

High Photocatalytic Activity of $\text{Gd}_2\text{O}_2\text{S:Tb}$ Modified Titanium Dioxide Films

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Fe_2O_3 , Ag_2O , CaWO_4 and $\text{Gd}_2\text{O}_2\text{S:Tb}$ loaded on titanium dioxide photocatalysts (P25, Degussa) were prepared by a calcination. Their composite films containing water-born polyurethane used as a material for immobilization were obtained by spray coating technique. The photocatalytic activity of the titanium dioxide films was characterized by decrease of UV-vis absorption spectra for methylene blue and gas chromatography for photocatalytic decomposition of formaldehyde diluted in water. It was shown that the $\text{Gd}_2\text{O}_2\text{S:Tb}$ modified titanium dioxide films had good photocatalytic properties and followed the first-order kinetic model with regard to photocatalytic decoloration of methylene blue. Especially in formaldehyde photodegradation experiment, decrease rate of concentration of the titanium dioxide films with $\text{Gd}_2\text{O}_2\text{S:Tb}$ modifying was about 35% larger than that of the unloaded titanium dioxide film.

Key Words: Titanium dioxide, $\text{Gd}_2\text{O}_2\text{S:Tb}$, Photocatalysts, PL

Introduction

One of the limiting factors that control the efficiency of photocatalysis in TiO_2 is the quick recombination within nanosecond between photoinduced charge carriers in semiconductor particulate system. Efforts have been made by several researchers to retard such a recombination of holes and electrons within the semiconductor particle and promote heterogeneous charge transfer at the semiconductor surface.^{1,2} Such efforts have included surface modification of the semiconductor with a noble metal or an oxide and simultaneous scavenging of holes and electrons by adsorbed redox species. Another interesting approach for achieving efficiency charge separation involves the coupling of two semiconductor particles with different energy levels. For example, in a semiconductor-titanium dioxide system a photogenerated electron can be transferred from a semiconductor into a titanium dioxide particle while the holes remain in the other semiconductor particle. The difference in energy levels of two semiconductor systems plays an important role in achieving such a charge separation.^{3,4}

Recently the essential subject to be resolved is the improvement in the efficiency of photocatalytic reaction. Some researches led to the enhancement in the efficiency of photocatalytic reduction. For example, the best results in the photocatalytic phenol degradation were obtained for dopant-free TiO_2 , Li(I)/TiO_2 , Zn(II)/TiO_2 and Pt/TiO_2 . However, in addition of ions Co(III) , Cr(III) , Mn(II) , Al(III) and Fe(III) in titanium dioxide films significantly lowered photocatalyst activity.⁵ It was well known that the incorporation of metal ions into titanium dioxide crystal lattice can significantly extend the absorption by the photocatalysts in visible region.^{6,7} Consequently, another disadvantage of the high band gap energy (3.2 eV) in titanium dioxide photocatalyst should be overcome its wide application in the visible light range. The applications of lanthanide or rare earth metal ions doped titanium dioxide photocatalysts were reported newly.⁸⁻¹⁰ This

interest is mainly due to their optical properties that affect emission lifetime, structure of emission spectra, luminescence quantum efficiency and concentration quenching.

In this paper, we have used a calcination with TiO_2 (P25) powder and synthetic terbium-activated oxysulfide of gadolinium ($\text{Gd}_2\text{O}_2\text{S:Tb}$) as X-ray luminophor, which has allowed us to obtain new photocatalysts that can be modified on their surface.^{11,12} And their composite films containing water-born polyurethane used as a material for immobilization were obtained by spray coating technique. Thus, in our case the term modifying should be considered as describing other locations of emissive ions as well, most likely bound to the capping ligands or absorbed on the photocatalytic surface. It was reported by Amiryan et al. that emission spectrum of $\text{Gd}_2\text{O}_2\text{S:Tb}$ is determined by the transitions of electrons from an upper ($^5\text{D}_3$) and a lower ($^5\text{D}_4$) excited level to the level of the multiplet term ^7F as a result of resonance (cross relaxation) interaction between the $^5\text{D}_3 \rightarrow ^5\text{D}_4$ and $^7\text{F}_6 \rightarrow ^7\text{F}_0$.¹³ To our knowledge, so far there were no reports on photocatalytic activity of $\text{Gd}_2\text{O}_2\text{S:Tb}$ modified titanium dioxide films. Herein, we report on photocatalytic activity of $\text{Gd}_2\text{O}_2\text{S:Tb/TiO}_2$ films in terms of decoloration of methylene blue and photodegradation of formaldehyde in aqueous solution.

