

Evaluation of Reaction Mechanism for Photocatalytic Degradation of Dye with Self-Sensitized TiO₂ under Visible Light Irradiation

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Abstract

The dye-sensitized TiO₂ method is one of the most promising methods for the visible-light-induced detoxification of pollutants. The reaction mechanism for photocatalytic degradation of orange II (OII) and rhodamine B (RhB) with self-sensitized TiO₂ under visible light irradiation ($\lambda > 400$ nm) has been evaluated. Radical scavenger studies were carried out to investigate the active species involved in the photodegradation of 5 mg/L of initial concentration of OII and RhB at room temperature. The trapping effects of different scavengers results proved that the oxidation of OII and RhB mainly occurred by the direct oxidization of h⁺ and $\cdot\text{O}_2^-$ radicals, while the $\cdot\text{OH}$ radicals played only a relatively minor role in the direct oxidization process.

Keywords

TiO₂, Photocatalytic Degradation, Visible Light, Dye-Sensitization, Reaction Mechanism

1. Introduction

The dye-sensitization technique has been reported as an innovative technology that could play an important role in developing efficient and cost-effective semiconductor photocatalyst in the near future [1]. It can extend the light absorption range, enhance photon harvesting efficiency, provide extra excited electron pairs from a dye and accelerate charge transfer, leading to a high efficiency of photoe-

lectric conversion [2]. The photo-sensitized mechanism of the dye-adsorbed TiO_2 under the visible light illumination can be simply expressed as follow: (1) the adsorbed dye is effectively excited to generate the electron/hole pair by the light illumination because of its narrower band gap in comparison with TiO_2 and (2) the photo-excited electrons are injected from the lowest unoccupied molecular orbital (LUMO) of adsorbed dyes into the conduction band (CB) of TiO_2 [3] [4] [5] [6]. Park *et al.* [7] reported that the dye-sensitization can be applied for the self-degradation of dyes. Shang *et al.* [8] studied the photocatalytic degradation of rhodamine B by dye-sensitized TiO_2 under visible-light irradiation. The present study is intended to investigate the photocatalytic degradation reaction mechanism of orange II (OII) and rhodamine B (RhB) with self-sensitized TiO_2 under the visible light irradiation ($\lambda > 400 \text{ nm}$) and the possible mechanism is discussed based on radical trapping experiments.

2. Experimental

2.1. Chemicals and Materials

All reagents were of analytical grade and were used without further purification. Orange II and rhodamine B used in this study were purchased from Nacalai Tesque. Ascorbic acid (AA), ammonium oxalate (AO) and *t*-butyl alcohol (TBA) were obtained from Wako Pure Chemicals. P-25 TiO_2 was purchased from Degussa Co. Ltd. Ultrapure water ($18 \text{ M}\Omega \text{ cm}$) was prepared by an ultrapure water system (Advantec MFS Inc.).

2.2. Photocatalytic Activity and Detection of Reactive Oxygen Species

The photocatalytic activities of TiO_2 were evaluated by the degradation of OII and RhB under visible light irradiation at ambient temperature. Typically, 30 mL of dye solution and 20 mg of photocatalyst were added to a 35 mL Pyrex glass cell. The initial concentration of dye in all experiments was 5 mg/L and the appropriate quantity of the photocatalyst powder was magnetically stirred before and during irradiation. Before irradiation, the photocatalyst suspension containing dye was allowed to equilibrate for 30 min in the dark. The sample solution was irradiated with a LED lamp (TOSHIBA LDA14L-G/100W) in conjunction with a UV cut filter (Y-44, HOYA), which was positioned on the side of the reaction cell. The luminous intensity was measured by a UV radio meter (UD-400, TOPCON TECHNOHOUSE Co., Japan). The light intensity of the LED lamp after the filter was 5.3 mW/cm^2 . After the desired irradiation time, TiO_2 was separated through the $0.45 \mu\text{m}$ Advantec membrane filter. The TiO_2 powder could be almost removed by the filtration. The absorbance of the remnant dye was measured using a UV-visible spectrometry (UV-1650PC, SHIMADZU Co., Tokyo, Japan). The relative concentration (C/C_0) of the OII solution was calculated by the relative absorbance (A/A_0) at 485 nm according to Beer-Lambert law. A_0 and A are the absorbance of the OII solution at the beginning time (t_0) of

visible light irradiation and at time t , respectively. C_0 and C are the concentrations of OII at the beginning of visible light irradiation and at time t , respectively. The photodegradation of RhB (5 mg/L) was similar to that of OII except that the detection wavelength was 554 nm.

