

Photodegradation of Rhodamine B catalyzed by TiO₂ thin films

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Abstract

Transparent TiO₂ thin films were prepared on glass substrates by a sol–gel method. They were confirmed to be anatase crystallites by X-ray diffraction (XRD) and Raman spectra analyses. The photocatalytic properties of the sol–gel derived films were assessed by measuring the photodegradative oxidation of Rhodamine B in aqueous solution and compared with Degussa P-25 coated films. These SG-TiO₂ films showed much higher photoactivity than P-25 coated films at the initial time of the reaction. Results of this study also indicate that the photodegradative mechanisms assisted by the two kinds of films are obviously different: highly efficient and fast *N*-de-ethylation accompanied the degradation of Rhodamine B catalyzed by a SG-TiO₂ thin film, whereas only degradative reaction took place when P-25 coated film existed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: TiO₂ thin films; Rhodamine B; Photodegradation; *N*-de-ethylation

1. Introduction

Semiconductor photocatalysis has attracted a great deal of attention over the last 20 years. The strong oxidative power of photogenerated holes on its surface has made TiO₂ the most practical photocatalytic material in fields such as environmental remediation [1,2]. The photodegradation of organic compounds in colloidal and particulate TiO₂ catalyst suspensions has been well studied [3–5]. From the standpoint of application, some shortcomings are apparent: It is difficult to separate the catalysts from the systems after the reaction and the particles are not very amenable to continuous flow system. Recently, TiO₂ films have been gaining much attention as useful photocatalysts [6–8] to offer practical benefits that are not available with the powder. However, the photoactivity of film-type photocatalysts is usually lower than that of powders and the mechanisms of their photocatalysis have not been extensively studied.

Dyestuffs are a ubiquitous class of synthetic organic pigments that represent an increasing environmental danger. Within the overall category of dyestuffs, Rhodamine B, one of the most important xanthene dyes, is used in a variety of applications such as paper and dyelasers. It has become a common organic pollutant, so the photodegradation of Rhodamine B is important with regard to the purification of dye effluents.

The aim of this work is to investigate the photocatalytic activity and properties of TiO₂ thin films through the degradation of Rhodamine B. In this paper, we focus on the high photoactivity and the different photocatalytic mechanisms of TiO₂ thin films recently prepared by us. They are compared with commercial Degussa P-25 coated films.

2. Experimental details

2.1. Materials and apparatus

Tetrabutyl titanate (Ti(OBu)₄), ethanol, polyethylene glycol (PEG) and Rhodamine B (RB) were analytical reagents. Degussa P-25 (an average particle size of 30 nm and BET surface area of 50 m² g⁻¹) were purchased from Japan (Ishihara Sangyo Kaisha) and used as received.

The X-ray diffraction pattern of the film on the glass substrate was measured on a RINT-2400 diffractometer (Rigaku Denki). Raman spectra were recorded on a Renishaw Raman-scope. Absorption spectra of solutions were obtained using a UV-visible double-beam spectrophotometer (Shimadzu UV-1601PC).

2.2. Preparation of SG-film

TiO₂ thin films were prepared by a conventional sol–gel process. Ti(OBu)₄ (7 ml) and acetylacetone (3 ml) were

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added to ethanol (70 ml) and the mixture was frequently stirred. Then PEG M-600 (100% by weight of $\text{Ti}(\text{OBU})_4$) was added and a stable coating solution was obtained. Glass slides used as substrates were submerged in the above solution. The slides were removed from the solution and dried in air for a few minutes. The samples were then sintered at 450°C for 1 h. The process was repeated several times until transparent thin films (SG-films) of 2 g m^{-2} coated TiO_2 were obtained.

Particles of P-25 TiO_2 were formed on the slides by dipping them several times in the TiO_2 ethanolic suspension (5 g dm^{-3}) and drying. The coated amount is the same as that of the SG-thin film.

2.3. Photocatalytic experiments

A 500-W mercury high-pressure resonance lamp was used as the light source. All photoreactions were carried out in a glass reactor containing 10 ml of Rhodamine B aqueous solution (initial concentration = $1 \times 10^{-5} \text{ mol dm}^{-3}$) which was 12 cm from the lamp. The solution was stirred continuously and open to air during the reaction. An SG-film (or a P-25 coated film) of 5 cm^2 was applied as photocatalyst. The photocatalytic decomposition of RB was monitored by the variation of the absorption spectra.

