen evolution is very low and many semiconductors will lose their activities after long-term irradiation [2,3]. In order to improve the efficiency and keep the activities of semiconductors, it is necessary to add electron donors to the reaction system. But if the sacrificial donors are more expensive than the H_2 produced, the use of electron donors is clearly not of interest. In our previous work, using oxalic acid as a model electron donor we have endeavored to combine photocatalytic hydrogen production with elimination of organic pollutants [3].

Organic pollutants are often encountered in practice as a multicomponent mixture. Studies on the photocatalytic hydrogen evolution in multicomponent systems have not been reported. Dye pollutants from the textile industry and photographic industry are a principal source of environmental contamination [4]. About 15% of the total world production of dyes is lost during the dyeing process and released in the textile effluents [5]. It is possible that dyes may often occur in practical multipollutant wastewater. What transformation will happen to these colored compounds in the multicomponent system and what is its effect on photocatalytic hydrogen evolution, these are two issues of interest.

Rhodamine B (Rh B), as an important representative of xanthene dyes, is famous for its good stability as dye laser material. Some studies on the photocatalytic degradation of Rh B in oxidative atmosphere (e.g. O_2) under UV or visible light irradiation have been reported [6–8], but no photocatalytic transformation of the dye in inert (e.g. N_2) atmosphere for hydrogen evolution has been reported. In the present study, we choose Rh B as a probe in order to demonstrate reactive behaviors of dye compounds and their effects on photocatalytic hydrogen evolution.

The adsorption of reactants on photocatalysts plays a very important role in photocatalysis [9,10]. TiO_2 with deposited platinum has been considered as a very effective photocatalyst for hydrogen evolution [11]. In the Pt/TiO_2 photocatalyst, there are two kinds of adsorption sites, namely Pt and TiO_2 moieties. Due to the Schottky barrier of metal Pt in contact with semiconductor TiO_2 surface, after excitation of TiO_2, the electron migrates to the metal Pt where it is trapped and reduction reaction takes place on Pt; whereas the hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur [10]. The action of Pt

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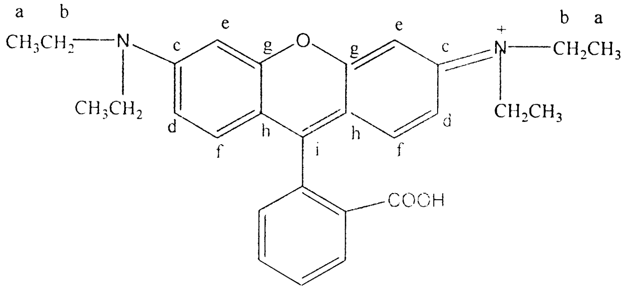
deposited on TiO_2 also involves the stabilization of intermediate $H^\bullet$ atoms as well as the catalysis of bimolecular combination reaction forming H_2 [12]. In this paper, we studied the photocatalytic transformation of Rh B in the presence of electron donors: disodium ethylene-diamine tetraacetate (EDTA), ethanol and oxalic acid. We observed that Rh B transformed in two reaction mechanisms (i.e., hydrogenation and ethanol radical addition) which are dependent on the adsorption behavior of Rh B on Pt/TiO_2 in the presence of the electron donors, and that the rates of photocatalytic hydrogen evolution by the donors were influenced simultaneously.

2. Experimental

Degussa P25 TiO_2 powder (70–30% anatase to rutile) was used. It had a negligible pore volume, a BET area of $55 \pm 15\,m^2\,g^{-1}$, and an average particle size of 30 nm. The Pt/TiO_2 photocatalyst was prepared as described in [13] by impregnation of Degussa P25 TiO_2 with a required amount of H_2PtCl_6, followed by the UV illumination (250 W high pressure Hg lamp) of the 100 ml stirred suspension under N_2 atmosphere at room temperature for 10 h. After washing and evacuation at 393 K for 10 h, this catalyst was used without any reduction under H_2. The sizes of Pt deposits observed by TEM were 1–2 nm. All reagents were of analytic grade and were used without further treatment. For reference, the structure of Rh B is shown below; the small letters labeled on the carbons denote reaction positions.



Rhodamine B

The photocatalytic reaction was carried out in a Pyrex flask of ca. 240 cm^3 with a flat window. The 120 ml reaction mixtures inside the cell were maintained in suspension by means of a magnetic stirrer. A 250 W high pressure Hg lamp was used as the light source. The IR fraction of the beam was removed by a water-cooling jacket outside the lamp. Prior to irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath and nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen. The top of the cell was sealed with a silicone rubber septum. Sampling was made intermittently through the septum during experiments. The reaction was carried out at room temperature.

