



# Photodegradation of rhodamine B in water assisted by titania films prepared through a novel procedure

Jin-Ming Wu\*, Tian-Wei Zhang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

Received 28 May 2003; received in revised form 25 June 2003; accepted 20 July 2003

## Abstract

Well-crystallized anatase thin films were prepared through direct oxidation of metallic titanium with 30 mass% hydrogen peroxide solution at 80 °C for 5 h, followed by soaking in distilled water at 80 °C for 3 days. The photodegradation of a dye solution, rhodamine B (RB), assisted by such deposited anatase films was studied. It was found that the well-crystallized anatase thin films induced complete degradation of RB in water with an initial concentration of less than 0.02 mM after 4–5 h of illumination under a 450 W high-pressure mercury lamp. The RB decayed directly to colorless end products of water and mineral acids. However, when the photocatalytic activity of the anatase films decreased after several repeated uses, an *N*-de-ethylation process producing rhodamine as an intermediate was evident during the photocatalytic degradation of RB.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Titanium dioxide; Thin films; Photocatalyst; Hydrogen peroxide; Rhodamine B

## 1. Introduction

Heterogeneous photocatalysis to eliminate pollutants, especially organic compounds, in water and air has attracted much attention in recent years [1–8]. This process involves the use of solid semiconductor (powders or films), oxygen as the electron scavenger and ultraviolet light. Due to its low-cost, non-toxic and high chemical stability, titania (titanium dioxide, TiO<sub>2</sub>) in anatase crystalline structure is an ideal n-type semiconductor serving as photocatalysts. The basic principle of the photodegradation of organic compounds in water by titania can be depicted as follows: once excited by light with energy larger than the band gap energy of titania (3.2 eV for anatase), pairs of holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) generate and migrate to the surface to react with adsorbed reactants. The holes, together with other oxidizing species such as hydroxyl radicals resulting from certain photochemical reactions, oxidize the organic pollutants to carbon dioxide, water and some simple mineral acids [1]. Although the photocatalytic activity is reduced a little for

the titania films compared to the suspended titania powders, the former is considered to be more applicable in practice [2–5]. This is because the reclamation of the powder suspensions from the reaction mixture is a nuisance.

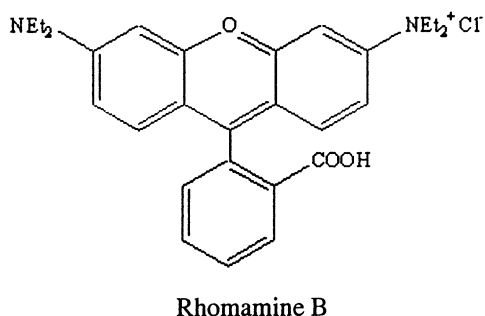
Except for the approaches to hinder the wasteful recombination of the hole and electron pairs [6,7], increasing the surface area of the titania film is another promising way to improve the photocatalytic property because almost all of the involved chemical reactions take place on the surface. Therefore, low-temperature synthesis of titania films has been the focus of many studies [8–12]. However, crystalline titania films obtained by all these methods are either a little complicated or susceptible to contaminations of organic or inorganic species, which would affect adversely the photocatalytic properties.

Dye pollutants from the textile industry are main sources of environmental contamination. Their annoying characters such as toxic, non-biodegradable and resistant to destruction by physico-chemical treatments greatly challenge the researchers [13]. The titania-assisted photodegradation of rhodamine B (RB, C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>Cl), one of the most important xanthene dyes, has been well studied [4,5,14–16]. In this paper, a novel low-temperature procedure suitable for mass production of contamination-free titania films was developed. The photodegradation of RB assisted by such films was studied.

\* Corresponding author. Tel.: +86-571-87953115;

fax: +86-571-87951358.

E-mail address: [msewjim@zju.edu.cn](mailto:msewjim@zju.edu.cn) (J.-M. Wu).



## 2. Experimental details

### 2.1. Preparation of titania thin films

Titanium sheets with sizes of 50 mm × 50 mm were cut from a commercially available pure titanium plate with thickness of 0.1 mm, supplied by Iron & Steel Research Institute, Shanghai, China. They were pickled with 10 mass% HF acidic solution, rinsed ultrasonically in ethanol and distilled water, subsequently. Each piece of the Ti samples was soaked in 50 ml of the 30 mass% H<sub>2</sub>O<sub>2</sub> solution, kept in an oven at 80 °C for 5 h, followed by soaking in distilled water at 80 °C for 3 days.

