Research Article

Solar Hydrogen Production Coupled with the Degradation of a Dye Pollutant Using TiO$_2$ Modified with Platinum and Nafion

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The simultaneous production of molecular hydrogen (H$_2$) and degradation of rhodamine B (RhB) was successfully achieved using TiO$_2$ modified with platinum and nafion (Pt/TiO$_2$/Nf) under visible light ($\lambda > 420$ nm). Pt/TiO$_2$/Nf exhibited high activity for H$_2$ production in the presence of RhB and EDTA as a photosensitizer (also an organic dye pollutant) and an electron donor, respectively. However, the activity of TiO$_2$ modified with either platinum or nafion for H$_2$ production was negligible under the same experimental conditions. The negatively charged nafion layer enhances the adsorption of cationic RhB and pulls protons, a source of hydrogen, to the surface of TiO$_2$ through electrostatic attraction. On the other hand, platinum deposits on TiO$_2$ can act as an electron sink and a temporary electron reservoir for the reduction of protons. With the production of H$_2$, RhB was gradually degraded through N-deethylation, which was confirmed by the spectral blue shift of the maximum absorption wavelength (λ_{max}) from 556 to 499 nm (corresponding to the λ_{max} of rhodamine 110). With Pt/TiO$_2$/Nf employed at [RhB] $= 20\,\mu$M (0.6 μmol), approximately 70 μmol of H$_2$ was produced and RhB and its intermediates were completely removed over a 12 h period. A detailed reaction mechanism was discussed.

1. Introduction

Dye-sensitized TiO$_2$ systems have been studied extensively for the remediation of environmental pollutants and the production of hydrogen under visible light [1–15]. Both applications are based on photo-induced electron transfer from the dyes to electron acceptors (e.g., pollutants and protons) through the TiO$_2$ conduction band (CB). Although the photonic efficiency of this system is high, expensive synthetic dyes (e.g., Ru-based [1, 3–6, 10], (metal) porphyrin [5, 7], and engineered organic dyes [2, 8, 11–15]) have been primarily used. In addition, most dye-sensitized TiO$_2$ systems suffer from the instability of the dye because dyes can be degraded after electron injection from the excited dye to the TiO$_2$ CB. The high price and low stability of dyes limit the practical applications of dye-sensitized TiO$_2$ systems.

Organic dyes are one of the most serious pollutants in the aquatic environment due to their high production volumes from industry, toxicity, and low biodegradability. The annual global production of organic dyes is approximately one million tons, and a significant amount (10–15%) of wastewater containing dyes is discharged to the surface water without any treatment [16, 17]. In addition, some organic dyes are carcinogenic to humans and negatively affect aquatic organisms by interfering with their metabolic processes [16–18]. However, the biological treatments widely employed in water treatment are usually inefficient for the degradation of organic dyes [19].

Recently, bifunctional TiO$_2$ photocatalysts have been developed, particularly for simultaneous hydrogen production and pollutant degradation. This bifunctionality was achieved through the surface modification of TiO$_2$ with metal nanoparticles or two different components (i.e., anions and metal nanoparticles) [20–25]. However, the previously developed bifunctional TiO$_2$ photocatalysts worked only under UV light, limiting their practical applications because UV light accounts for only 3% of natural sunlight at ground level. Visible active photocatalysts can be used to achieve the

simultaneous hydrogen production and pollutant degradation under visible light [26]. Another approach to addressing this challenge would be to use the organic dyes to be treated as a photosensitizer for hydrogen production instead of expensive synthetic dyes, while simultaneously degrading these organic dyes under visible light (44% of natural sunlight).

In this work, we successfully achieved the simultaneous production of hydrogen and degradation of rhodamine B (RhB, an azo dye that accounts for more than 65% of total dye production [16]) using TiO_2 modified with platinum and nafion (Pt/TiO_2/Nf) under visible light. The effects of various experimental parameters (e.g., initial pH (pH$_i$), RhB concentration, and EDTA concentration) on H_2 production were investigated. In addition, a detailed reaction mechanism for the simultaneous production of hydrogen and degradation of RhB was suggested.

2. Experimental

2.1. Materials and Reagents.

The materials and reagents were used as received without further purification. These substances include TiO_2 powder (Hombikat, UV-100), rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$, Aldrich), chloroplatinic acid (H_2PtCl_6, Aldrich), methanol (CH_4O, J. T. Baker), nafion perfluorinated resin solution (5 wt% solution in a mixture of alcohol and water, Aldrich), and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, Aldrich). Ultrapure deionized water (18.3 MΩ cm) prepared by a water purification system (Barnstead) was used.

2.2. Catalyst Preparation.

Platinum (Pt) nanoparticles were deposited onto the surface of TiO_2 using a photodeposition method [27]. An aqueous TiO_2 suspension (0.5 g/L, 500 mL) containing chloroplatinic acid as a Pt precursor (100 μM) and methanol as an electron donor (1 M) was irradiated with a 200 W mercury lamp for 30 min. Next, the Pt-deposited TiO_2 (Pt/TiO_2) powder was collected by filtration through a 0.45 μm PVDF disc filter (Pall), washed with distilled water, and dried in an oven at 70°C. The typical Pt loading on TiO_2 was estimated to be ca. 3 wt% by measuring the concentration of unused chloroplatinic acid remaining in the filtrate solution after the photodeposition using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Corp.). To obtain Pt/TiO_2/Nf (TiO_2 modified with Pt and nafion), an aliquot of nafion solution (0.1 mL) was added to the Pt/TiO_2 powder (0.1 g), mixed well, and dried at room temperature overnight [28].

