

Enhanced Photocatalytic Activity of 3,4,9,10-Perylenetetracarboxylic Diimide Modified Titanium Dioxide Under Visible Light Irradiation

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Received August 9, 2010, Accepted August 18, 2010

A method to improve the photocatalytic activity of titanium dioxide by modification with a sensitizer and a metal oxide is proposed. To achieve this goal, we used metal oxides as dopants. In particular, CaWO₄ and Gd₂O₂S:Tb were used because their 2.6 eV and 2.2 eV band gap energy and optical properties have a large positive effect on photocatalysis. The improvement in the photocatalytic activity of TiO₂ modified with Gd₂O₂S:Tb under ultraviolet light irradiation is described in a previous study. The present work focuses on the sensitization of metal oxide-modified TiO₂. Having observed the ultraviolet-visible absorption spectra of 3,4,9,10-Perylenetetracarboxylic diimide in the wide visible-light region from 400 nm to 650 nm and the broad peaks in its photoluminescence spectra at 695 nm and 717 nm, we decided to use this perylene dye to sensitize modified TiO₂ to enhance its activity as a visible-light harvesting photocatalyst. We also explored the positive effects thin-film surface changes stemming from ultraviolet pre-treatment have on photocatalytic activity. Finally, we subjected several metal oxide-modified TiO₂ products sensitized by the perylene dye to ultraviolet pre-treatment, obtaining the most active photocatalysts.

Key Words: Titanium dioxide, TiO₂, Photocatalyst, Sensitizer, 3,4,9,10-Perylenetetracarboxylic diimide

Introduction

With increasing calls for a cleaner environment, photocatalytic applications used by industry are attracting renewed interest. For example, many concerned scientists see decomposition of organic pollutants by photocatalysis as one way to achieve the goal of an eco-friendly economy. And another advantage of photocatalytic technology is that it can be very cost effective because sunlight can be used as an energy source.¹⁻⁵

Semiconductor materials, such as TiO₂, ZnO, SnO₂, CdS, GaP, and WO₃, are applied in photocatalysis. Among them, TiO₂ is the most popular for this purpose because it is nontoxic, chemically stable, inexpensive, and very efficient. In fact, TiO₂ photocatalysts are frequently employed in environmental clean-ups. However, their photocatalytic activity is restricted by the wide band gap of TiO₂ (3.03 eV for rutile and 3.18 eV for anatase) and fast electron-hole recombination.⁶⁻⁹ TiO₂ can absorb only about 3% - 4% of solar light in the ultraviolet, or UV, region. To increase the amount of visible light (to about 45%) TiO₂ absorbs from the sun, researchers are working on the development of TiO₂ visible-light harvesting photocatalysts.¹⁰

The visible-light sensitivity of TiO_{2-x}N_x is a result of the narrowing of the band gap by mixing the 2p states of nitrogen and 2p states of oxygen.^{5,11} In semiconductor photocatalysis the visible or UV light forms electrons and holes in the semiconductor material, which are essential to the catalytic reactions. We investigated metal-oxide doping because of its ability to narrow the band gap. Under UV light irradiation, the photocatalytic activity of metal oxide-modified TiO₂, or TiO₂/metal oxide, was 13% - 35 % higher than that of TiO₂ (P25) under UV light irradiation; however, the activity was still low under visible light (≥ 400 nm) irradiation. This makes practical use difficult. We addressed these drawbacks by sensitizing TiO₂/

metal oxide to obtain a visible-light harvesting photocatalyst. The fluorescent dye 3,4,9,10-Perylenetetracarboxylic diimide or PTCDI was used as the sensitizer because of its high thermal stability and photostability. PTCDI is used extensively as an industrial pigment, and its derivatives are effective n-type organic semiconductors with various applications. For example, they are used as tunable laser dyes, light-harvesting materials, transistors, solar cells, and optoelectronic devices, such as light-emitting diodes, because of their unique optical and electrochemical properties.^{12,13}

In the present work, we report the enhanced photocatalytic activity under visible-light irradiation of metal oxide-modified TiO₂ sensitized with PTCDI. We also propose an efficient method for the preparation of photocatalyst thin film.