3. Results and discussion

3.1. Structural properties of the SG-films

The X-ray diffraction and Raman spectra of the SG-films attached to the glass substrates were measured, and an X-ray diffraction pattern for 2θ diffraction angles between 20 and 60° is given in Fig. 1. Three primary peaks can be seen at 25.2° , 37.8° and 48.0° . They can be assigned to diffraction from (101), (004) and (200) planes of anatase, respectively [9]; they show that the thin film consists of only anatase within the detection limits of the measurements. Anatase crystallites were also confirmed by Raman spectra.

3.2. Photocatalytic activity of the SG-films

Rhodamine B in aqueous solution containing an SG-film disappeared completely after illumination for 5 h by the mercury lamp. Whereas the absorption spectrum of the solution without the film was not changed under similar conditions. Fig. 2 shows the change in RB concentration vs. irradiation time with an SG-film and a P-25 coated film. From it, we can see that the initial rate of decomposition assisted by the SG-film is much faster than the one catalyzed by the P-25 film (the half-life of RB is 33 and 57 min, respectively). With further reaction, the rate of the former decays gradually and becomes smaller than that of the latter. This is related to the mechanisms of the reactions in the two systems.

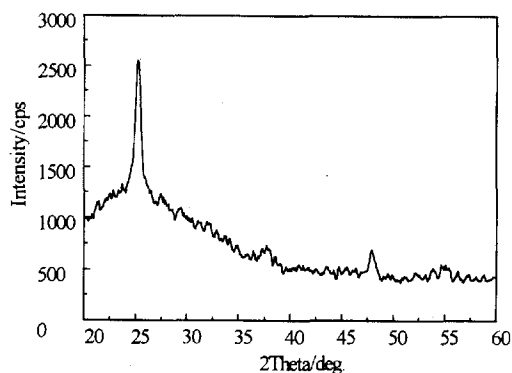


Fig. 1. X-ray diffraction pattern of the SG- TiO_2 film.

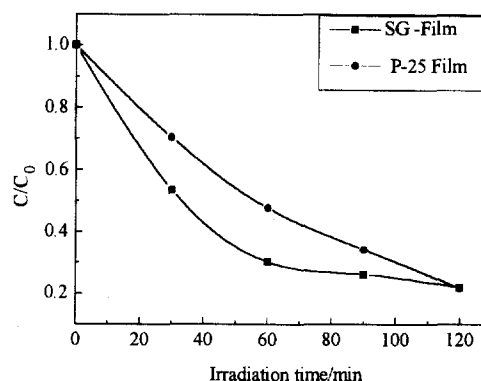


Fig. 2. Dependence of the normalized concentration of Rhodamine B on the irradiation time.

3.3. Comparison of the photocatalytic mechanisms

The absorption spectra of the solutions during irradiation in both systems are illustrated in Fig. 3. As seen from a comparison of Fig. 3a and b, the degradation processes of RB assisted by the two films are very different. The maximum absorption of the solution with a P-25 film decreased gradually with irradiation time and no peak shift was observed (Fig. 3a). However, the solution with an SG-film showed two types of change (Fig. 3b). One is a fast decrease in absorbance; the other is a hypsochromic shift in the absorbance maximum. The loss of absorbance was probably caused by destruction of the dye chromogen. Furthermore, since no new peaks appeared, degradation of RB has occurred. The blue shift of the absorption maximum has been confirmed by T. Watanabe to be due to the *N*-de-ethylation of RB, and the product is Rhodamine ($\lambda_{\text{max}} = 498 \text{ nm}$) [10]. Although the absorbance of RB is larger than that of Rhodamine [10,11], the difference is very small. So the sharp decrease of absorbance in Fig. 3b is mainly attributed to a degradative reaction. This result can also be confirmed by the further decrease of the absorbance after the *N*-de-ethylation was completed. That is to say, catalyzed *N*-de-ethylation by an SG-film took place simultaneously with the photodegradation of RB. Furthermore, the different reaction rates between Rhodamine and RB may lead to the smaller rate of SG-film than that of P-25 film with prolonging a reaction time.