Hydrogen was analyzed by gas chromatography (TCD, N_2 as gas carrier, zeolite NaX column). After irradiation, the catalyst was removed by centrifugation or Millipore filter under N_2 atmosphere. The filtrates of Rh B suspensions containing oxalic acid, EDTA and ethanol, were used to monitor the changes of UV–Vis spectra of Rh B directly. The sample of the hydrogenation products in oxalic acid solution for FABMS (fast atom bombardment mass spectrometry) was prepared as follows: after the Rh B solution containing oxalic acid in Pt/TiO_2 dispersion was bleached under irradiation, the filtrate was extracted by dichloromethane in the dark [14]. The samples of ethanol addition for ^1H NMR and FABMS measurement were prepared as follows: an aqueous dispersion (120 ml) of Rh B (1.0×10^{-5} M), ethanol (1.0×10^{-2} M) and 0.020 g 0.3 wt.% Pt/TiO_2 was irradiated for 0 or 5.5 h, and the Pt/TiO_2 particles were removed by Millipore filter; the H_2O in samples for ^1H NMR (360 ml) and FABMS (50 ml) was removed by rotary evaporation (below 328 K), and the residue was dissolved in 0.5 ml $CDCl_3$ for ^1H NMR and was dissolved in 0.5 ml CH_3OH for FABMS. Glycerin was used as the substrate for FABMS analysis. The sample of ethanol addition for ^{13}C NMR was prepared as follows. The 5.0 l of the filtrate from ethanol addition reaction prepared as described above was evaporated by rotary evaporation, then the residue was redissolved in acetone (15 ml), and then the solution was purified by silica gel column chromatography using acetone and acetone–H_2O (4:1) as eluents to give unreacted Rh B and the orange addition product solution, respectively. The solvent of the product solution was removed by rotary evaporation, and the residue was dissolved in $CDCl_3$–CD_3SOCD_3 for ^{13}C NMR.

The photodecomposition of leuco Rh B was carried out with the same light source and reaction cell as used in the photocatalytic reaction. The solution of leuco Rh B for photodecomposition was prepared as follows: a suspension of 120 ml 1.0×10^{-5} M Rh B solution and 0.020 g 1.0 wt.% Pt/TiO_2 was dispersed in an ultrasonic bath and nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen, then hydrogen was bubbled for 3 min through the mixture and stirred for 10 min in the dark; the Pt/TiO_2 in dispersion was removed by Millipore filter under N_2 atmosphere in the dark. Before irradiation, nitrogen was bubbled through the bleached filtrate for 30 min.

3. Results

3.1. Photocatalytic activities of various substrates for hydrogen evolution

Table 1 shows that oxalic acid, EDTA and ethanol are good electron donors for hydrogen evolution; whereas Rh B has no activity, which can be attributed to its stability. By increasing the concentration (1.0×10^{-3} M Rh B), the rate of hydrogen evolution is much smaller than that in distilled water. This fact would be explained by the fact that Rh B screened TiO_2 from the ultra-bandgap light.

Table 1
Comparison of activities of various organic substrates in aqueous solution as electron donors for hydrogen evolution[a]

Organic substrates	Initial concentration of the substrate (M)	Irradiation time (h)	Amount of hydrogen evolution (μmol)
$H_2C_2O_4$	1.0×10^{-3}	1	75
EDTA	1.0×10^{-3}	1	72
Ethanol	1.0×10^{-3}	2	32
Rh B	1.0×10^{-3}	2	Trace
Rh B	1.0×10^{-5}	2	2.4
None	–	2	2.3

[a] Conditions: 0.020 g 0.3 wt.% Pt/TiO$_2$, 120 ml solution.

3.2. Adsorption measurements

The degree of adsorption of Rh B onto TiO$_2$ or Pt/TiO$_2$ was evaluated by monitoring the decrease of the concentration of Rh B (ΔC) in the aqueous solutions containing powdered TiO$_2$ or Pt/TiO$_2$ stirred in the dark at room temperature for 30 min. The concentration of Rh B was measured spectrophotometrically. Table 2 illustrates that Rh B can be adsorbed more strongly on Pt/TiO$_2$ than on TiO$_2$ in the single Rh B solution, whereas it exhibits different adsorption behaviors on TiO$_2$ or Pt/TiO$_2$ in the presence of other solutes. Because the deposited Pt particles of 1.0 wt.% Pt/TiO$_2$ occupy only a very small portion of TiO$_2$ surface based on TEM analysis, it is believed that the adsorption of Rh B on TiO$_2$ should be much stronger on Pt than on TiO$_2$. In the presence of oxalic acid or EDTA, the competitive adsorption between Rh B and oxalic acid or EDTA on TiO$_2$ can be observed, while in the presence of ethanol, the adsorption of Rh B on TiO$_2$ is not influenced. Carboxylic acid undergoes inner-sphere complexation at TiO$_2$ surface sites, while ethanol interacts with the sites via weaker hydrogen-bonding interactions [15]. Thus, the adsorption of Rh B on TiO$_2$ via carboxyl radical cannot compete with that of oxalic acid and that of EDTA, because oxalic acid is adsorbed strongly on TiO$_2$ [16] and EDTA is a strong chelate agent; whereas Rh B and ethanol can be adsorbed on different kinds of adsorbed sites, respectively, so that the adsorption of Rh B is not affected by ethanol. Electrostatic action between Rh B and TiO$_2$ is another reason for the decrease of the adsorption on TiO$_2$. The pH of 1.0×10^{-3} M oxalic acid and disodium ethylene-diamine tetraacetate solution were 3.0 and 4.8, respectively. In the pH range of 3.0–4.8, Rh B is present as the cation, since the carboxy-phenyl group dissociates with p$K_a = 9$ [17]. The surface of TiO$_2$ is amphoteric due to hydroxyl groups [15]. The pH of zero point of charge (pHzpc) for Degussa P25 in water is 6.25 [18].

$$>\text{Ti–OH} + \text{H}^+ \leftrightarrows\ >\text{TiOH}_2{}^+ \quad \text{at pH} < 6.25$$

$$>\text{Ti–OH} + \text{OH}^- \leftrightarrows\ >\text{TiO}^- + \text{H}_2\text{O} \quad \text{at pH} > 6.25$$

In acidic media of pH below 6.25, both Rh B and TiO$_2$ surface are positively charged. Because of strong electrostatic repulsion between these similarly charged species, Rh B cannot be adsorbed easily on TiO$_2$ surface. The conclusion is also suitable for the adsorption of Rh B on TiO$_2$ moiety of Pt/TiO$_2$, because a small amount of deposited Pt hardly influences the pHzpc [19]. For the adsorption of Rh B on Pt moiety of Pt/TiO$_2$, oxalic acid has a small effect on the adsorption but EDTA decreased it greatly. However, still a small amount of Rh B can be adsorbed on Pt. On the other hand, ethanol suppresses the adsorption of Rh B on Pt, which could be attributed to that ethanol is adsorbed more strongly on Pt than Rh B.