Experimental

Material. Titanium dioxide powder (Degussa, P25) was used as the photocatalyst base material. It was composed of 80% anatase and 20% rutile, with a specific surface area of BET 60 ± 5 m²g⁻¹. The metal oxides were Ag₂O, CaWO₄, Fe₂O₃ (Aldrich Co., USA; analytic reagent grade), and Gd₂O₂S:Tb. 3,4,9,10-Perylenetetracarboxylic diimide (Tokyo Chemical Industry Co., first grade reagent) was used as the sensitizer. Ethanol (Wako Chemical, USA) was used as the dispersion medium. The thin-film substrate was a petri dish (8.6 cm \times 1.7 cm). Methylene blue and formaldehyde (Aldrich Co., first grade reagent) were used as is. Water-borne polyurethane dispersion (SamMyung Biochem Co., Korea, pH 7, M.W 8000, MTU-06) was used as binder.

We used a furnace (Muffle-1125, Dongyang Science Co.) to prepare the TiO₂/metal oxide. The thin films were prepared by spray coating (NCF 035CC, Air Maker, Korea) under a pre-

ssure of 7 bar. The specific surface area was measured by BET (ASAP 2020, Micromeritics Ins., USA). The absorbance of methylene blue was investigated by ultraviolet-visible, or UV-vis, spectrophotometry (DT 1000 CE, Ocean optics Inc., USA), and the decomposition rate of the formaldehyde was measured by gas chromatography (HP 6890 Series, USA).

Sensitization of TiO₂ thin films. 0.013 g of PTCDI was added to TiO₂ and a Vortex mixer was used to mix them for 5 minutes. At this point the specific surface area ratio of the PTCDI to TiO₂ was BET 5% - 10%. Distilled water (60 mL) as solvent was added to the mixture, which was stirred at room temperature for 16 hrs. The water was removed by drying the mixture for 22 hr in an oven (HST501VS, HST Co.) at 120 °C. Preparation of the TiO₂/metal oxide was according to our previous study,¹⁴ with 0.005 g of metal oxide added to 0.04 g (5×10^{-4} mol) of TiO₂. Using the identical procedure described above, we sensitized the TiO₂/metal oxide and calcinated it at 400 °C for 45 minutes.

Ethanol (15 mL) was added to each of the powder mixtures as a dispersant and then water-born polyurethane was added to the dispersed solutions, after which they were sonicated for 1 hr. The water-born polyurethane acted as a binder, immobilizing TiO₂ particles and preventing the degradation of photocatalytic potential. Thin films were prepared from the dispersed solutions by a spray coating technique.

Photocatalytic activity measurements. The photocatalytic activity of each sample, including the PTCDI-modified TiO₂, was determined by the change in absorbance. The change in absorbance was determined by measuring the percent of decoloration of aqueous methylene blue solution by photocatalysis. The photocatalyst thin films were coated with 40 μM of aqueous methylene blue solution and placed under a UV cut-off filter (N-169 (400 nm ≤)). Visible light was irradiated with two fluorescent light lamps (20 W, ≥ 380 nm, 9 W/m²) placed at a distance of 20 cm. During a 5-hr period, we took absorbance measurements once an hour. The photodegradation of formaldehyde was measured by the method described earlier.¹⁴ We added 0.1 M formaldehyde to the photocatalyst thin films and measured its decomposition rate during a 2-hr period of visible-light irradiation.

Characterization of thin film transmittance and photocatalytic activity. Photocatalytic activity and transmittance were measured for each of the thin-film coatings, which were numbered from 1 through 20. The measurements, by UV-vis spectrophotometry, discolored the methylene blue.

Characterization of UV pre-treatment effect. UV pre-treatment was started when the photocatalytic activity was at its highest level. An earlier investigation of 5 hr through 28 hr of activity showed the 16th hr to be optimum. UV pre-treatment was carried out using two black lamps (Sankyo denki black light blue (20 W, 352 nm, 16 W/m²)) placed at a distance of 15 cm.