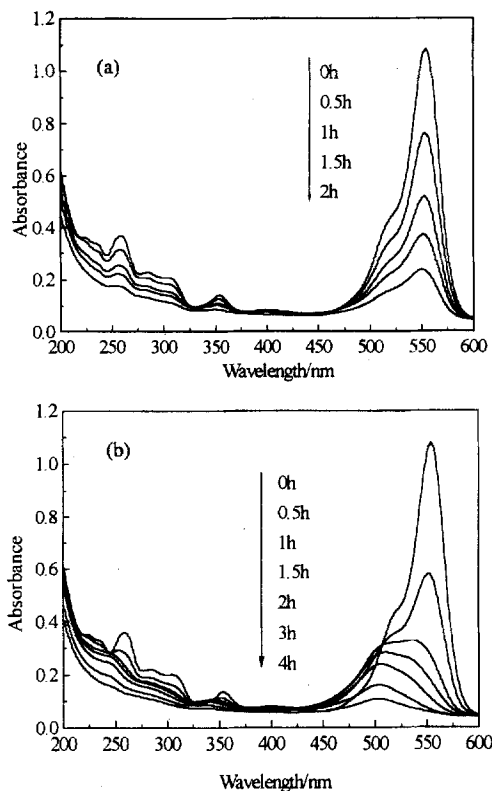
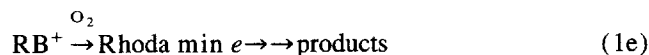
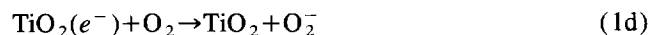
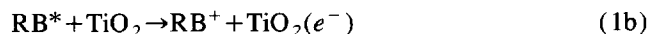
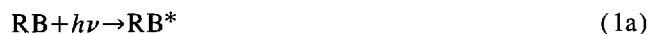


Fig. 3. Absorption spectra of Rhodamine B aqueous solutions during irradiation. (a) P-25 coated film; (b) SG-TiO₂ film.

N-de-ethylation is usually initiated by visible light [10,12]. The radiator of the mercury lamp in this experiment includes ultraviolet and visible light. To determine the source of the two photocatalytic mechanisms, the two types of radiation were separated.

Visible light was isolated with a colored glass filter to remove radiation below 500 nm. Fig. 4 shows the degradation of RB under visible irradiation. It is evident that the decomposition rate of RB with an SG-film is much faster than that with a P-25 film. At the same time, fast *N*-de-ethylation was observed. RB molecules are known to react with TiO₂ after excitation by visible light [4,10,12]:



The excited RB molecules can inject electrons into the conduction band of TiO₂ particles according to the energy level correlation between RB and TiO₂ [2,10,14], and the dye cationic radicals (RB⁺) can be formed. They can also be formed by transferring electrons to the adsorbed oxygen, but reaction (1b) has been verified as the principal pathway [10,12]. Oxygen not only acts as a major acceptor of conduction band electrons (Eq. (1d)), but also plays an impor-

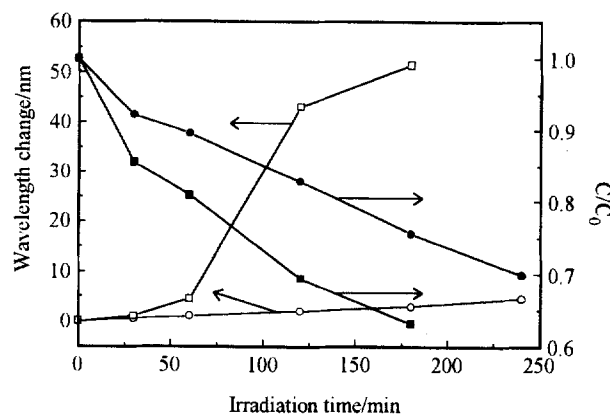


Fig. 4. Change of normalized concentration of Rhodamine B and the shifts of maximum absorbance under visible light. (●, ○) P-25 coated film; (■, □) SG-TiO₂ film.

tant role in the photochemical *N*-de-ethylation process [12]. Among these reactions, Eq. (1b) is the key in both photosensitization and photocatalysis processes of semiconductors [4,13,14]. One of the important criteria for an efficient charge transfer is to adsorb the dyes strongly on the semiconductor surface [15]. In other words, preadsorption of the dye molecules is very important. Fig. 5 indicates that RB is much easier to be adsorbed on the SG-films than on the P-25 films. About 4.2% RB molecules were adsorbed on the former overnight, whereas only 0.8% of RB molecules were adsorbed on the latter. Thus charge transfer between excited RB molecules and TiO₂ is more efficient on the surface of an SG-film. This leads to the higher photocatalytic activity under visible light.