Experimental

Materials. Titanium dioxide powder P25, obtained by Degussa Corp. is composed of 70% anatase and 30% rutile with a surface area of $50 \pm 5 \text{ m}^2\text{g}^{-1}$. The modified titanium dioxide samples containing Fe_2O_3 , Ag_2O , CaWO_4 (Aldrich Co. analytic reagent grade) and $\text{Gd}_2\text{O}_2\text{S:Tb}$ were prepared by a calcination. Terbium-activated oxysulfide of gadolinium ($\text{Gd}_2\text{O}_2\text{S:Tb}$) was synthesized as described.¹⁴ After Gd_2O_3 (5 g, 0.014 mol) was mixed with S (1.33 g, 0.04 mol), Na_2CO_3 (2.195 g) and Na_2HPO_4 (0.98 g) was added to the mixture respectively, and then was pulverized that with a mortar. Herein in addition of Tb_4O_7 (0.005 g, 1×10^{-5} mol) and NH_4 -

PF₆ (0.008 g), the mixture was stirred with vortex mixer for 1 hour. The mixture calcined into a melting pot with furnace at 1100 °C for 30 min. The powders obtained were vacuum dried. Gd₂O₃:S:Tb and CaWO₄ have a characteristic property, which absorbed light in visible region. If excitation by photons is occurred, an inherent luminescent phenomenon is appeared. In traditional, these materials were used as X-ray intensifying agent. The efficiency of luminescence in these materials was over 5% higher, whereas that of Ag₂O or Fe₂O₃ was only less than 4%. Also due to have low band gap energy 2.2 eV and 2.6 eV respectively, it is expected that photocatalytic efficiency would be increased acting as a dopant of titanium dioxide surface. Methylene blue and formaldehyde were purchased by Aldrich Co. without further purification. Water-borne polyurethane dispersion (pH 7, M.W 8000, MTU-06) was supplied by SamMyung Bio Chem Co. (Korea).

Preparation of metal oxide modified TiO₂ photocatalysts and the films. After 0.005 g metal oxide was added at 0.04 g (5×10^{-4} mol) titanium dioxide, the mixture was stirred for 10min with vortex mixer. Then the photocatalysts were prepared by calcination with furnace (Muffle-1125, Dongyang Science Co.) at 400 °C during 45 min. Ethanol (Wako Chemical) was used as a dispersion medium, and homogeneous dispersed solutions were prepared in addition of water-borne polyurethane dispersion through sonication for 30min. Polyurethane dispersion was made use of an additives for coating substrate and an immobilizers for titanium dioxide photocatalyst coincidentally. Since the dispersed solution was coated at petri dish (8.6 cm \times 1.7 cm) and ITO substrate by air sprayer (NCF 035CC, Air maker, Korea) under 7 bar. In order to retard aggregation, the distance between spray gun and the substrate kept up 40 cm. The thickness of films was characterized by microprocessor thin film thickness gauge (M.K.C Korea Co.). Surface area of prepared samples were measured by BET (ASAP 2020, Micromeritics Ins., U.S.A.) method. The values of TiO₂ (P25), TiO₂/Ag₂O, TiO₂/Fe₂O₃, TiO₂/CaWO₄ and TiO₂/Gd₂O₃:S:Tb were 54, 51, 49, 48 and 52 (m²/g) respectively. In addition, the thickness of films was measured in the range from 6.5 to 6.7 (μ m).

Characterization of decoloration for methylene blue and photodegradation for formaldehyde. The photocatalytic activity of metal oxide modified titanium dioxide was characterized by decrease in absorbance of aqueous methylene blue solution as a result of photoreduction. Each film of modified titanium dioxide photocatalyst in 10⁻⁵ M aqueous methylene blue solution was irradiated in photoreactor for 30, 60, 90, 120, 180, 210 and 240 min respectively. The photoreactivity runs lasted 240min. The decrease in absorbance was investigated by UV-Vis spectrophotometer (DT 1000 CE, Ocean optics Inc.). The distance between petri dish, the substrate of modified TiO₂ photocatalyst film, and two black lamp (Sankyo denki black light blue (10W, UV-A, 9W/m²)) kept up 20 cm perpendicularly. At that time, intensity of photon was calculated to be 8×10^{14} photons/cm². As well, photodegradation of formaldehyde was characterized by GC (HP-6890, HP-1 column, He carrier gas at 1.0 mL/min) due to decrease in concentration by photolysis. Each film of modified titanium dioxide photocatalyst in 0.10M aqueous formaldehyde