Characterization of photoluminescence. Measurement of the photoluminescence of the sensitizer-modified TiO₂/metal oxide was performed as described previously.¹⁴

Results and Discussion

Absorption spectrum of 3,4,9,10-perylenetetracarboxylic

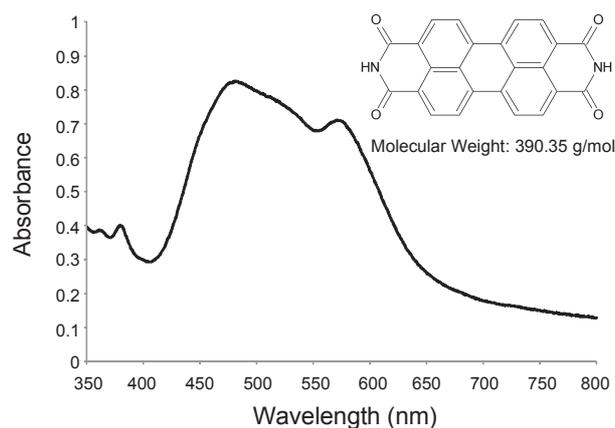


Figure 1. The chemical structure and UV-vis spectrum of 3,4,9,10-perylenetetracarboxylic diimide.

diimide. The level of photocatalytic activity of a photocatalyst depends on the number of excited electrons created by the energy supplied. If the intensity of the supplied energy equals an intensity within the visible-light region, the photocatalyst might be active under visible-light irradiation. Sensitization can improve performance by expanding photocatalytic activity to the visible-light region. The chemical structure and UV-vis spectra of the sensitizer, PTCDI, are shown in Figure 1. Since the UV-vis absorption spectra of PTCDI are in the wide visible-light region (400 nm - 650 nm), we expected sensitization to enhance the activity of visible-light harvesting photocatalysts. Moreover, PTCDI displays a high degree of photostability, making it even more effective.

Thin film transmittance and methylene blue decoloration rate.

The most important consideration in the preparation of photocatalyst thin films is how to efficiently optimized the photocatalytic activity. Although TiO₂ photocatalyst powders have identical properties, significant differences in photocatalytic activity arise among them because of variations in the amount of TiO₂ dispersed in solution or the thickness of their thin films. Various methods are used to prepare thin films, including spray coating, dip coating and spin coating. In the present study, we used spray coating, because it is effective regardless of the characteristics of the thin-film substrate. A coating speed of 2.0 ± 0.05 cm/sec was adhered to as closely as possible. Figure 2 confirms that this coating technique optimized the thin-film photocatalytic activity.

Although binder in the dispersed solution decreased thin-film transmittance, the decoloration rate of methylene blue indicates that photocatalytic activity did increased (Figure 2). This result is explained by the fact that photocatalysis occurs at the surface of the thin films. Increasing the number of coatings enhances photocatalytic activity because of the dense distribution of photocatalyst particles (Figure 3). But, excessive coating number cause the disturbance of photocatalytic activity by increased binder amount. For the reason, Eight coatings showed the highest methylene-blue decoloration rate, and this number maintained the transmittance of the thin films at more than 85%.

UV pre-treatment effect. The degree of unsaturation of surface bonds effects the photohydrophilicity of thin films. UV irradiation can produce hydroxyl groups, promoting photo-

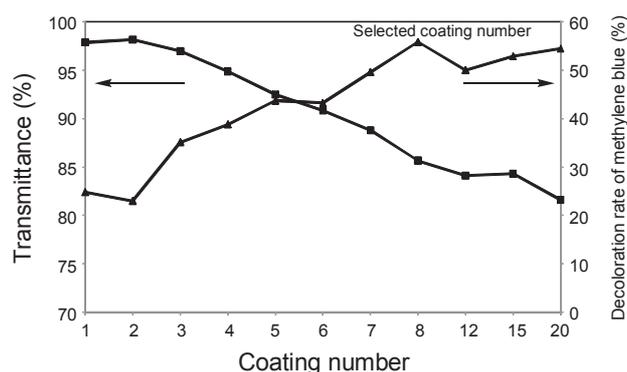


Figure 2. Relations with thin film transmittance and decoloration rate of methylene blue. Increasing the number of coating, decoloration rate of methylene blue means photocatalytic activity increase to a certain portion compared with decreased transmittance of thin film.