2.3. Photocatalysis.

The catalyst powder was dispersed in distilled water by sonication for 30 s in an ultrasonic cleaning bath. An aliquot of the RhB and EDTA stock solution was subsequently added to the suspension to yield the desired initial concentration. The initial pH (pH$_i$) of the suspension was adjusted with $HClO_4$ solution. The total volume of the suspension was 30 mL. Prior to visible light irradiation, N_2 gas (99.9%) was purged through the suspension for 1 h to remove dissolved oxygen, and then the reactor was sealed with a rubber septum. A 300 W Xe arc lamp (Oriel) was used as a light source. Light was passed through a 10 cm IR water
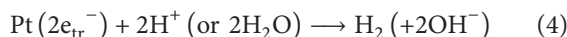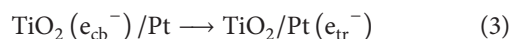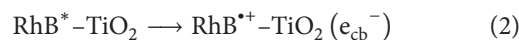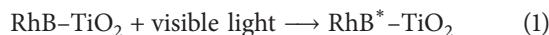
filter and a cutoff filter ($\lambda > 420$ nm), and then the filtered light was focused onto a cylindrical glass reactor with a quartz window.

2.4. Analysis.

The amount of photogenerated molecular hydrogen (H_2) in the headspace of the reactor was analyzed using a gas chromatograph (GC, HP6890A) equipped with a thermal conductivity detector and a 5 Å molecular sieve column. Sample aliquots were withdrawn from the visible-light-irradiated reactor and filtered through a 0.45 μm PTFE syringe filter (Millipore) to remove catalyst particles prior to the analysis of RhB. The color disappearance of RhB and its maximum absorption wavelength (λ_{max}) shift resulting from the stepwise N-deethylation [29] were monitored using a UV-visible spectrophotometer (Shimadzu UV-2401PC). It should be noted that RhB (colored) is transformed to leuco RhB (colorless) through the addition of H$^\bullet$ (formed from the reduction of H$^+$) in the absence of oxygen, but leuco RhB is dehydrogenated back to RhB in the presence of oxygen [30]. To exclude the color disappearance through the formation of leuco RhB, the absorption spectrum of samples was measured after exposure to air. The concentrations of RhB adsorbed on the catalyst surface were calculated by subtracting the equilibrated concentrations (with catalyst, after 30 min in the dark) from the initial concentrations (without catalyst). The concentration of RhB was determined by measuring the absorbance at 556 nm.

3. Results and Discussion

3.1. Effect of Nafion Coating on H_2 Production.

RhB, a representative azo dye pollutant, was selected as a photosensitizer, and the production of H_2 in the presence of EDTA (electron donor) was compared between Pt/TiO_2 and Pt/TiO_2/Nf (Figure 1(a)). The production of H_2 in the suspension of Pt/TiO_2 was very low but was markedly enhanced by the nafion coating of Pt/TiO_2.

Under visible light, RhB adsorbed on the TiO_2 surface is excited (see, reaction (1)), and then electrons are transferred from the excited RhB to protons (or water molecules) through the TiO_2 CB and Pt nanoparticles (see, reactions (2)–(4)):

$$RhB–TiO_2 + \text{visible light} \longrightarrow RhB^*–TiO_2 \qquad (1)$$

$$RhB^*–TiO_2 \longrightarrow RhB^{\bullet+}–TiO_2 \left(e_{cb}^{-}\right) \qquad (2)$$

$$TiO_2 \left(e_{cb}^{-}\right)/Pt \longrightarrow TiO_2/Pt \left(e_{tr}^{-}\right) \qquad (3)$$

$$Pt \left(2e_{tr}^{-}\right) + 2H^+ \left(\text{or } 2H_2O\right) \longrightarrow H_2 \left(+2OH^-\right) \qquad (4)$$

In these processes, Pt nanoparticles enhance the interfacial electron transfer from the TiO_2 CB to protons as an electron sink (Schottky-barrier electron trapping) and a temporary electron reservoir that enables the two-electron reduction of protons (see, reactions (3) and (4)) [32, 33]. In the absence of Pt nanoparticles (i.e., in the cases of TiO_2 and TiO_2/Nf), the production of H_2 was negligible (data not shown). The coating of nafion, an anionic perfluorinated polymer with a sulfonate group ($-SO_3^-$), changes the surface charge of TiO_2 (pH$_{zpc}$ = 6.0 [9]) from positive to negative under
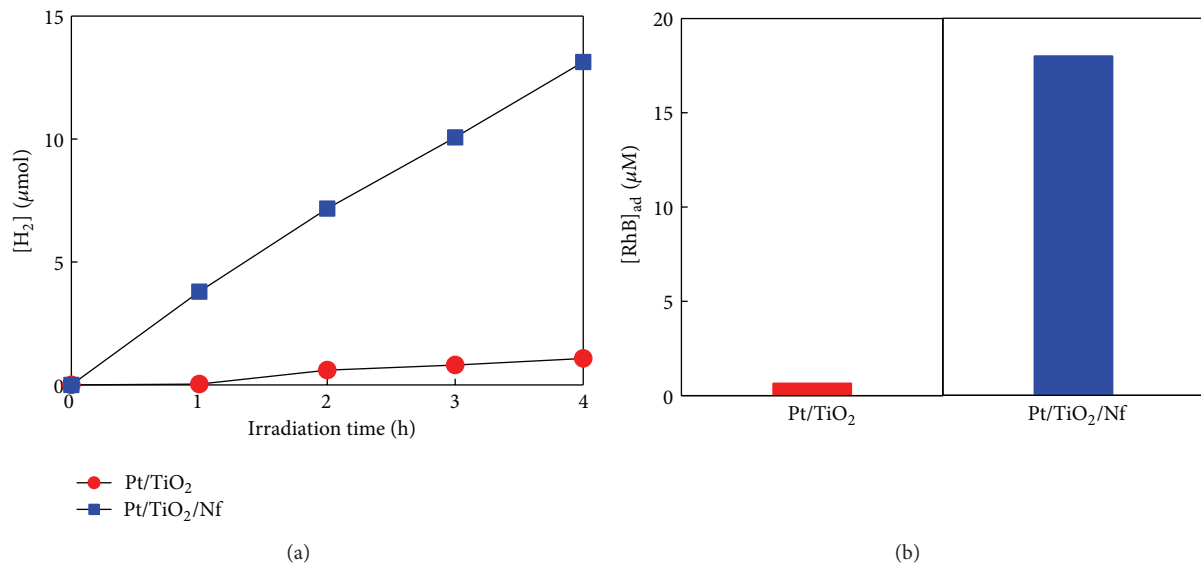
(a)