The X-ray diffraction (XRD) tests were performed using a RAD IIA powder diffractometer. The samples were scanned at a (1/3)° min<sup>-1</sup> scanning rate using Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm) at 40 kV and 25 mA.

### 2.2. Photodegradation of RB

The photoreaction was carried out in a pyrex reactor surrounded with a water-jacket to maintain the reaction temperature at ambient temperature of near 20 °C. One hundred milliliters of the RB solution with an initial concentration  $c_0$  of 0.005–0.04 mM in the presence of the titania thin film with 50 mm × 50 mm × 0.1 mm in size, was illuminated with a 450 W high-pressure mercury lamp 10 cm high over the solution. The solution was stirred continuously and exposed to air during the photocatalytic reaction. Potassium ferrioxalate actinometry was used to measure the near-UV intensity entering the reactor [17]. The photon absorption rate in the reactor was calculated to be  $1.8 \times 10^{-6}$  Einsteins/min. The change of the RB concentration with the illumination time was monitored by determining the absorbance at 555 nm [16], using a 752 UV-Vis spectrophotometer. The molar extinction coefficient  $\epsilon_{\max}$  was determined to be  $8.8 \times 10^4$  (cm mol/l)<sup>-1</sup>. Three parallel experiments were conducted to obtain a point in the related curves.

To detect the possible organic intermediates, 100 ml of the RB aqueous solutions photodegraded to a final concentration of 36%( $c_0$ ) and 3%( $c_0$ ) ( $c_0 = 0.01$  mM) were extracted by 10 ml diethyl ether and subjected to the gas chromatography/mass spectrometry (GC/MS) analysis, which was carried out in Trace 2000 GC/MS (Thermo Quest), equipped

with a DB-5MS capillary column (length = 30 m, i.d. = 0.25 mm, and film thickness = 0.25  $\mu$ m).

## 3. Results

### 3.1. Characterization of the titania films

Fig. 1 shows the XRD patterns of Ti soaked in the H<sub>2</sub>O<sub>2</sub> solution at 80 °C for 5 h (pattern a), followed by soaking in distilled water at 80 °C for 3 days (pattern b). Broad bands around 25.3° and 48.1° in  $2\theta$ , which correspond to the two main anatase peaks of (1 0 1) and (2 0 0), respectively, can be found on the H<sub>2</sub>O<sub>2</sub>-oxidized Ti sheet. This suggests that the titania formed on the Ti surface after 5 h of soaking in the H<sub>2</sub>O<sub>2</sub> solution was mainly amorphous, or consisted of poorly crystallized anatase. Subsequent soaking in the hot water resulted in well-crystallized anatase film on the Ti sheet.

According to the Scherrer formula,  $d_{hkl} = k\lambda/(B \cos(2\theta))$ , where  $\lambda$  is the wavelength of the Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm),  $\theta$  the Bragg's diffraction angle,  $B$  the full-width at half maximum (FWHM) intensity of the peak, and  $k$  a constant (usually  $\sim 0.94$ ) [18]; crystallite size of anatase ( $d_{101}$ ) was estimated to be  $\sim 9.2$  nm. The anatase film thickness was estimated to be  $\sim 1$   $\mu$ m according to the cross-section examination under a scanning electron microscope.

Fig. 2 indicates the adsorption curve of the anatase film soaked in 100 ml RB in the dark ( $c_0 = 0.01$  mM). The RB concentration decreased to 86%( $c_0$ ) within 6 h and further decreased gradually to reach a value of 78%( $c_0$ ) with the prolonged soaking time. Soaking in the dark for 12 h, about  $4 \times 10^{-9}$  mol RB molecules were adsorbed on 1 cm<sup>2</sup> of the anatase film.

### 3.2. Photodegradation of the RB aqueous solution

Fig. 3a shows the photodegradation of RB with different initial concentrations assisted by the anatase film used for

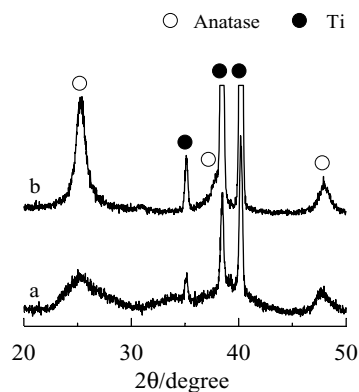


Fig. 1. XRD patterns of the Ti sheet after soaking in 30 mass% H<sub>2</sub>O<sub>2</sub> solution at 80 °C for 5 h (a), followed by ageing at 80 °C for 3 days in distilled water (b).