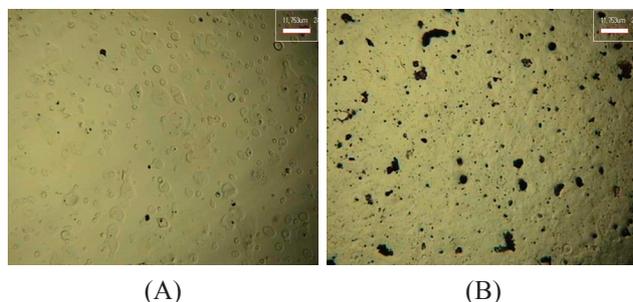


Figure 3. Micrograph of thin film surface (Video microscope (SV-35, Sometech Co. ($\times 600$))). (A) Characterized TiO₂ thin film with coating number 1, (B) Characterized TiO₂ thin film with coating number 8. Increasing the number of coating, distribution of the TiO₂ photocatalysts particles is densely packed.

hydrophilicity. This change on the thin-film surface increases the number of water molecules absorbed on the surface. The UV-vis spectra, which shifted to the shorter wavelength after UV irradiation, indicated the photohydrophilicity of the TiO₂ thin films.¹⁵ This confirmed the positive effect UV pre-treatment

had on photocatalytic activity. Also, the increased rate of decoloration of methylene blue by UV pre-treatment of the TiO₂/metal oxide thin films was confirmed, showing that UV pre-treatment improved their photocatalytic activity. For TiO₂ (P25), the decoloration of methylene blue increased by 24.26 percentage points, from 4.88% to 29.14% as a result of UV pre-treatment. And the photocatalytic activity of the other TiO₂/metal oxide thin films increased by 4.70 - 9.06 percentage points (Table 1). The activity of the PTCDI-modified TiO₂ increased by 4.77 percentage points, from 36.73% to 41.50% as a result of UV pre-treatment. And UV pre-treatment increased the activity of the PTCDI-modified TiO₂/metal oxide by 4.70 - 14.20 percentage points (Table 2). However, after UV light irradiation, the photocatalytic activity of the TiO₂/Gd₂O₂S:Tb decreased despite PTCDI modification. Perhaps, this phenomenon can be explained by the disturbance created between alternations in the characteristics of the thin-film surface and the transition of an electron from ⁵D₃ state to the conduction band or to the ⁵D₄ level in the identical anionic environments of the Tb³⁺ ion.¹⁴ Further theoretical study is necessary to elucidate the reason for the lower photocatalytic activity of TiO₂/Gd₂O₂S:Tb after UV pre-treatment.

Photodecoloration of methylene blue solution. Before measuring photocatalytic activity, we compared the initial absorbance of the aqueous methylene blue solution with its final absorbance after photocatalysis. Next, we compared the results of the photodecoloration rate of methylene blue (%) shown in Table 1 and Table 2. Table 1 shows the photocatalytic activity of TiO₂ (P25) and TiO₂/metal oxide. TiO₂ (P25) was nearly photocatalytically inactive, but the activity of TiO₂/metal oxide increased by 23.35 - 46.47 percentage points under visible light. In particular, because of their lower band gap energy (2.6 eV and 2.2 eV) CaWO₄ and Gd₂O₂S:Tb showed increased photocatalytic activity compared with the other metal oxides. In addition, the behavior of Gd₂O₂S:Tb was greatly influenced by its optical properties, such as the transition of an electron from the ⁵D₃ state to the conduction band or to the ⁵D₄ level in the identical anionic environments of the Tb³⁺ ion. Table 2 shows the photocatalytic activity of TiO₂ sensitized with PTCDI.