(b)

FIGURE 1: (a) RhB-sensitized H_2 production in the suspension of Pt/TiO$_2$ and Pt/TiO$_2$/Nf. (b) Adsorption of RhB on the surface of Pt/TiO$_2$ and Pt/TiO$_2$/Nf. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [RhB] = 20 μM, [EDTA] = 0.4 mM, pH$_i$ = 5, and $\lambda > 420$ nm (for part (a)).
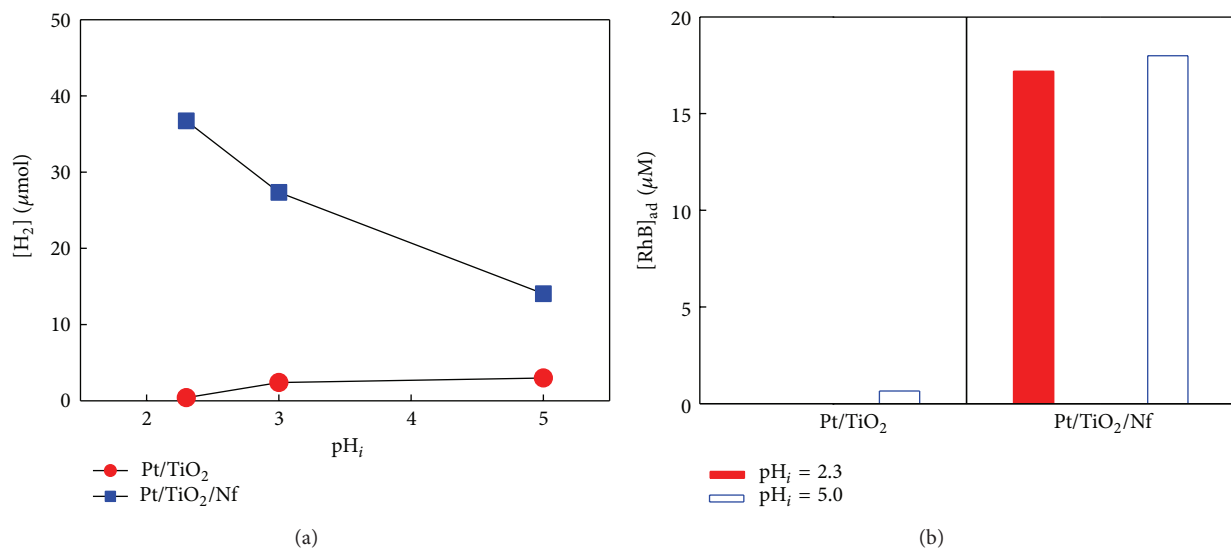

(a)

(b)

FIGURE 2: (a) Production of H_2 for 4 h and (b) adsorption of RhB in the suspension of Pt/TiO$_2$ and Pt/TiO$_2$/Nf as a function of pH$_i$. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [RhB] = 40 μM (for part (a)) or 20 μM (for part (b)), [EDTA] = 4 mM, and $\lambda > 420$ nm (for part (a)).

acidic conditions [27, 28, 34]. Therefore, the adsorption of cationic RhB on the TiO$_2$ surface should be enhanced, which accelerates the electron transfer from the excited RhB to the TiO$_2$ CB and, eventually, the production of H_2.

Figure 1(b) shows the adsorption of RhB on the surfaces of Pt/TiO$_2$ and Pt/TiO$_2$/Nf under the same conditions ([RhB] = 20 μM and pH$_i$ = 5). The amount of RhB adsorbed on Pt/TiO$_2$ was very low (0.7 μM, 3.5%) because the positively charged surface of Pt/TiO$_2$ at pH$_i$ = 5 repels the cationic RhB molecules. Under this condition, the interfacial electron transfer from the excited RhB to the Pt/TiO$_2$ CB should be limited. On the other hand, the adsorption of RhB on the surface of Pt/TiO$_2$/Nf was significant (18.0 μM, 90.0%)

because the negatively charged surface induced by nafion attracts cationic RhB molecules. This result can help to explain why the production of H_2 is markedly enhanced by the nafion coating.