3.3. Effect of Rh B on photocatalytic hydrogen evolution and its transformation

As comparative study, in the presence of electron donors, oxalic acid, EDTA and ethanol, profile of the ratio of the photocatalytic hydrogen evolution rate with Rh B to the rate without Rh B as a function of illuminated time is shown in Fig. 1. In the presence of EDTA, Rh B decreases the rate of hydrogen evolution to some extent at the first 30 min, but scarcely influences the rate after that time; while in the presence of oxalic acid or ethanol, Rh B decreases the rate to a great extent.

Table 2
Adsorption of Rh B on Pt/TiO$_2$ and Degussa P25 TiO$_2$ in various solutions[a]

Solution	Amount of adsorbed Rh B (mol/g catalyst)	
	Degussa P25 TiO$_2$	1.0 wt.% Pt/TiO$_2$
1.0×10^{-5} M Rh B	5.5×10^{-7}	7.6×10^{-7}
1.0×10^{-5} M Rh B + 1.0×10^{-3} M $H_2C_2O_4$	1.7×10^{-7}	4.2×10^{-7}
1.0×10^{-5} M Rh B + 1.0×10^{-3} M EDTA	0.63×10^{-7}	1.4×10^{-7}
1.0×10^{-5} M Rh B + 1.0×10^{-2} M ethanol	5.5×10^{-7}	4.9×10^{-7}
1.0×10^{-5} M Rh B + 1.0×10^{-1} M ethanol	5.2×10^{-7}	4.8×10^{-7}

[a] Adsorption conditions: 0.10 g catalyst, 10 ml solution, stirring time: 30 min, room temperature (290–295 K).

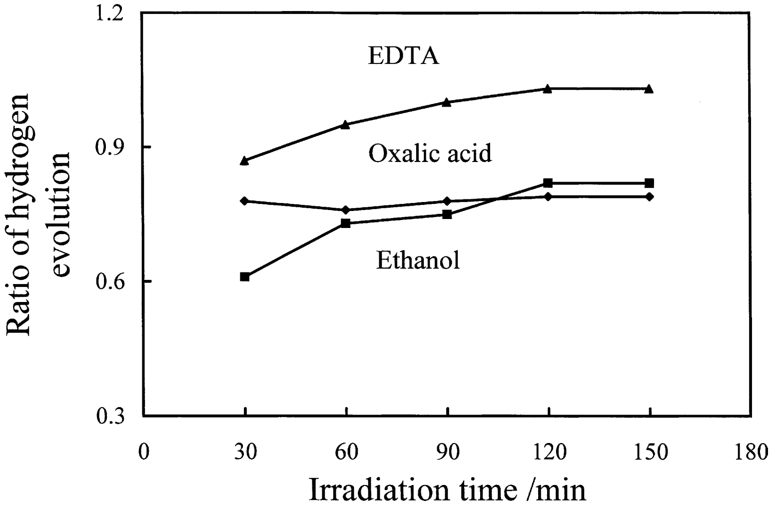
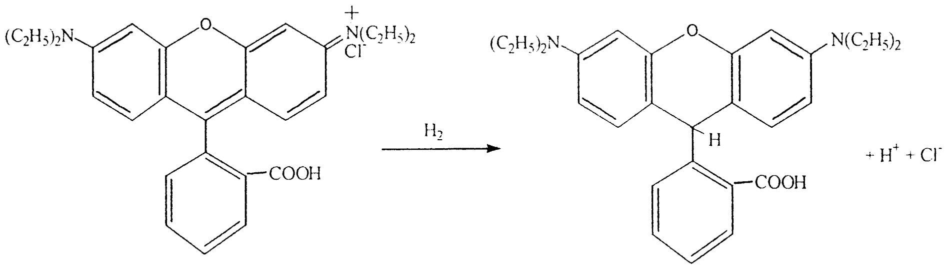


Fig. 1. Plot of the ratio of the photocatalytic hydrogen evolution rate with Rh B to the rate without Rh B vs. irradiation time in the presence of various electron donors. Reaction conditions: 0.020 g 0.3 wt.% Pt/TiO_2, 120 ml 1.0×10^{-3} M EDTA (▲), 5.0×10^{-3} M oxalic acid (◆) and 1.0×10^{-2} M ethanol (■) solution containing 1.0×10^{-5} M Rh B, respectively.

Fig. 2a shows that in the presence of oxalic acid, the characteristic absorption band of Rh B at about 556 nm, which can be attributed to the conjugated chromophore ring structure, disappears quickly. The result indicates that the conjugated structure of Rh B is destroyed. Control experiment established that in the absence of oxalic acid, the absorption of Rh B at 556 nm did not decrease markedly after 2 h irradiation except for its adsorption on Pt/TiO_2. It can be seen from Fig. 1 that Rh B decreases the rate of the hydrogen evolution, thus we can assume that the hydrogenation of Rh B takes place in the process.