Table 1. Confirmation of the UV pre-treatment effect on metal-oxide modified TiO₂ thin film

Sample	Non UV pre-treatment			UV pre-treatment	
	Photodecoloration of MB by visible light absorption (%)	1st order rate constant for photodecoloration of MB (%)	Photocatalytic degradation of formaldehyde by GC (%)	Photodecoloration of MB by visible light absorption (%)	1st order rate constant for photodecoloration of MB (%)
TiO ₂ (P25)	4.88 ^a	1.03 ^b	2.29 ^c	29.14 ^a	6.69 ^b
TiO ₂ /Ag ₂ O	+ 23.352 28.23 ± 0.41 ^a	+ 5.522 6.55 ± 0.32 ^b	+ 19.173 21.46 ^c	+ 8.155 37.29 ± 0.17 ^a	+ 2.114 8.80 ± 0.23 ^b
TiO ₂ /Fe ₂ O ₃	+ 29.257 34.13 ± 0.27 ^a	+ 7.483 8.51 ± 0.26 ^b	+ 16.568 18.85 ^c	+ 10.029 39.16 ± 0.21 ^a	+ 2.537 9.22 ± 0.26 ^b
TiO ₂ /CaWO ₄	+ 39.541 44.42 ± 0.18 ^a	+ 10.582 11.61 ± 0.21 ^b	+ 11.872 14.09 ^c	+ 19.984 49.12 ± 0.32 ^a	+ 5.913 12.60 ± 0.30 ^b
TiO ₂ /Gd ₂ O ₂ S:Tb	+ 46.473 51.35 ± 0.34 ^a	+ 11.249 12.27 ± 0.23 ^b	+ 31.834 34.09 ^c	+ 14.144 43.28 ± 0.29 ^a	+ 3.586 10.27 ± 0.35 ^b

^aDecrease in concentration (%), ^bRate constant ($\times 10^{-2}$ M hr⁻¹), ^cPercentage of photocatalytic degradation (%).

Table 2. The enhanced photocatalytic activity of metal-oxide modified TiO₂ after sensitization with 3,4,9,10-perylenetetracarboxylic diimide and confirmation of the UV pre-treatment effect

Sample	Non UV pre-treatment			UV pre-treatment	
	Photodecoloration of MB by visible light absorption (%)	1st order rate constant for photodecoloration of MB (%)	Photocatalytic degradation of formaldehyde by GC (%)	Photodecoloration of MB by visible light absorption (%)	1st order rate constant for photodecoloration of MB (%)
TiO ₂ (P25)	36.73 ± 0.35 ^a	8.74 ^b	20.57 ^c	41.50 ± 0.14 ^a	10.50 ^b
TiO ₂ /Ag ₂ O	+ 16.032 52.76 ± 0.43 ^a	+ 6.542 15.28 ± 0.24 ^b	+ 9.859 30.42 ^c	+ 25.461 66.96 ± 0.16 ^a	+ 10.352 20.85 ± 0.32 ^b
TiO ₂ /Fe ₂ O ₃	+ 17.876 54.60 ± 0.27 ^a	+ 7.441 16.18 ± 0.18 ^b	+ 4.873 25.44 ^c	+ 23.728 65.22 ± 0.30 ^a	+ 9.313 19.81 ± 0.41 ^b
TiO ₂ /CaWO ₄	+ 13.471 50.20 ± 0.18 ^a	+ 4.09 12.83 ± 0.19 ^b	+ 23.701 44.27 ^c	+ 13.406 54.90 ± 0.26 ^a	+ 3.349 13.84 ± 0.21 ^b
TiO ₂ /Gd ₂ O ₂ S:Tb	+ 22.290 59.02 ± 0.31 ^a	+ 8.10 16.84 ± 0.29 ^b	+19.255 39.82 ^c	+ 8.957 50.45 ± 0.26 ^a	+ 2.374 12.87 ± 0.22 ^b

^aDecrease in concentration (%), ^bRate constant ($\times 10^{-2}$ M hr⁻¹), ^cPercentage of photocatalytic degradation (%).