3.2. Effect of Various Parameters on H_2 Production. In dye-sensitized TiO$_2$ systems, the solution pH has a significant effect on the production of H_2 because the adsorption kinetics of dyes on the TiO$_2$ surface strongly depends on the pH-dependent surface charge of TiO$_2$. Figure 2 shows the production of H_2 and the adsorption of RhB in the suspension of Pt/TiO$_2$ and Pt/TiO$_2$/Nf as a function of pH$_i$. The pH-dependent H_2 production trends for Pt/TiO$_2$ and Pt/TiO$_2$/Nf

were opposite: as the pH_i increased, H_2 production gradually increased for Pt/TiO$_2$ but decreased for Pt/TiO$_2$/Nf (Figure 2(a)). However, it should be noted that the H_2 production in the suspension of Pt/TiO$_2$/Nf was much higher than that in the suspension of Pt/TiO$_2$ over the whole pH range of 2.3 to 5.0.

The surface charge of Pt/TiO$_2$ is strongly positive at pH_i = 2.3 because most of the surface hydroxyl groups are protonated. Under this condition, the adsorption of cationic RhB on TiO$_2$ should be inhibited, which results in the negligible production of H_2. However, the number of surface hydroxyl groups that are not protonated increases as the pH increases. This makes the surface charge of TiO$_2$ less positive and enables the adsorption of cationic RhB on TiO$_2$ (see, reaction (5)) and H_2 production. As expected, the adsorption of RhB on the surface of Pt/TiO$_2$ was negligible at pH_i = 2.3 but was clearly observed at pH_i = 5.0, albeit in small amounts (Figure 2(b)):

$$> \text{Ti–OH}_2]^{(2/3)+} + \text{RhB} \tag{5}$$
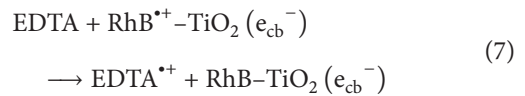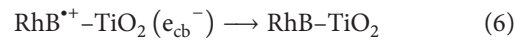$$\longleftrightarrow > \text{Ti–OH}]^{(1/3)-}-\text{RhB} + \text{H}^+$$
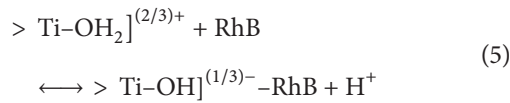
(pK_a = 3.9 [35]) (the surface charge of TiO$_2$ is determined by assuming that the surface Ti having +4 formal charge is located at the octahedral site surrounded by five lattice oxygen atoms and one surface group).

On the other hand, the surface charge of Pt/TiO$_2$/Nf is highly negative, even at acidic pH, because the anionic sulfonate groups (–SO$_3^-$) in the nafion layer outnumber the protonated surface hydroxyl groups of TiO$_2$($>$Ti–OH$_2$]$^{(2/3)+}$) [27, 28]. Therefore, sufficient RhB to have little effect on H_2 production can be adsorbed on the surface of Pt/TiO$_2$/Nf at both pH_i = 2.3 and 5.0 (Figure 2(b)). Under this condition, the decrease in the production of H_2 with increasing pH implies the existence of another mechanism for H_2 production with Pt/TiO$_2$/Nf. It has been reported that the concentration of protons in the nafion layer is much higher than that in the aqueous bulk phase due to the electrostatic attraction between the positively charged protons and anionic sulfonate groups [36]. Because the electron transfer from Pt nanoparticles to protons is kinetically more favorable than that to undissociated water molecules [$k(e^- + H_2O) = 1.9 \times 10^1$ M^{-1} s^{-1} and $k(e^- + H^+) = 2.3 \times 10^{10}$ M^{-1} s^{-1}] [37], the locally concentrated protons within the nafion layer provide good conditions for H_2 production. At lower pH, more protons can be trapped within the nafion layer, which enhances the electron transfer from Pt nanoparticles to protons. Therefore, the production of H_2 with Pt/TiO$_2$/Nf increases as the pH decreases, in contrast to the case of Pt/TiO$_2$. Overall, the nafion-enhanced H_2 production in the RhB-sensitized Pt/TiO$_2$/Nf system is ascribed to two factors. First, the negatively charged nafion layer enhances the adsorption of cationic RhB. Second, protons, which are more favorably reduced to H_2 than undissociated water molecules, are concentrated within the nafion layer.

Figure 3 shows the effect of RhB and EDTA concentrations on the production of H_2 in the suspension of Pt/TiO$_2$/Nf. The production of H_2 was negligible in the absence of either RhB or EDTA, which clearly indicates that RhB and EDTA act as a photosensitizer and an electron donor in the RhB-sensitized Pt/TiO$_2$/Nf system, respectively. The production of H_2 rapidly increased with increasing RhB and EDTA concentrations and then saturated at [RhB] = 10 μM and [EDTA] = 2 mM.

The fact that H_2 was not produced in the absence of EDTA (electron donor) indicates that the electron transfer from the TiO$_2$ CB to RhB$^{\bullet+}$ (i.e., charge recombination, reaction (6)) is much faster than that from the TiO$_2$ CB to Pt nanoparticles (see, reaction (3)), which is consistent with other dye-sensitized TiO$_2$ systems using expensive synthetic dyes for H_2 production [3, 7]. However, EDTA can prevent the charge recombination process by regenerating RhB$^{\bullet+}$ to RhB (i.e., electron transfer from EDTA to RhB$^{\bullet+}$, reaction (7)), which enables the electron transfer from the TiO$_2$ CB to Pt nanoparticles and, eventually, the production of H_2:

$$\text{RhB}^{\bullet+}-\text{TiO}_2 \left(e_{cb}^-\right) \longrightarrow \text{RhB–TiO}_2 \tag{6}$$

$$\text{EDTA} + \text{RhB}^{\bullet+}-\text{TiO}_2 \left(e_{cb}^-\right)$$
$$\longrightarrow \text{EDTA}^{\bullet+} + \text{RhB–TiO}_2 \left(e_{cb}^-\right) \tag{7}$$

3.3. Mechanism of RhB Degradation.

The stability of dye molecules is an important parameter for the evaluation of dye-sensitized TiO$_2$ systems using expensive synthetic dyes. On the other hand, the degradation of dye during the course of H_2 production should increase the utility of dye-sensitized TiO$_2$ systems if organic dye pollutants are used as a photosensitizer. This is conceptually similar to bifunctional photocatalysis (i.e., the simultaneous production of hydrogen and degradation of pollutants) [20–26].