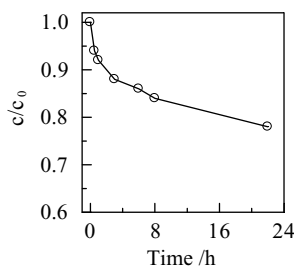


Fig. 2. The adsorption curve of the anatase film soaked in 100 ml 0.01 mM rhodamine B aqueous solution in the dark.

the first time. Without any photocatalysts, RB decayed very slowly. At the present experimental condition, 95% RB remained in the solution after 8 h of the illumination. In the presence of the anatase thin film, the rose-red RB with initial concentrations of 0.005–0.02 mM decayed to colorless end products with concentrations of less than 10% of the initial ones. The photodegradation rate decreased with the increasing initial concentration. For the initial concentration of 0.04 mM, 70% of the RB remained in the solution even after 8 h of the illumination. It should be mentioned that, during the irradiation, some RB molecules would be adsorbed to the back side of the anatase film (the side opposite to the light). However, they are minor compared to the photodegraded RB, as Fig. 2 indicates that only about 7% ( $c_0$ ) of the RB was adsorbed after 6 h in case  $c_0 = 0.01$  mM.

Re-plotting Fig. 3a in the  $\ln(c_0/c)$ – $t$  coordinates (Fig. 3b), it is clear that the photodegradation of RB follows roughly the pseudo first-order reaction [4]

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (1)$$

where  $c/c_0$  is the normalized RB concentration and  $k$  the apparent reaction rate in term of  $\text{min}^{-1}$ . For the RB solution with an initial concentration of 0.01 mM, the value of  $k$  is determined to be  $0.01173 \text{ min}^{-1}$ .

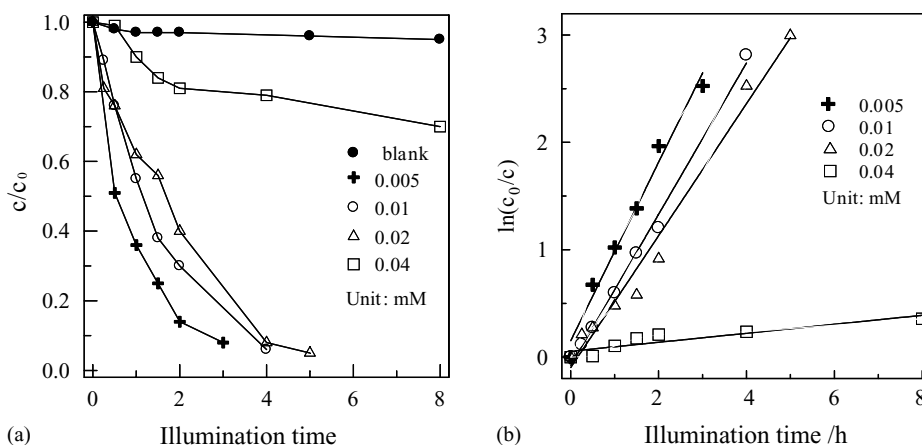
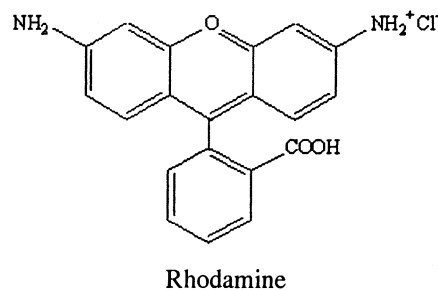


Fig. 3. (a) Photodegradation of rhodamine B with different initial concentrations assisted by the titania films used for the first time; (b) re-plot of (a) in the  $\ln(c_0/c)$ – $t$  coordinates, assuming that the photodegradation of RB follows the pseudo first-order reaction.