Radical scavenger studies were carried out to investigate the active species involved in the photodegradation of dye. The scavenging experiments of reactive oxygen species were similar to the photodegradation experiments. Three scavengers were selected, namely, *t*-butyl alcohol ($\cdot\text{OH}$ radical scavenger), *di*-ammonium oxalate monohydrate (hole scavenger) and ascorbic acid ($\cdot\text{O}_2^-$ radical scavenger). Different quantity of *t*-butyl alcohol, *di*-ammonium oxalate monohydrate [9] and ascorbic acid [10] were added into the dye solution prior to addition of catalysts.

3. Result and Discussion

3.1. Radical Scavenger Studies on TiO_2 Using OII

To determine the possible degradation mechanism of Orange II by TiO_2 , different scavengers were introduced to quench the relevant active species. In this study, *t*-butyl alcohol (TBA), *di*-ammonium oxalate monohydrate (AO) and ascorbic acid (AA) were adopted to be the scavengers of hydroxyl radicals ($\cdot\text{OH}$), superoxide radical ($\cdot\text{O}_2^-$) and holes (h^+), respectively. As shown in **Figure 1**, the photocatalytic degradation efficiency of OII (5 mg/L) with TiO_2 was about 100% after 6 h under visible light irradiation. The photodegradation of OII over the TiO_2 was affected slightly by the addition of TBA, demonstrating that $\cdot\text{OH}$ active species played a small role in the photocatalytic degradation of OII. However, the photocatalytic degradation efficiency of OII decreases significantly in the presence of AA, which indicates that $\cdot\text{O}_2^-$ is an important active species in the process of OII degradation. In addition, the photocatalytic activity of the TiO_2 was completely suppressed by AO, suggesting that h^+ can be also involved in the process of OII degradation.

3.2. Radical Scavenger Studies on TiO_2 Using RhB

In order to investigate the active species involved in photodegrading RhB, scavenger studies were also carried out on TiO_2 . As shown in **Figure 2**, photocatalytic degradation of RhB over TiO_2 was retarded with the presence of di-ammonium oxalate monohydrate (AO) and ascorbic acid (AA). The results strongly indicated that h^+ , and $\cdot\text{O}_2^-$ were the active species involved in the photodegradation of RhB. However, $\cdot\text{O}_2^-$ was more dominant in photodegrading RhB, with h^+ as the most important active species. As aforementioned, the enhanced photocatalytic degradation of MB was contributed by the photosensitizing of RhB toward TiO_2 . The electron ejected from HOMO to conduction band of TiO_2 could have been utilized for the reduction of surface adsorbed oxygen to produced $\cdot\text{O}_2^-$ [11]. The photocatalytic degradation of RhB was retarded most significantly with the presence of AO, conveying that oxidation reaction occurred