Figure 4 shows the absorption spectral change (i.e., degradation) of RhB in the suspension of Pt/TiO$_2$ and Pt/TiO$_2$/Nf as a function of irradiation time. In accordance with the absence of H_2 production with Pt/TiO$_2$ at pH_i = 2.3 (Figure 2(a)), the degradation of RhB was negligible (Figure 4(a)). On the other hand, with Pt/TiO$_2$/Nf, the intensity of the RhB absorption spectrum decreased and its position shifted to shorter wavelengths with irradiation time (Figure 4(b)). This result clearly indicates that RhB is degraded with H_2 production in the suspension of Pt/TiO$_2$/Nf.

Some dyes including RhB can be degraded through two pathways: the cleavage of the chromophoric ring and N-dealkylation [29, 38, 39]. Between these pathways, the cleavage of the chromophoric ring is not favored under our experimental conditions (i.e., in the absence of oxygen) because it is primarily initiated by the reaction between reactive oxygen species (e.g., O$_2^{\bullet-}$ and $^\bullet$OH) and RhB$^{\bullet+}$ in the bulk phase [29, 38]. On the other hand, it has been reported that the N-deethylation proceeds through the electron transfer from RhB to the TiO$_2$ CB and subsequent hydrolysis of RhB$^{\bullet+}$ [29], leading to a blue shift of the maximum absorption wavelength (λ_{max}) because N-de-ethylated RhB intermediates exhibit λ_{max} at shorter wavelengths than RhB (λ_{max} = 556 nm) [29, 38]. With Pt/TiO$_2$/Nf, the λ_{max} shifted from 556 to 502 nm after 4 h of visible light irradiation. This significant spectral
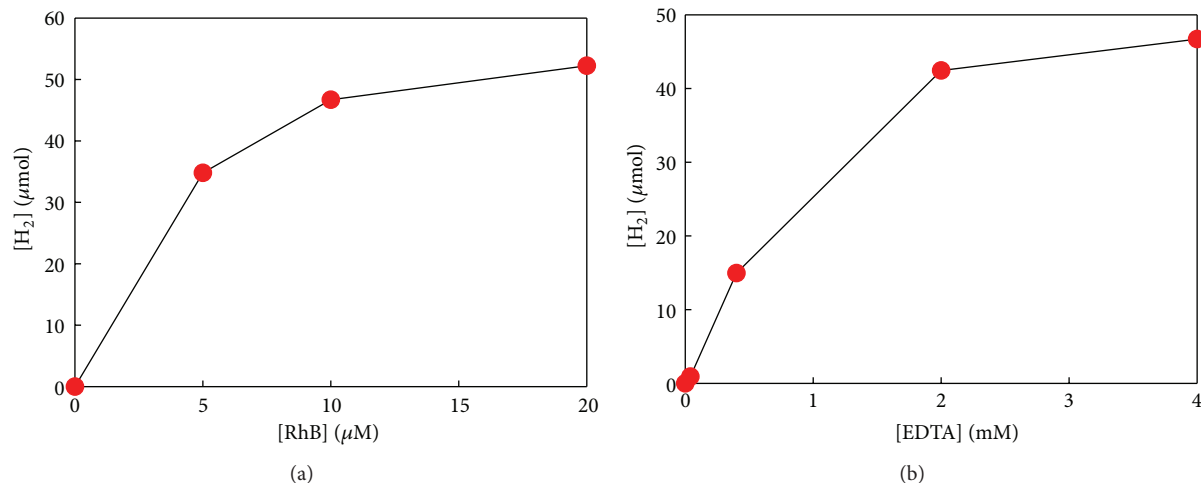
(a)

(b)