Fig. 4a shows the absorbance spectra of the RB solution ( $c_0 = 0.005$  mM) in the presence of the anatase thin film used for the first time during the irradiation, with wavelength covering from 450 to 600 nm. With the increasing irradiation time of up to 2 h, the intensity of the maximum peak located near 555 nm decreased gradually to a value near 0. No remarkable peak shift was observed. Unfortunately, the repetitive photodegradation experiments, that is, an identical anatase film was used repetitively to assist the complete photodegradation of the RB with the same initial concentration, showed that the photocatalytic activity of the present anatase film decayed gradually. For the 10th cycle, the peak absorbance decreased much slower compared to that of the 1st cycle. Meanwhile, the absorbance peak shifted to near 498 nm after 2 h of the illumination (Fig. 4b). This change was more significant when the RB solution with an initial concentration of 0.02 mM was used (Fig. 5). Fig. 5a shows that only the decrease of the peak absorbance located near 555 nm can be discerned when the anatase film was used for the first time. For the 5th cycle, the absorbance peak near 498 nm appeared after about 4 h of the illumination. This shifted absorbance maximum also decreased with the prolonged irradiation time (Fig. 5b). However, doubled irradiation time was needed to induce the complete photodegradation of the RB, compared to the 1st cycle. Watanabe et al. [16] have ascribed the peak shift to *N*-de-ethylation of RB to rhodamine. Therefore, the decreased photocatalytic activity of the anatase film resulted in rhodamine as the most remarkable intermediate.



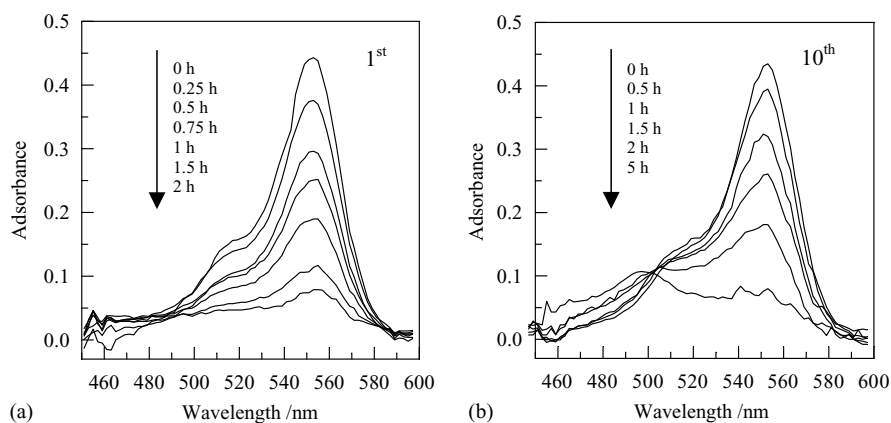


Fig. 4. Absorbance spectra of the 0.005 mM rhodamine B aqueous solution after irradiation for different durations, in the presence of the anatase film: (a) the 1st cycle and (b) the 10th cycle.

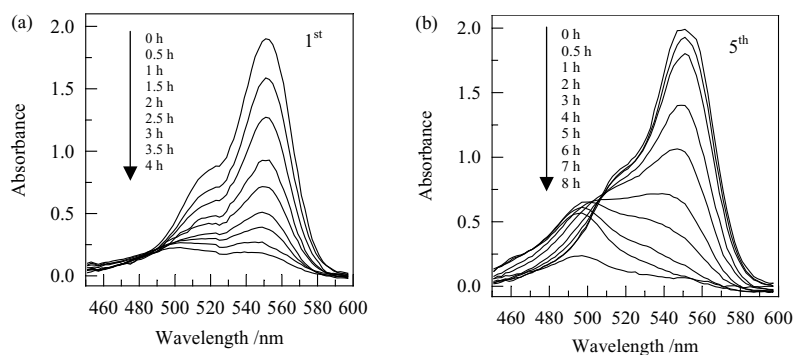


Fig. 5. Absorbance spectra of the 0.02 mM rhodamine B aqueous solution after irradiation for different durations, in the presence of the anatase film: (a) the 1st cycle and (b) the 5th cycle.