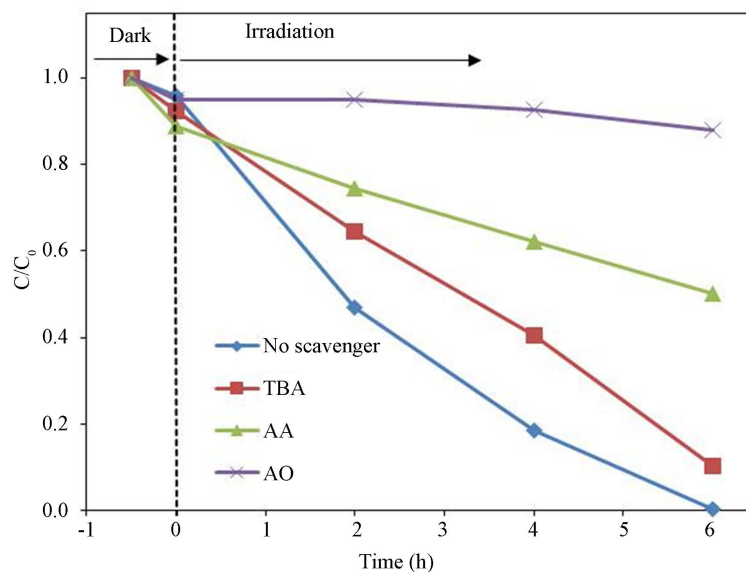


Figure 1. Effects of different radical scavengers on OII degradation in presence of TiO_2 under visible light Irradiation.

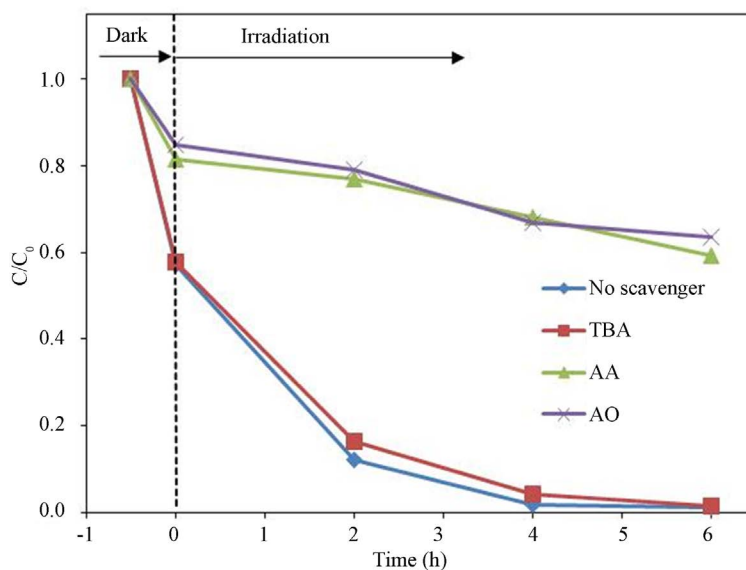


Figure 2. Effects of different radical scavengers on RhB degradation in presence of TiO_2 under visible light irradiation.

mainly via photogenerated holes, not via hydroxyl radical [12]. Therefore, the presence of holes scavenger has decreased the most the photocatalytic degradation of RhB. The presence of TBA had little effect on the decolorization rate, indicating that RhB was almost not degraded by $\cdot\text{OH}$.

3.3. Reaction Mechanism

Figure 3(a) demonstrates the valence band (VB) and conduction band (CB) levels and the band gap energy of orange II and rhodamine B and TiO_2 vs NHE reference electrodes. The energy bands of rhodamine B, orange II and TiO_2