In order to confirm this assumption, we carried out the hydrogenation of Rh B over TiO_2 and Pt/TiO_2 in the dark under pure H_2 atmosphere. Rh B (1.0×10^{-5} M) bleached quickly (in 10 min) over 1.0 wt.% Pt/TiO_2, whereas bleaching of Rh B could not be observed over TiO_2 within several hours. It is well known that Pt–H formed by adsorption of H_2 on Pt is responsible for the hydrogenation of unsaturated compounds. The result shows that Rh B can undergo hydrogenation over Pt in the photocatalytic reaction.

Rh B can be reduced with zinc in acid solution [14] to produce its leuco form. The reaction is hydrogenation and can be expressed as follows:



DH^+ DH_2 (leuco Rh B, M=444) (1)

Similarly, Koizumi and coworkers [20] reported that hydrogenation of xanthene dye can result in three separated benzene rings as shown in formula (1). To further identify the structure of photocatalytic hydrogenation product of Rh B, the reaction product was analyzed by mass spectrometry. Fig. 3 shows the FAB mass spectrum of the bleached Rh B solution extracted by dichloromethane after irradiation. The peaks at m/z 445.2 and 443.2 can be attributed to $[DH_2+H]^+$ and $[DH]^+$, respectively (formula (1)). The reason for that the $[DH]^+$ peak is much stronger than the peak $[DH_2 + H]^+$ is that $[DH]^+$ has a more stable conjugated π-bonding structure. Based on the peak at m/z 445.2, we conclude that hydrogenation reaction of one Rh B molecule with one H_2 molecule takes place. Judging from the structure of Rh B, we are sure that only the addition of $H^\bullet$ to the position i as shown in above formula takes place so that the conjugated structure is destroyed completely. The photocatalytic hydrogenation can be attributed to that Rh B can be adsorbed strongly on Pt and there are a large amount of $H^\bullet$ atoms on it.

Interestingly, as shown in Fig. 2b, when the bleached solution with Pt/TiO_2 was exposed to air, the color of the

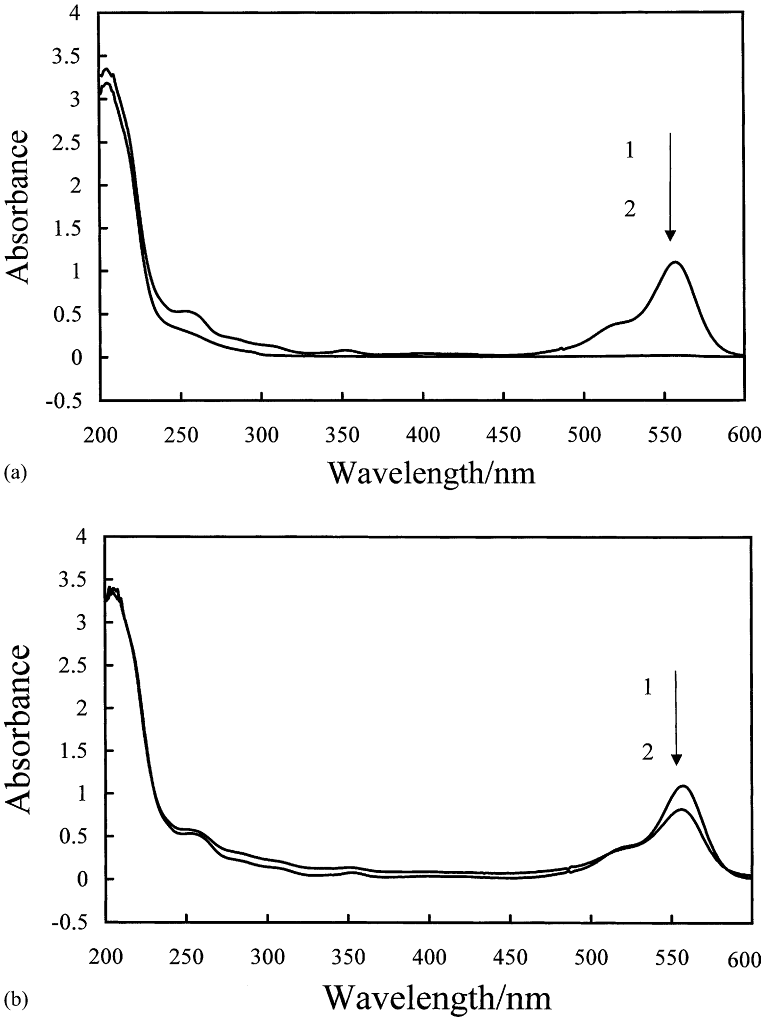


Fig. 2. Absorption spectra of Rh B (1.0×10^{-5} M) solution containing initial 5.0×10^{-3} M oxalic acid under various conditions: (a) 1, the original solution; 2, the filtrate of bleached suspension of 120 ml 0.020 g 1.0 wt.% Pt/TiO$_2$ dispersion after 18 min irradiation under N$_2$ atmosphere; (b) 1, the original solution; 2, the filtrate of the bleached suspension after exposure to air for 16 h.