FIGURE 3: Time-profiled H_2 production in the suspension of Pt/TiO$_2$/Nf as a function of (a) RhB and (b) EDTA concentration. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [EDTA] = 4 mM (for part (a)), [RhB] = 10 μM (for part (b)), pH$_i$ = 2.3, and λ > 420 nm.
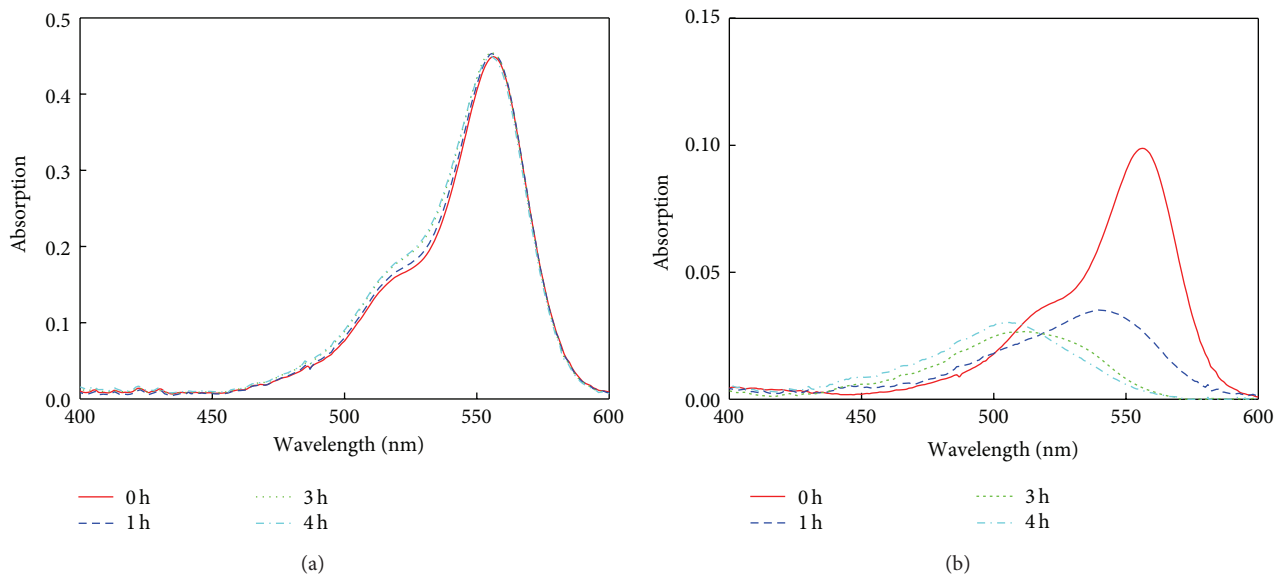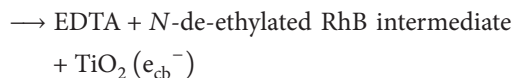

(a)

(b)

FIGURE 4: Absorption spectral change of RhB in the suspension of (a) Pt/TiO$_2$ and (b) Pt/TiO$_2$/Nf as a function of irradiation time. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [RhB] = 20 μM, [EDTA] = 4 mM, pH$_i$ = 2.3, and λ > 420 nm. Samples were diluted by 3 times for the analysis.

shift of $\lambda_{\max}$ ($\Delta\lambda_{\max}$) clearly indicates that the degradation of RhB is primarily initiated by N-deethylation.

RhB was not degraded in the absence of EDTA (data not shown), which implies that EDTA$^{•+}$, not the hydrolysis of RhB$^{•+}$, plays a critical role in the N-deethylation of RhB in our system. This seems to be because the N-deethylation through the hydrolysis of RhB$^{•+}$ is much slower than the reduction of RhB$^{•+}$ by the TiO$_2$ CB electron (see, reaction (6)) in the absence of oxygen. In this situation, the N-deethylation of RhB should be due to the oxidation of RhB (or more preferentially RhB$^{•+}$) by EDTA$^{•+}$ (see, reaction (8)) generated from the oxidation of EDTA by RhB$^{•+}$ (see, reaction (7)):

$$\text{EDTA}^{•+} + \text{RhB}^{•+} - \text{TiO}_2 \left(\text{e}_{cb}^{-}\right)$$

$$\longrightarrow \text{EDTA} + N\text{-de-ethylated RhB intermediate} + \text{TiO}_2 \left(\text{e}_{cb}^{-}\right)$$

(8)

It has been reported that EDTA$^{•+}$ can oxidize N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD), which has electron-donating alkyl groups [40]. Likewise, EDTA$^{•+}$ could react with the ethyl group of RhB$^{•+}$ to generate N-de-ethylated RhB intermediates. It should be noted that RhB is regenerated when RhB$^{•+}$ accepts one electron from the TiO$_2$ CB or EDTA (see, reactions (6) and (7)). However, N-de-ethylated RhB intermediates generated by further oxidation of RhB$^{•+}$ (see, reaction (8)) should not be regenerated to RhB and undergo further degradation.
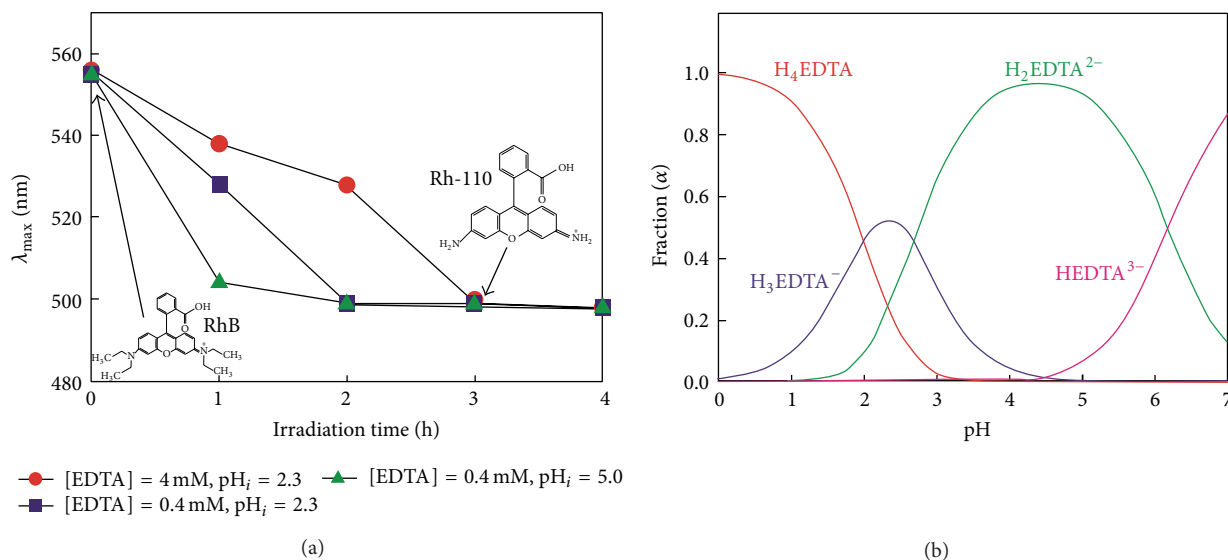
(a)