A CoSO₄ aqueous solution (I) and a CuSO₄ aqueous solution (II) were placed between the lamp and the reactor to isolate radiation of 330–400 nm; maximum transmittance is 31.6% at 359 nm. The dependence of RB concentration on UV irradiation time is given in Fig. 6. The absorption spectra of the solutions are depicted in the corner illustrations. Under this condition, the degradation rates for two films are apparently different, which are similar to the cases of UV + VIS. A general mechanism for heterogeneous photocatalysis on TiO₂ under UV irradiation is [1,2]:

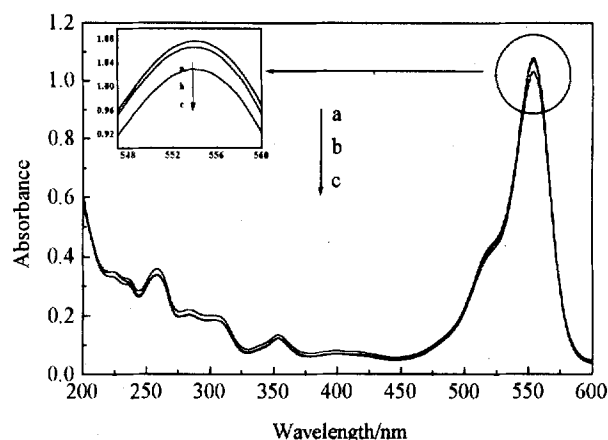


Fig. 5. Absorption spectra of Rhodamine B aqueous solution after adsorption for 12 h in the dark. (a) Blank; (b) P-25 coated film; (c) SG-TiO₂ film.

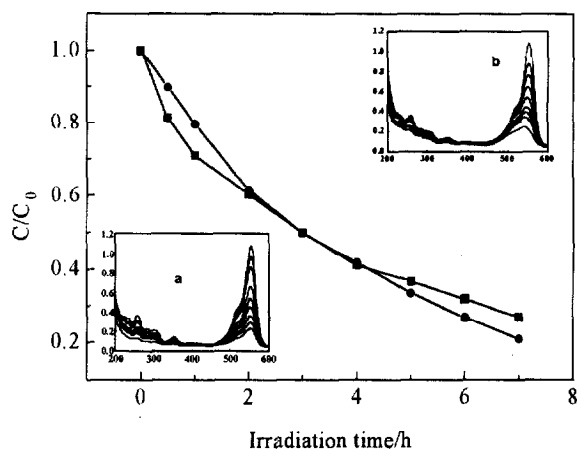


Fig. 6. Degradation of Rhodamine B by UV light. (●, a) P-25 coated film; (■, b) SG-TiO₂ film.



Upon excitation, a conduction-band electron and a valence-band hole separate. Then the hole initiates an oxidative reaction while the electron initiates a reductive reaction if recombination does not occur. Organic compounds are believed to be destroyed through direct oxidation by the trapped holes or attack by hydroxyl groups [1,2]. Because neither the concentration of RB is high nor the RB molecules are strongly adsorbed on the surface under our experimental condition, the direct reaction with holes (reaction 2b) cannot compete with reaction (2c) [16], reaction (1e) does not happen as the result of reaction (2b). At the same time, since RB can be also excited by UV irradiation, reactions (1b) and (1c) are also expected. So the results between UV and UV + VIS are similar. The role of oxygen in the processes is needed for further study.

From the discussion above, the differences in photocatalytic properties between an SG-film and a P-25 film under irradiation by a mercury high-pressure resonance lamp lies in the different adsorption capacities. Since SG-thin films can

utilize effectively ultraviolet light as well as visible light, they improve the efficiency of the degradation of RB. This result is probably due to the different interactions between the dye molecules and TiO₂ surfaces or the differences in surface properties between the two kinds of films.

4. Conclusions

TiO₂ thin films prepared on glass substrates have comparable photocatalytic activity to P-25 coated films. The capacity of SG-films to adsorb RB is greater than that of P-25 films and, as a result, SG-films display not only a different photocatalytic mechanism, but also a higher photocatalytic activity than P-25 coated films.

Acknowledgements

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