Table 1. The effect of absorbance decreasing percent in TiO₂ on calcined condition

	(Unit: %)		
	300 °C	400 °C	500 °C
30 min	77.2	80.7	79.3
45 min	83.1	84.9	82.0
60 min	72.6	78.4	79.5

solution was irradiated for 2hrs.

Characterization of photocurrent. In order to investigate generative efficiency of photocurrent in surface of metal oxide modified titanium dioxide photocatalyst, three electrode potentiostat (Electronical BAS, Epsilon Co.) system (reference electrode: Ag/AgCl, counter electrode: Pt wire, working electrode: ITO substrate of modified titanium dioxide photocatalyst film) was used. The electrolyte was 0.1 M aqueous KCl solution. The photoelectrochemical cell was equipped with plat pyrex vial kept bubbling nitrogen gas and two 10W UV light source.

Characterization of photoluminescence. The photoluminescence measurement for metal oxide modified TiO₂ powders was carried out at room temperature, emission range 280 nm~880 nm and scan rate 10 sec⁻¹. It was characterized by UV-Micro Raman spectrometer (Renishaw inVia-Reflex). Powders were prepared at TiO₂ (P25), TiO₂/Ag₂O, TiO₂/Fe₂O₃, TiO₂/CaWO₄ and Gd₂O₃:S:Tb modified TiO₂.

Results and Discussion

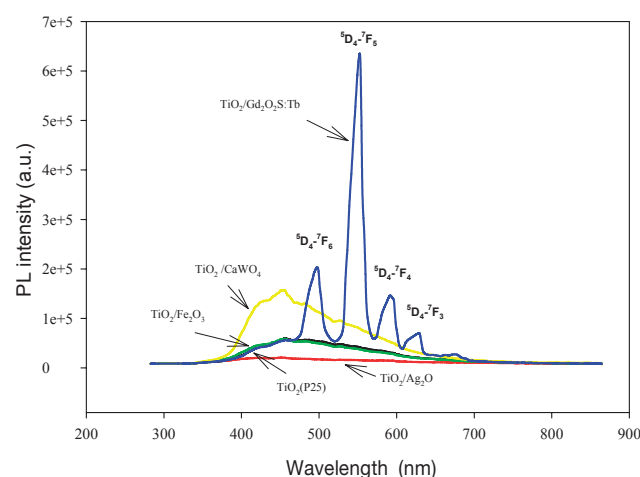
Effect of calcination on photocatalytic activity. Metal oxide modified titanium dioxide photocatalysts were prepared by calcination and impregnation with each of metal oxide source onto titanium dioxide surface. Here, the experimental results report the photocatalytic activity depends on the condition of calcination like calcined temperature and time. Table 1 shows the difference of photocatalytic activity with respect to the decrease in absorbance in aqueous methylene blue solution according to condition of calcination. The best condition was observed at 400 °C for 45 min. At that condition, the photocatalytic activity of calcined titanium dioxide photocatalyst was similar to that of the bare TiO₂ (P25) without calcination.

Absorbance of aqueous methylene blue solution. Before the photocatalytic activity of metal oxide modified titanium dioxide photocatalysts for aqueous methylene blue solution was investigated, the adsorption of aqueous methylene blue solution for the substrate was examined in dark state for 240min, as shown in Figure 1. Total amount of adsorption for the substrate was measured with small value $3.0 \pm 0.13\%$. Hence it is worth nothing that the adsorption for the substrate has an effect on photocatalytic activity directly. One might have expected amount of adsorption for the substrate slight depended on photocatalytic activity. Table 2 shows the photocatalytic decoloration for the film of titanium dioxide (P25) and metal oxide modified TiO₂ photocatalysts. Metal oxide modified TiO₂ samples proved effective in decolorizing methylene blue in a comparable than that found for the TiO₂

Table 2. The relative increase of efficiency against TiO_2 (P25) as characterization.