Compared with Table 1, the photocatalytic activity of PTCDI-modified TiO₂ is 31.85 percentage points higher than that of TiO₂ (P25). Furthermore, the activity of PTCDI-modified TiO₂/metal oxide increased by 7.67% - 24.53% compared with that of TiO₂/metal oxide. These results represent an improvement in photocatalytic activity through PTCDI and metal-oxide modification. The UV-vis absorption spectra with PTCDI as sensitizer were observed in the wide visible-light region, and PTCDI properties, such as high fluorescence quantum yields in solution ($\Phi_F \geq 95\%$), chemical inertness, and photochemical stability, had a positive influence on photocatalytic activity.¹⁶

Kinetics of photodecoloration for methylene blue through the 1st order rate constant. Table 1 and Table 2 give the first-order rate constants for the photodecoloration of methylene blue. These results were obtained by calculating the correlation between the length of time of visible-light irradiation and the decreasing ratio of methylene blue. This correlation is described with the following equation, using the first-order rate constant (k)

$$-k = \ln(C/C_0) / (t - t_0) \quad (1)$$

C₀ is the initial concentration of methylene blue solution and C is its concentration after photocatalysis. t - t₀ is the time for photocatalysis to proceed. The first-order rate constant (k) shows a linear relationship with the photodecoloration of methylene blue solution. This shows that the photocatalysis rate varies with the type of prepared thin film. In the case of non UV-pre-treatment, each of the first-order rate constants of PTCDI-modified TiO₂ and PTCDI-modified TiO₂/metal oxide increased 8.74 - 16.84 ± 0.29 × 10⁻² M hr⁻¹ more than the rate constants of TiO₂ (P25) and TiO₂/metal oxide increased, which was 1.03 - 12.27 ± 0.23 × 10⁻² M hr⁻¹. And, the first-order rate constants of the UV pre-treated thin films showed more improvement than the constants of the non UV pre-treated thin films regardless of PTCDI sensitization. Finally, the present work shows that among the several metal oxides studied, TiO₂/metal oxide pre-treated with UV and sensitized with PTCDI was the kinetically

superior photocatalyst.

Photodegradation of formaldehyde. The photodegradation of formaldehyde was studied with reference to the "sick house syndrome," a phrase used to describe a situation in which the residents of a house become ill and their illness is linked to the house's air quality. Formaldehyde is often cited as one cause of such a malaise.

Our investigation was performed in the dark because of the low photostability of formaldehyde. The decomposition rates of formaldehyde were measured by gas chromatography. In the procedure, 13.2 M aqueous formaldehyde was diluted to 0.1 M followed by photocatalytic degradation for 2 hrs under visible-light irradiation. Table 1 shows the effect of UV pre-treatment. The photodegradation of formaldehyde with TiO₂ (P25) is negligible, 2.29%. Photodegradation with TiO₂/metal oxide is 11.8% - 31.8% higher than with TiO₂ (P25). Sensitization of TiO₂ (P25) with PTCDI increases photocatalytic degradation with TiO₂ (P25) from 2.29% (Table 1) to 20.57% (Table 2), confirming the sensitizer effect. The photocatalytic activity of PTCDI-modified TiO₂/metal oxide is 5.73% - 30.18% higher than that of TiO₂/metal oxide. These results show different tendencies with respect to the decoloration of methylene blue, but improved photocatalytic activity with CaWO₄, Gd₂O₂S:Tb, and PTCDI is confirmed.

Photoluminescence spectra of sensitizer-modified TiO₂ powders. Figure 4 shows the photoluminescence spectra of TiO₂/Gd₂O₂S:Tb and PTCDI-modified TiO₂ under excitation at 254 nm. Definitions and the correlation of the photocatalytic activity of TiO₂/Gd₂O₂S:Tb with its photoluminescence spectra are given in the previous study.¹⁴ The peak of the photoluminescence spectra of TiO₂ (P25) is located near 490 nm; the PTCDI peak, including the lower shoulder peak, is located near 695 nm. The detected emission peak in the longer wavelength corresponds to the vibration modes in PTCDI (~1340 - 1790 cm⁻¹). This means PTCDI modification was carried out successfully and it enhanced photocatalytic activity.¹⁷ The shape of the photoluminescence spectrum of PTCDI is very similar to the shape of the UV-vis spectrum. The main peak and lower shoulder peak