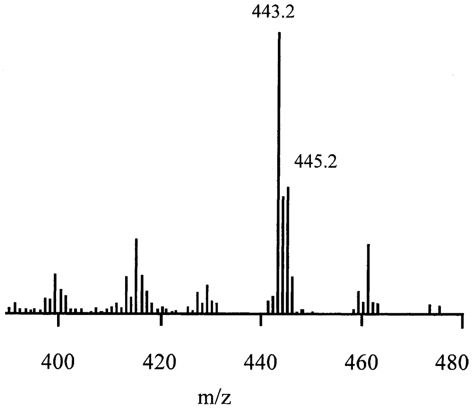


Fig. 3. FAB mass spectrum of the leuco form of Rh B in glycerin.

solution can be resumed slowly. It can be attributed to that the conjugated π-bonding structure can be resumed by oxidation or dehydrogenation because the conjugated π-bonding molecule form is more stable, which indicates that hydrogenation of Rh B is reversible. Compare curve 1 with curve 2 in Fig. 2b, only 75% of the absorbance of Rh B at 556 nm can be restored. We speculate that there are three possibilities to explain this result: (1) the adsorption of Rh B on Pt/TiO$_2$; (2) incomplete oxidation of leuco Rh B within 16 h exposure time; (3) other photocatalytic reactions which cannot be returned reversibly by oxidation.

In the presence of EDTA, the temporal profile of the changes in the Rh B chromophore was monitored by UV–Vis spectroscopy (Fig. 4). The spectra illustrate that after 2 h irradiation there is a small decrease in the absorbance at ca. 554 nm, which can be attributed to the adsorption of Rh B on Pt/TiO$_2$ and the hydrogenation of Rh B. However, comparing the absorbance after 2 h with that after 4 h irradiation, no apparent change can be found.

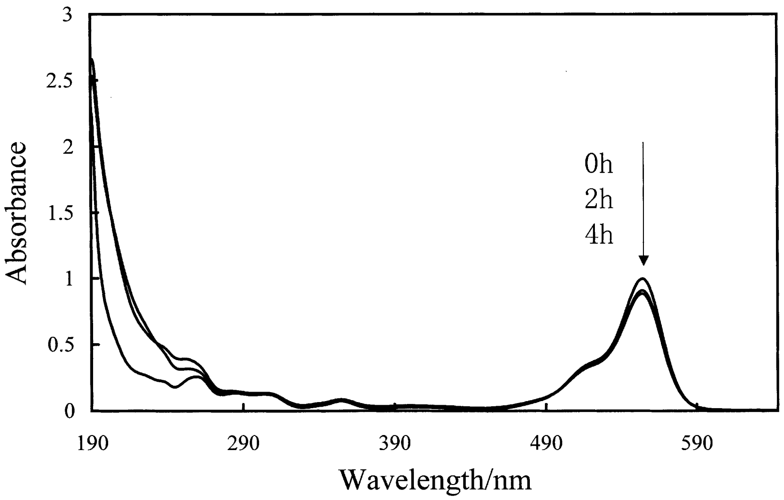


Fig. 4. Temporal UV–Vis spectra of the changes for Rh B in the presence of EDTA at different irradiation times. Conditions: 120 ml 1.0×10^{-5} M Rh B solution containing initial 1.0×10^{-3} M EDTA and 0.020 g 0.3 wt.% Pt/TiO_2.

In our work we found that leuco Rh B solution derived from hydrogenation was sensitive to irradiation. Fig. 5 shows that the leuco dye can return to dye form under irradiation in N_2 atmosphere and the concentration of Rh B reaches a plateau (6.8×10^{-6} M) in about 30 min. The initial concentration of Rh B before hydrogenation was 1.0×10^{-5} M (pH 5.4). The large difference between the initial and formed concentration would be attributed to the stronger adsorption ability of leuco dye on TiO_2. From formula (1) we can consider that at pH 5.4, leuco Rh B can exist as a neutral molecule or an anion (if we assume that pK_a of carboxy-phenyl group of leuco Rh B is near to pK_a of benzoic acid, 4.2). Owing to no electrostatic repulsion between the positively charged TiO_2 surface and the neutral molecule or electrostatic attraction between the TiO_2 surface and the anion, the adsorption ability of leuco Rh B on TiO_2 is much stronger than that of Rh B. The amount of hydrogen produced in the process determined by gas chromatography was consistent with the reverse reaction shown in (1) within experimental error. If we assume that initial concentration of leuco Rh B (DH_2) is 6.8×10^{-6} M, the photodecomposition of leuco Rh B follows a zero-order kinetics and the rate constant is 0.25×10^{-6} mol l^{-1} min^{-1} (Fig. 5, inset).

If we assume that photodecomposition of leuco Rh B can compete with hydrogenation of Rh B over Pt/TiO_2, we can explain that the absorbance at 554 nm after 2 h and that after 4 h irradiation were almost the same. The reason is that in the presence of EDTA there was only a small amount of Rh B adsorbed on Pt and the hydrogenation rate of Rh B was slower. However, in the case of oxalic acid, due to its larger adsorption amount on Pt, the rate of hydrogenation of Rh B could be much faster than that of photodecomposition of leuco Rh B, thus the photobleaching could be observed.