(b)

FIGURE 5: (a) Spectral shift of $\lambda_{\max}$ depending on [EDTA] and pH_i. (b) Speciation of EDTA depending on pH. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [RhB] = 20 μM, [EDTA] = 4 mM, pH_i = 2.3, and $\lambda > 420$ nm. Samples were diluted by 3 times for the analysis. The stepwise acid dissociation constants ($\text{p}K_a$) of EDTA are $\text{p}K_{a1}$ = 1.99, $\text{p}K_{a2}$ = 2.67, $\text{p}K_{a3}$ = 6.16, and $\text{p}K_{a4}$ = 10.26 [31].

Figure 5(a) shows the spectral shift of $\lambda_{\max}$ depending on [EDTA] and pH_i. In all cases, $\lambda_{\max}$ shifted from 556 to 499 nm and then remained constant. Rh-110 (the fully N-de-ethylated form of RhB) exhibits an absorption maximum at 499 nm [28]. Therefore, the generation of Rh-110 further confirms that RhB is degraded through N-deethylation in the suspension of Pt/TiO$_2$/Nf with EDTA.

The N-deethylation rate, which is proportional to the $\Delta\lambda_{\max}$ rate, was greatly dependent on both [EDTA] and pH_i. The N-deethylation at [EDTA] = 4 mM was slower than that at [EDTA] = 0.4 mM, as the reaction of RhB$^{\bullet+}$ with EDTA (regeneration of RhB, reaction (7)) becomes more favored than that with EDTA$^{\bullet+}$ (N-deethylation of RhB, reaction (8)) as the concentration of EDTA increases. On the other hand, the N-deethylation at pH_i = 5.0 was faster than that at pH_i = 2.3 at the same [EDTA], which is related to the pH-dependent speciation of EDTA. At pH_i = 5.0, EDTA primarily exists as H$_2$EDTA^{2-}, which can be repelled from the negatively charged surface of TiO$_2$ induced by the nafion (Figure 5(b)). On the other hand, H$_4$EDTA and H$_3$EDTA$^-$, which can more favorably approach the negatively charged surface, are the main species at pH_i = 2.3 (Figure 5(b)). Therefore, the concentration of EDTA within the nafion layer at pH_i = 5.0 should be lower than that at pH_i = 2.3 despite the concentration of EDTA added being the same. A lower concentration of EDTA within the nafion layer at higher pH reduces the regeneration of RhB and therefore enhances the degradation of RhB. The lower production of H$_2$ at higher pH (see Figure 2(a)) should also be related to the faster degradation of RhB at higher pH (see Figure 5(a)). The degradation of RhB reduces the number of RhB molecules adsorbed on the surface of Pt/TiO$_2$/Nf and eventually decreases the production of H$_2$. Overall reactions occurring in the suspension

of Pt/TiO$_2$/Nf with RhB and EDTA under visible light are illustrated in Scheme 1.

3.4. Long-Term Experiment. In the suspension of Pt/TiO$_2$/Nf, H$_2$ was continuously produced up to 12 h at [RhB] = 20 μM (0.6 μmol), [EDTA] = 4 mM, and pH_i = 2.3, although the RhB (i.e., absorbance at λ = 556 nm) was completely removed within 4 h (Figure 6). This result implies that not only RhB but also the intermediates generated from the degradation of RhB can act as a photosensitizer. However, the rate of H$_2$ production gradually decreased (9.0 μmol/h for 0–3 h, 6.4 μmol/h for 3–6 h, 3.6 μmol/h for 6–9 h, and 2.3 μmol/h for 9–12 h) as RhB and its intermediates were degraded (Figure 6(a)). The degradation of Rh-110 ($\lambda_{\max}$ = 499 nm) resulting from the complete N-deethylation of RhB proceeded (i.e., the absorbance at λ = 499 nm continuously decreased) after 4 h and was completed after 12 h (Figure 6(b)). In accordance with the complete degradation of RhB and its intermediates after 12 h, the production of H$_2$ stopped after 12 h.