Sample	Photodecoloration of MB by UV absorption (%)	1 st order rate constant for photodecoloration of MB (%)	Photocatalytic degradation of formaldehyde by GC(%)	Generation of photocurrent (%)
TiO_2 (P25)	- 84.9 ^a	- 81.0 ^b	- 31.53 ^c	- 1.32 ^d
$\text{TiO}_2/\text{Ag}_2\text{O}$	+5.535 89.6 ± 0.35 ^a	+20.987 98.0 ± 0.29 ^b	-15.857 26.53 ^c	-23.484 1.01 ^d
$\text{TiO}_2/\text{Fe}_2\text{O}_3$	+6.360 90.3 ± 0.14 ^a	+22.222 99.0 ± 0.21 ^b	+13.257 35.71 ^c	-11.363 1.17 ^d
$\text{TiO}_2/\text{CaWO}_4$	+6.949 90.8 ± 0.19 ^a	+23.703 100.2 ± 0.24 ^b	+25.118 39.45 ^c	+42.424 1.88 ^d
$\text{TiO}_2/\text{Gd}_2\text{O}_3\text{:Tb}$	+7.656 91.4 ± 0.24 ^a	+27.283 103.1 ± 0.21 ^b	+35.014 42.57 ^c	+119.69 2

^aDecrease in concentration (%) ^bRate constant ($\times 10^{-4} \text{ min}^{-1}$) ^cPercentage of photocatalytic degradation (%) ^dPhotocurrent (μA)

**Figure 1.** The photoluminescence spectra of TiO_2 (P25), $\text{TiO}_2/\text{Ag}_2\text{O}$, TiO_2/WO_4 , $\text{TiO}_2/\text{Fe}_2\text{O}_3$ and $\text{TiO}_2/\text{Gd}_2\text{O}_3\text{:Tb}$ powders calcined at 400 °C for 45 min in air. ($T = \text{R.T.}$, $s.r = 10 \text{ sec}^{-1}$)

(P25). The most active photocatalyst was the $\text{Gd}_2\text{O}_3\text{:Tb}$ modified TiO_2 sample. CaWO_4 and $\text{Gd}_2\text{O}_3\text{:Tb}$ were stable metal oxide, which had little effect on water or thermal. They have lower band gap energy 2.6 eV and 2.2 eV respectively than that of TiO_2 (P25). In addition, it was well known that they are used as an X-ray intensifying agent, which had long lifetime of excited electrons. In particular, in identical anionic environments of the Tb^{3+} ion, the probability of the transition of an electron from the $^5\text{D}_3$ state to the conduction band or to the $^5\text{D}_4$ level will be greater than the probability of the radiative transition to the ground state during external quenching. Due to these physical properties, it can be noticed that the increase in the probability of the transition of an electron enhanced photocatalytic activity of $\text{Gd}_2\text{O}_3\text{:Tb}$ modified titanium dioxide photocatalysts.¹⁰

The photocatalytic activity of the TiO_2 films with $\text{Gd}_2\text{O}_3\text{:Tb}$ modifying was about 7.65% larger than that of the unloaded TiO_2 (P25) film. Comparative data of Fe_2O_3 and Ag_2O modified sample exhibits lower photoactive than that of the $\text{Gd}_2\text{O}_3\text{:Tb}$ modifying sample, but beneficial effect with respect to the TiO_2 (P25) was observed for the Fe_2O_3 and Ag_2O

modified sample.

Kinetics of decoloration for methylene blue. Table 2 summarizes first order rate constant for photodecoloration of methylene blue (%). It is a result of the plots of decreasing ratio of methylene blue with TiO_2 (P25) and metal oxide modified titanium dioxide photocatalysts ($\ln C/C_0$) versus UV irradiation time. It appears highly probable that methylene blue was decolorated by using each of the modified titanium dioxide photocatalysts, following first order kinetics. It results that the linear relationship between the decrease in absorption ($91.3 \pm 0.24\%$) and the rate constant ($103.1 \pm 0.21 \times 10^{-4} \text{ M} \cdot \text{min}^{-1}$) has been at the $\text{Gd}_2\text{O}_3\text{:Tb}$ modified TiO_2 sample. Moreover, it was far better than that of the TiO_2 (P25). Additionally the most active photocatalyst tested in this work was the $\text{TiO}_2/\text{Gd}_2\text{O}_3\text{:Tb}$ sample.