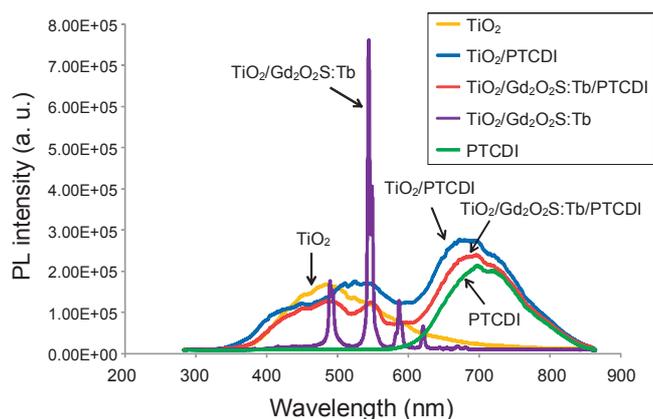


Figure 4. Photoluminescence spectra of TiO₂ (P25)/3,4,9,10-perylene-tetracarboxylic diimide modified TiO₂/3,4,9,10-perylenetetracarboxylic diimide and Gd₂O₂S:Tb modified TiO₂/Gd₂O₂S:Tb modified TiO₂/3,4,9,10-perylenetetracarboxylic diimide (PTCDI) (T = R.T., s.r = 10 sec⁻¹).

of the photoluminescence spectra of PTCDI-modified TiO₂ were detected at 695 nm and 717 nm by comparing the PTCDI spectra with that of TiO₂ (P25). This means that PTCDI-modified TiO₂ absorbs visible light and emits light in the longer wavelength of 695 nm. This shows that its photocatalytic activity as a visible-light harvesting photocatalyst improved. In the photoluminescence spectra of PTCDI-modified TiO₂/Gd₂O₂S:Tb, the PTCDI peak is high near 695 nm compared with that of TiO₂/Gd₂O₂S:Tb, which is nearly flat. Furthermore, the photoluminescence spectra of PTCDI-modified TiO₂/Gd₂O₂S:Tb include a peak at 480 nm and at 545 nm. The highest photocatalytic activity (59.02 ± 0.31%, Table 2) shows the modifying effect of PTCDI and Gd₂O₂S:Tb. Overall, the results in Table 2 show that photocatalytic activity can be greatly increased by PTCDI and metal oxide.

Conclusions

We have shown here that TiO₂ sensitized with the dye 3,4,9,10-Perylenetetracarboxylic diimide out performs TiO₂ (Degussa, P25) in photocatalytic activity and also acts as a visible-light harvesting photocatalyst.

The case of TiO₂ modified with Gd₂O₂S:Tb and then further modified with 3,4,9,10-Perylenetetracarboxylic diimide illustrates the gains in photocatalytic activity achieved by this process. This study points the way to the commercialization of a light-harvesting photocatalyst through a thin film optimized for photocatalytic activity and transmittance.

The UV-vis absorption spectra of PTCDI were observed in

the wide visible-light region (400 nm - 650 nm). Its main peak and lower shoulder peak were observed at 695 nm and 717 nm in the photoluminescence spectra. These results support our conclusion that PTCDI improves the photocatalytic activity of semiconductor materials, resulting in a visible-light harvesting photocatalyst. Also, we confirmed that UV pre-treatment enhances photocatalytic activity. UV pre-treatment caused drastic changes on the thin film surface, subsequent to which the thin film exhibited super hydrophilicity, a property that has a large positive effect on photocatalytic activity. However, in one case that deviated from the observed trend, the activity of the Gd₂O₂S:Tb-modified TiO₂ decreased after UV light irradiation. Perhaps, this is related to disturbances created by the interaction between characteristic changes in the thin film surface and the optical properties of Gd₂O₂S:Tb. Further study is needed to explain this apparent anomaly.

Acknowledgments. The author would like to thank KAST (Kanagawa Academy of Science and Technology) photocatalyst laboratory researcher for help and guidance during 2010.01.18 - 2010.01.29 and also much useful information.

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