Using Pt/TiO$_2$/Nf under visible light, approximately 70 μmol of H$_2$ was produced and 20 μM (0.6 μmol) of RhB and its intermediates were completely degraded over a 12 h period without the use of external energy or chemical oxidants (Figure 6). Although high concentrations of EDTA (millimolar levels) are required in the RhB-sensitized Pt/TiO$_2$/Nf system for the simultaneous production of H$_2$ and degradation of RhB, many industrial wastewaters (e.g., pulp and paper, textile, and cosmetics wastewaters) contain high concentrations of EDTA [41]. In addition, EDTA can be easily degraded through conventional biological treatment, unlike RhB [42, 43]. Therefore, the application of Pt/TiO$_2$/Nf for the simultaneous production of H$_2$ and degradation of organic dye pollutants could become practicable by using
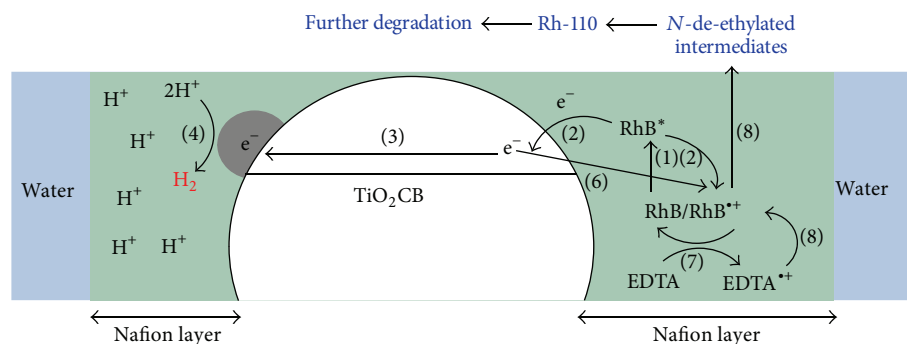
SCHEME 1: Schematic illustration of the simultaneous production of H_2 and degradation of RhB occurring on Pt/TiO$_2$/Nf. (1) excitation of RhB, (2) electron transfer from excited RhB to TiO$_2$ CB with RhB$^{\bullet+}$ generation, (3) electron transfer from TiO$_2$ CB to Pt nanoparticles, (4) reduction of protons (H_2 production), (6) electron transfer from TiO$_2$ CB to RhB$^{\bullet+}$ (charge recombination) with RhB regeneration, (7) electron transfer from EDTA to RhB$^{\bullet+}$ with EDTA$^{\bullet+}$ generation and RhB regeneration, and (8) reaction between RhB$^{\bullet+}$ and EDTA$^{\bullet+}$ (N-deethylation of RhB). The number in parentheses indicates the number of reactions in the text.
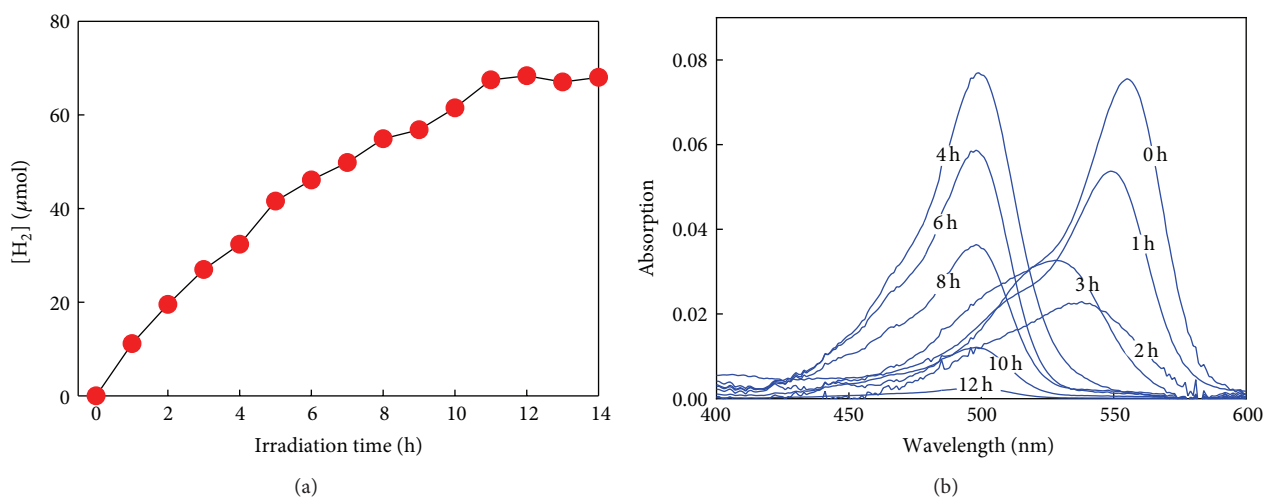

FIGURE 6: Long-term experiment for the simultaneous (a) production of H_2 and (b) degradation of RhB in the suspension of Pt/TiO$_2$/Nf. Experimental conditions: [catalyst] = 0.5 g L^{-1}, [RhB] = 20 μM, [EDTA] = 4 mM, pH$_i$ = 2.3, and λ > 420 nm. Samples were diluted by 3 times for the analysis (for part (b)).

industrial wastewaters containing high concentrations of EDTA.

4. Conclusions

The present study introduces a new strategy for visible-light-induced bifunctional photocatalysis (i.e., the simultaneous production of hydrogen and degradation of pollutants) using TiO$_2$ modified with platinum and nafion (Pt/TiO$_2$/Nf) and organic dye pollutants. In the presence of RhB (as both a photosensitizer and an organic dye pollutant) and EDTA (as an electron donor), Pt/TiO$_2$/Nf exhibited considerably higher activity for H_2 production than Pt/TiO$_2$. This is ascribed to the negatively charged surface of TiO$_2$ induced by the nafion, which enhances the adsorption of cationic RhB and pulls protons, a source of hydrogen, to the surface of TiO$_2$. In addition, the degradation of RhB was accompanied by the concurrent production of H_2. The intensity of the RhB absorption spectrum decreased and its position shifted to shorter wavelengths, which indicates that RhB is primarily degraded through N-deethylation. EDTA$^{\bullet+}$, which is generated from the oxidation of EDTA by RhB$^{\bullet+}$, is found to be involved in the degradation mechanism, as RhB was not degraded in the absence of EDTA. Rh-110, a fully N-de-ethylated form of RhB, was further degraded and the production of H_2 continued until RhB and its intermediates were completely degraded. Based on its high efficiency, bifunctionality, and visible light activity, this organic dye pollutant-sensitized TiO$_2$ system using Pt/TiO$_2$/Nf can be proposed as a viable photocatalytic system for the simultaneous production of hydrogen and degradation of organic dye pollutants.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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