Photodegradation for formaldehyde. The dual cases of experiment for the photocatalytic activity were carried out in this work. One way is the decoloration for methylene blue. The other is the photodegradation for formaldehyde. The former accounted on the better efficiency of photocatalytic activity in our system comparing with already reported in the literature. However, it is not easy to obtain probably direct experimental evidence for reaction pathway, the presence of various related intermediates or reaction mechanism. Whereas, the latter can explain the better performance observed in terms of decomposition for formaldehyde.

Table 2 shows photocatalytic degradation of formaldehyde by GC (%). 13.2 M aqueous formaldehyde solution was diluted to 0.10 M concentration. With GC measurement, the photocatalytic degradation of the samples with respect to 0.10 M aqueous formaldehyde solution was carried out after irradiation during 2 h. An almost complete disappearance of the formaldehyde can be observed after 4 h for $\text{TiO}_2/\text{Gd}_2\text{O}_3\text{:Tb}$ sample that was the most efficient. At 2 h irradiation, 42.57% of degradation was observed. On the contrary, the photocatalytic degradation of Ag_2O modified photocatalyst is lower than that of the TiO_2 (P25). This finding is opposed to the result of the photocatalytic decoloration for methylene blue. Interestingly, the presence of water-born polyurethane used as a binder had a slightly effect on the photocatalytic activity.

This finding hits the mark in choice of polymer, but more work is necessary to elucidate this fact.

Photocurrent for metal oxide modified titanium dioxide films.

The characteristic photocurrent for metal oxide modified TiO₂ films onto ITO substrate was carried out under irradiation for 7 sec at room temperature. Results reported in Table 2 that the generation of photocurrent for the TiO₂/Gd₂O₂S:Tb film was twice higher than that of the TiO₂ (P25). The results summarized in Table 5. On the contrary, the photocurrent for Fe₂O₃ and Ag₂O modified sample were lower than that of the TiO₂ (P25). It seemed to that these results may reflect low photocatalytic activity in case of Fe₂O₃ and Ag₂O modified sample.

Photoluminescence spectra of metal oxide modified titanium dioxide powders. Under the excitation of 254 nm, the PL spectra of metal oxide modified titanium dioxide powders are shown in Figure 1. In particular, four peaks arise from the transitions of ⁵D₄ excited state levels to ⁷F_J (*J* = 6, 5, 4, 3) ground state levels, respectively, and belong to the characteristic emission of Tb³⁺ in the TiO₂/Gd₂O₂S:Tb sample. The emission lines between the 370 nm and 480 nm corresponds to the ⁵D₃ → ⁷F_J (*J* = 0~6) transitions could be observed because of its weakness and overlapping with emission of the TiO₂ (P25). The peak at 545 nm arising from the ⁵D₄ → ⁷F₅ transition is the strongest. The peak at In general, the ⁵D₄ → ⁷F_{1,2} transitions are difficult to be observed at room temperature.^{15,16,17,18} The high photocatalytic property of TiO₂/Gd₂O₂S:Tb sample is probably attributed to those green emission. It is noted that an energy transfer between Gd³⁺ and Tb³⁺ ions plays an important role in achieving photocatalytic effect. On the contrary, emission lines for the Ag₂O modified TiO₂ sample were preferably disappeared between 380 nm and 700 nm, which is the characteristic emission of the TiO₂ (P25). There is no difference between emission lines for Fe₂O₃ modified TiO₂ sample and that of the TiO₂ (P25).

Conclusions

Our experiments have shown that the newly terbium-activated oxysulfide of gadolinium (Gd₂O₂S:Tb) modified TiO₂ photocatalyst are of improved significantly photocatalytic properties over pure the TiO₂ (P25), and have been proved to be used as more efficient photocatalyst than any other single or heterogeneous photocatalyst. Moreover, it can

be noted that enhancement of the photocatalytic efficiency is remarkable in terms of low intensity of irradiation and low amounts consumed due to characteristics of lanthanide and the increase in the probability of the transition of an electron from the ⁵D₃ state to the conduction band or to the ⁵D₄ level in the presence of Tb³⁺. A Comprehensive explanation of the slight differences in reactivity between samples has not been possible at this stage of investigation, so further dedicated experimental evidence is necessary to elucidate this point.

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