Fig. 6 shows that in the case of ethanol and Rh B, with increase of irradiation time, absorbance of the solution at ca. 554 nm decreases quickly and the absorption band

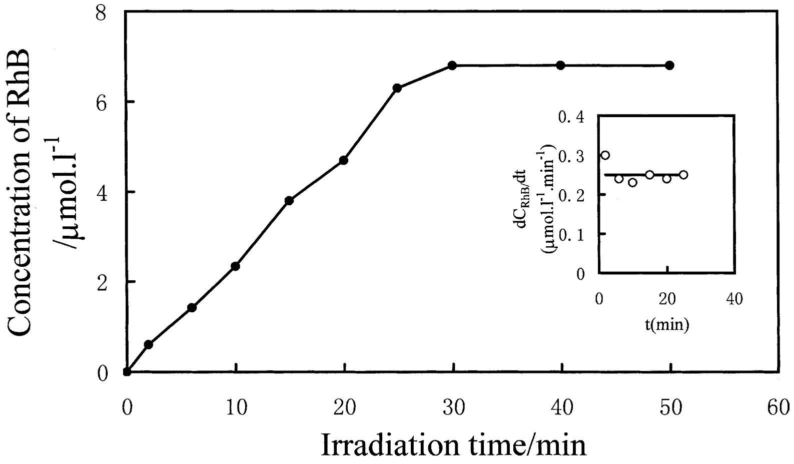


Fig. 5. Photodecomposition of leuco Rh B prepared by hydrogenation of 1.0×10^{-5} M Rh B solution over 1.0 wt.% Pt/TiO_2.

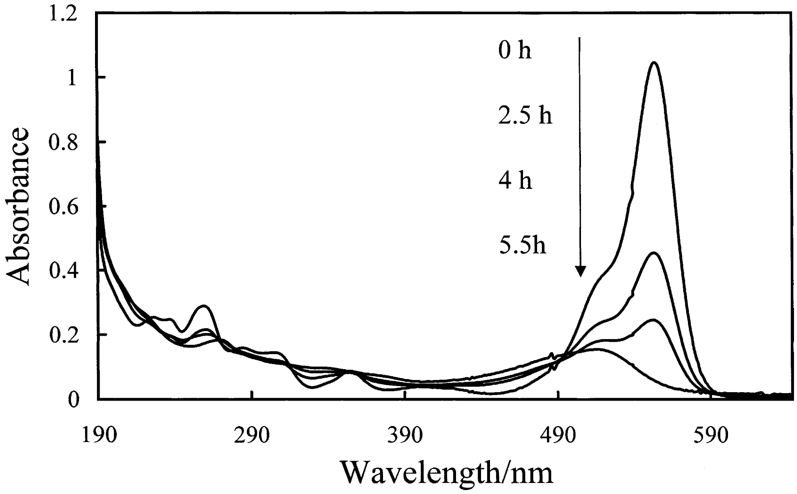


Fig. 6. Temporal UV–Vis spectra of the changes for Rh B in the presence of ethanol at different irradiation times. Conditions: 120 ml 1.0×10^{-5} M Rh B solution containing initial 1.0×10^{-2} M ethanol and 0.020 g 0.3 wt.% Pt/TiO_2.

shifts from 554 nm (0 h) to 553 nm (2.5 h), 552 nm (4 h) and 521 nm (5.5 h) in sequence. The result demonstrates that some transformation of Rh B has taken place. Interestingly, using 0.10 M instead of 0.010 M CH_3CH_2OH, we observed that Rh B transformed from violet (absorption band at 554 nm) to orange (the band at 521 nm) in 1.5 h, indicating that ethanol plays an important role in this transformation. In order to determine what kind of reaction Rh B underwent, the product of 5.5 h irradiation was determined by FABMS. Fig. 7 shows that compared product of 5.5 h irradiation with initial Rh B, a new strong peak appears at *m*/*z* 489.3 which can be attributed to $[DH–H_4C_2OH+H]^+$ (vide infra), demonstrating that the addition of ethanol radical is the main reaction.

α-Hydrogen of ethanol can be abstracted by photogenerated hydroxyl radical on TiO_2 to form α-hydroxyalkyl radical as follows [21]:

$$CH_3CH_2OH + {>}TiOH^{\bullet}\ (\text{or } h_{vb}^{+}) \rightarrow CH_3CHOH^{\bullet} + {>}TiOH_2 \quad (2)$$

The rate constant for hydrogen-abstraction from an ethanol molecule by a free hydroxyl radical is $1.9 \times 10^9\ M^{-1}\ S^{-1}$ [22]. Thus, on the surface of TiO_2 there would be a certain amount of ethanol radicals. Since Rh B and ethanol can be adsorbed on TiO_2 concurrently, the formed ethanol radical can combine with Rh B additively.

The half-wave potential $E_{1/2}$ of oxidation of α-hydroxyalkyl radical has been determined to be −0.94 V (vs. NHE at pH 7) [23]. The potential is negative enough to inject electrons to the conduction band (current doubling) to promote hydrogen evolution. The reaction can be expressed as follows:

$$CH_3CHOH^{\bullet} \rightarrow CH_3CHO + H^+ + e^- \quad (3)$$

In view of the combination of ethanol radical with Rh B additively, the rate of hydrogen evolution was decreased.

4. Discussion

The reaction is initiated by the photoexcitation of TiO_2 particles, which leads to the formation of electron–hole pairs:

$$TiO_2 \xrightarrow{h\nu} TiO_2\ (e_{cb}^{-} + h_{vb}^{+}) \quad (4)$$

Photogenerated conduction band electrons e_{cb}^- can be transferred to electron acceptor H^+ or Rh B. With Pt on TiO_2, electrons can be trapped by Pt and $H^{\bullet}$ intermediates and dihydrogen can be produced on Pt [12]. Rh B can be reduced by electron directly or by H atom to semireduced radical which is a long-lived radical [14]

$$H^+ + e_{cb}^- \rightarrow H^{\bullet} \rightarrow \tfrac{1}{2}H_2 \quad \text{on Pt} \quad (5)$$

$$DH^+ + e_{cb}^- \rightarrow DH^{\bullet} \quad (6)$$

$$DH^+ + H^{\bullet} \rightarrow DH^{\bullet} + H^+ \quad (7)$$

According to electrochemistry, combination of two $H^{\bullet}$ on Pt to produce H_2 is a rate-determining step for hydrogen evolution:

$$Pt–H + Pt–H \rightarrow H_2 + 2Pt \quad (8)$$

There should be a large amount of $H^{\bullet}$ on Pt. Thus, Rh B should be reduced mainly by H atoms, and the reduction of Rh B by electrons could not compete with the former. The produced free radical ($DH^{\bullet}$) is very stable; its structure is shown as follows [14]:

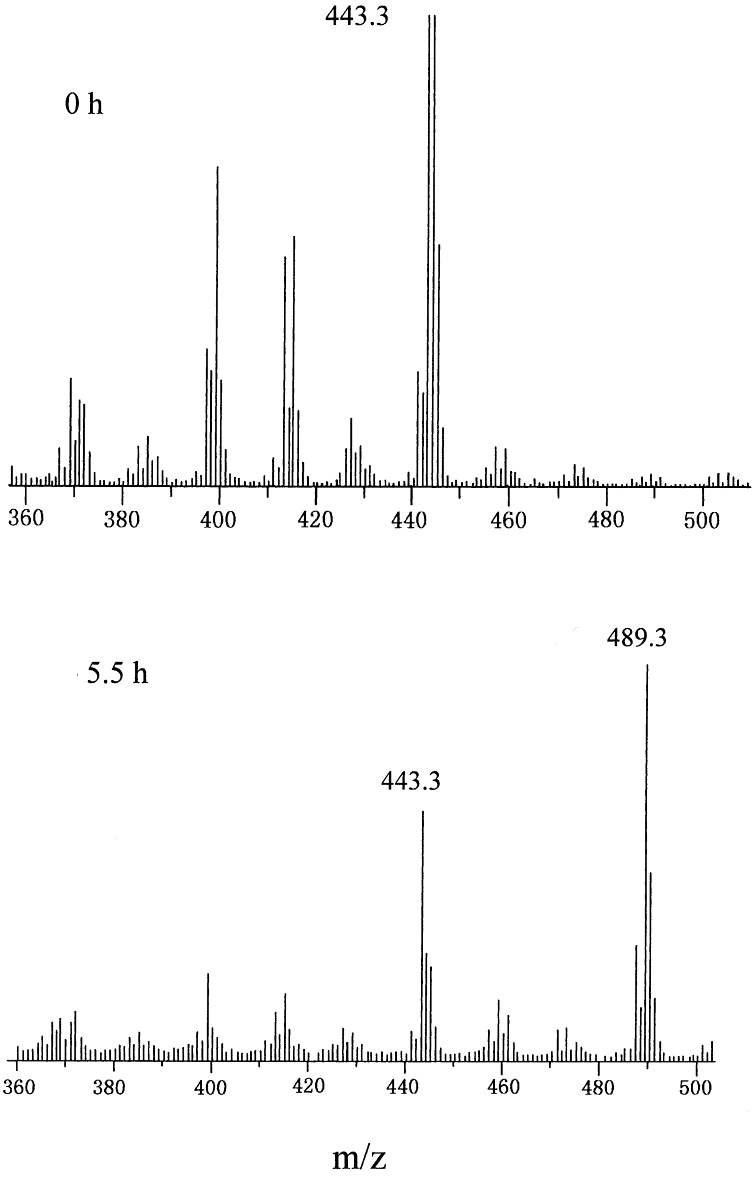
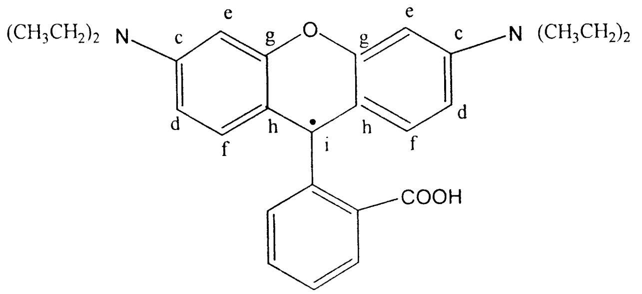


Fig. 7. FAB mass spectra of Rh B in the presence of ethanol before irradiation (a) and after 5.5 h irradiation (b). Conditions: the same as in Fig. 6.



The formed DH$^\bullet$ can combine at the position i with produced H atom on Pt

$$DH^\bullet + H^\bullet \rightarrow DH_2 \qquad (9)$$

The structure of the product (leuco Rh B) is the same as what has been shown in (1).

In the presence of oxalic acid, due to the large adsorption amount of Rh B on Pt, hydrogenation could take place quickly and the rate of photocatalytic hydrogen evolution was decreased greatly. However, in the presence of EDTA, owing to the adsorption behavior of Rh B, Rh B would undergo the hydrogenation slowly, and as a result of the photodecomposition of leuco dye, Rh B had less influence on the rate.