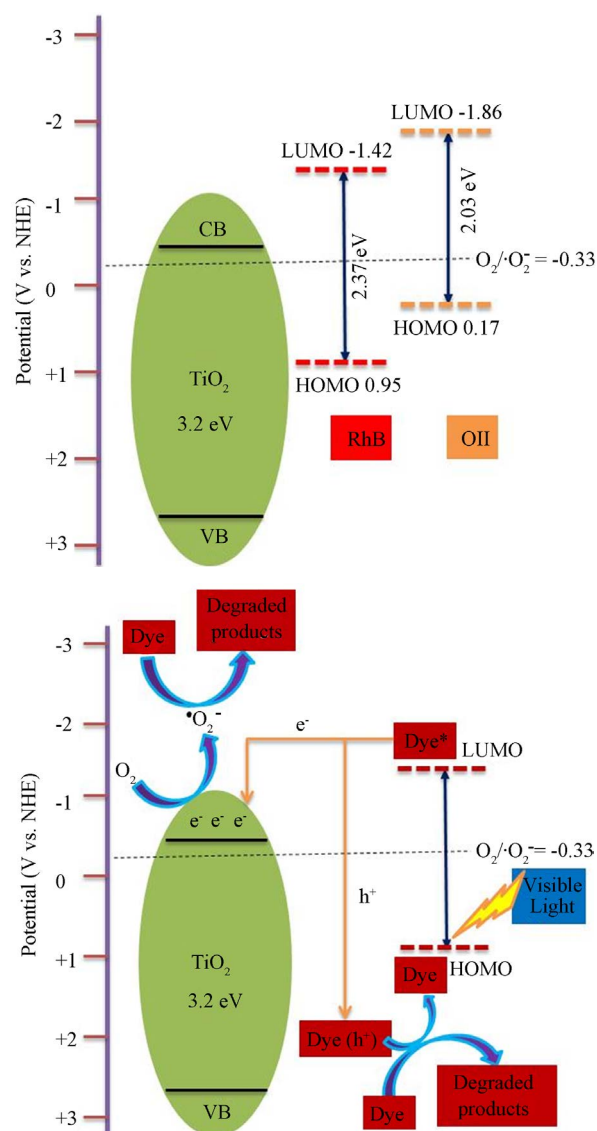
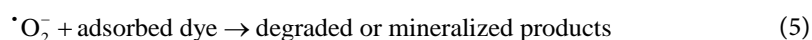
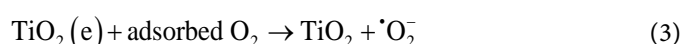
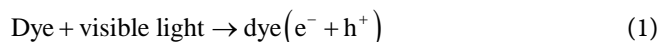


Figure 3. Schematic (a) energy level diagram of TiO₂ with respect to potential of O₂/[•]O₂⁻ and the HOMO-LUMO levels of dye and (b) mechanisms of self-sensitized TiO₂ reaction of superoxide radical ([•]O₂⁻) and holes (h⁺) formation under visible light irradiation.

are 2.37 [13], 2.03 [14] and 3.2 eV [13], respectively. The band gap energies of orange II and rhodamine B are narrow enough to absorb visible light. Otherwise, as the more negative potential of OII and RhB lowest unoccupied molecular orbital (LUMO) level than the conduction band (CB) of TiO₂ [13] [14], the electron transfer from the LUMO of dyes to the CB of TiO₂ is feasible. It is reported the redox potential of O₂/[•]O₂⁻ is -0.33 V vs NHE [15], which is less negative than conduction band potential of TiO₂ (-0.5 V vs NHE) [16].

Under visible light irradiation, a dye sensitized mechanism has been depicted in **Figure 3(b)**. Upon irradiation of visible light, a dye absorbs the light to create an electron and hole in the conduction and valence bands (LUMO and HOMO)

of the dye [17]. The electron in the LUMO then transfers to the CB of TiO₂. The adsorbed molecular oxygen on the catalyst captures electron from the CB of TiO₂ to form $\cdot\text{O}_2^-$. The oxidant ($\cdot\text{O}_2^-$) radical reacts with adsorbed dye to degrade it. The holes in the HOMO react with adsorbed OH⁻ species to form $\cdot\text{OH}$ radical. However, the formation channel to $\cdot\text{OH}$ is minor under visible light [17], which is similar with the result shown in **Figure 1** and **Figure 2**. According to the results of the radical scavengers, OII and RhB were attacked by the super oxides, $\cdot\text{O}_2^-$ and holes, h^+ for the degradation of dye. A possible degradation reaction mechanism is described below.



4. Conclusion

The radical scavenger studies were carried out to investigate the active species involved in the photodegradation of orange II and rhodamine B with self-sensitized TiO₂ under the visible light irradiation ($\lambda > 400$ nm). Investigation of the photocatalytic mechanism showed that the TiO₂ self-sensitized degradation of OII and RhB under visible-light irradiation could be mainly attributed to the direct oxidization by h^+ and $\cdot\text{O}_2^-$ radicals, while the $\cdot\text{OH}$ radicals played only a relatively minor role in the direct oxidization process. The present work may provide deep insight into the photosensitization induced photocatalytic mechanism, and also offer new opportunities for their industrial application in the elimination of dye pollutants from wastewater.

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