Likewise, valence band hole, h_{vb}^{+} can be filled by electron donors $H_2C_2O_4$, EDTA, CH_3CH_2OH and surface hydroxyl groups on TiO_2. The oxidized EDTA undergoes a facile, irreversible decomposition to produce formaldehyde and ethylene-diamine-*N*,*N*′-triacetic acid [24]. Because of its good stability, the oxidation of Rh B in the presence of electron donor is negligible. The formed hydroxyl radical can continuously oxidize oxalic acid, EDTA and CH_3CH_2OH:

$$OH^- + h_{vb}{}^+ \rightarrow OH^\bullet \tag{10}$$

$$HC_2O_4{}^- + h_{vb}{}^+ \rightarrow HC_2O_4{}^\bullet \tag{11}$$

The potential for Rh B taking up an electron is −0.75 V (vs. NHE) in aqueous alkaline solution [25]. The decomposition product of $HC_2O_4{}^\bullet$, $CO_2{}^{\bullet -}$ (normal potential $E^0(CO_2/CO_2{}^{\bullet -}) = -1.8\,V$ [26]) is also able to reduce Rh B to $DH^\bullet$ or inject electron to conduction band (current doubling):

$$CO_2{}^{\bullet -} + DH^+ \rightarrow CO_2 + DH^\bullet \tag{12}$$

$$CO_2{}^{\bullet -} \rightarrow CO_2 + e^- \rightleftarrows \tag{13}$$

Since Rh B is adsorbed mainly on Pt, current doubling effect will be predominant, and $HC_2O_4{}^\bullet$ or $CO_2{}^{\bullet -}$ has less contribution to the reduction of Rh B.

Similarly, $CH_3CHOH^\bullet$ can also reduce Rh B to $DH^\bullet$ or inject electron to conduction band as shown in (3). The former also decreases the rate of photocatalytic hydrogen evolution:

$$CH_3CHOH^\bullet + DH^+ \rightarrow CH_3CHO + DH^\bullet + H^+ \tag{14}$$

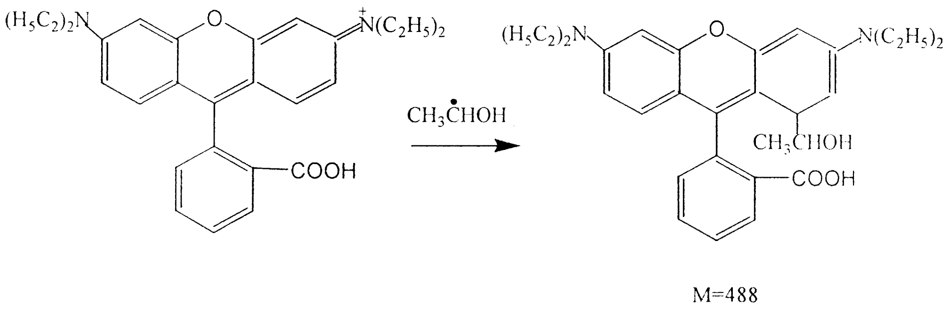
The produced $DH^\bullet$ can be protonated and dismutated [17] as follows:

$$DH^\bullet + H^+ \rightarrow DH_2{}^{\bullet +} \tag{15}$$

$$2DH_2{}^{\bullet +} \rightarrow DH_2 + DH^+ + H^+ \tag{16}$$

The process should undergo slowly, since in the presence of ethanol the hydrogenation could not be observed.

Due to the stability of $DH^\bullet$, combination of $DH^\bullet$ with ethanol radical should take place completely at position i. However, ^1H NMR signals showed that after 5.5 h irradiation, the characteristic signal of Rh B for $-CH_2-$ at the position b appeared at $\delta = 3.55$ ppm shifted upfield, and two signals for $-CH_2-$ of addition product appeared at $\delta = 3.33$ and 3.42 ppm, demonstrating that symmetrical addition of ethanol radical to the position i was at least not the main reaction. The reason is that there is a large steric hindrance for ethanol radical addition to the position i. According to the resonance theory, Rh B can also undergo addition of ethanol radical at positions c, g, and f. The UV–Vis spectroscopic evidence established that the conjugated structure of Rh B was not destroyed after 5 h irradiation, indicating that the addition of ethanol radical to the positions has taken place. Since there is a larger repulsion for the addition at the positions c and g, the products of addition to these positions should be smaller or even none. Due to steric conditions the carboxy-phenyl group remains almost perpendicular to plane of the chromophore of Rh B [25]. The block for the addition to the position f should be smaller. Thus, the additive reaction would take place mainly as follows:



In order to confirm the proposed mechanism, ^{13}C NMR spectrum of the addition product was measured. Compared with the two characteristic signals of two symmetrical c and g carbons for Rh B at $\delta = 155.2$ and 157.4 ppm [27], the corresponding signals for the product shifted upfield and four signals appeared in the range of $\delta = 150$–154 ppm, indicating that the addition does not take place at the positions c and g. The reason is that the product molecule is not symmetrical any more after the addition. The single peak at $\delta = 156.9$ ppm for the product can be assigned to the i carbon (for Rh B the corresponding peak at $\delta = 159.1$ ppm), demonstrating that the addition does not take place at this position. Based on these results, we are sure that the addition takes place at the position f.

5. Conclusions

In the presence of oxalic acid as the electron donor for photocatalytic hydrogen evolution, due to the strong adsorption of Rh B on Pt, the hydrogenation of Rh B takes place quickly on Pt of Pt/TiO_2. In the presence of ethanol, since ethanol and Rh B are adsorbed on TiO_2 concurrently, Rh B undergoes the addition of ethanol radical. In the two cases, the rates of photocatalytic hydrogen evolution decrease markedly. On the other hand, in the presence of EDTA, Rh B can only be adsorbed on Pt in a very small amount, the rate of the hydrogenation is slow, so the rate of photodecomposition of leuco dye can compete with it. In this case, notable transformation of Rh B and decrease in the rate of photocatalytic hydrogen evolution cannot be observed.

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