Fig. 6 shows the GC/MS spectra of the solution extracted from the RB aqueous solution photodegraded to a final concentration of 36%( $c_0$ ) and 3%( $c_0$ ) ( $c_0 = 0.01$  mM), respectively, using diethyl ether as an extraction reagent. Comparing the spectrum of the sample to the blank, the peaks located at the retention times of 7.13, 16.79 and 18.74 min were evident for Fig. 6a. These peaks were designated respectively to be cyclohexane, 1,3-dicyclohexylurea and piperidine according to retention times of standards. Although the exact photodegradation route is not clear at present time, Fig. 6a does suggest that some colorless complex organic intermediates existed in the RB solution photodegraded to 36%( $c_0$ ). On the contrary, compared to the blank, no extra peaks can be identified for the RB solution photodegraded to 3%( $c_0$ ), suggesting the complete degradation of the RB to end products of water and some simple mineral acids (Fig. 6b). The complete mineralization of the RB subjected to the 5th cycle ( $c_0 = 0.02$  mM, Fig. 5b) was also confirmed by the GC/MS analysis. Therefore, no matter which path the RB underwent, thorough degradation can be realized when assisted by the present anatase thin film, providing that the irradiation time was long enough.

#### 4. Discussion

Mass production of titania films with high photocatalytic activity is one of the main factors inhibiting the wide use of the heterogeneous photocatalysis for removal of contaminations from water or air. Here, we developed a novel procedure to prepare contamination-free anatase thin films, since the hydrogen peroxide was used as an oxidant and hence brought no extra species to the reaction system, which was unavoidable for the methods reported till now. In an attempt to induce apatite deposition on Ti, we have deposited anatase thin films on much smaller Ti pieces with sizes of 10 mm × 10 mm × 1 mm, using the similar procedure [19]. In this experiment, anatase thin films with much larger area were prepared using somewhat different processing parameters. This suggests that scaled-up production of the nanocrystalline anatase films can be realized easily using the present low-temperature approach. In addition, as the titania films came directly from the oxidation of the titanium substrates, a high interfacial strength between the films and the substrates can be anticipated.

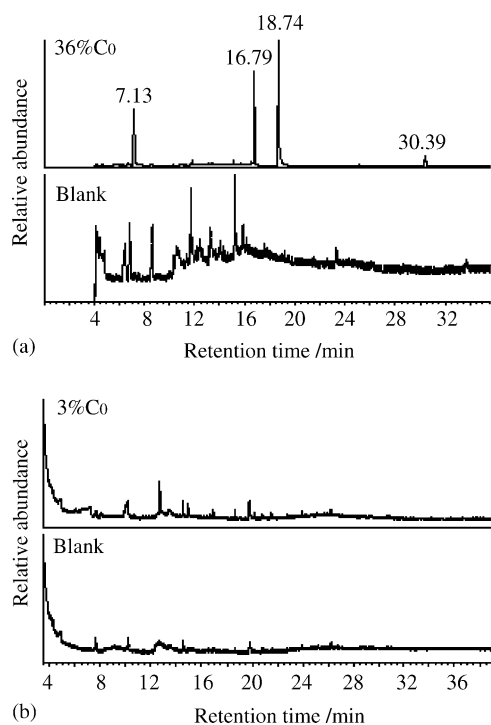
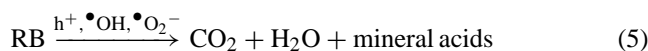
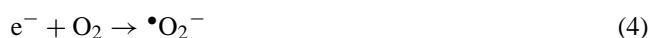
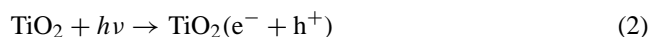


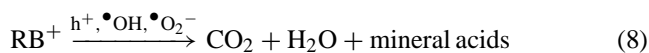
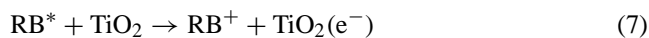
Fig. 6. The GC/MS spectra of the solution extracted from the rhodamine B aqueous solution photodegraded to a final concentration of (a) 36% ( $c_0$ ) and (b) 3% ( $c_0$ ) ( $c_0 = 0.01$  mM), using diethyl ether. The GC/MS spectrum of the blank diethyl ether was shown below that of the sample.

Under the irradiation of the high-pressure mercury lamp, which produces both ultraviolet light and visible light, assisted by titania, the RB in water undergoes two possible pathways: photocatalytic and photosensitization [14]. The photocatalytic pathway can be summarized as follows [1,5,14,20]: titania adsorbs ultraviolet photons and excites electrons in the valence band to the conduction band, creating highly reactive electron and hole pairs (Eq. (2)). Some of the pairs recombine while some migrate to the titania surface to be involved in the photocatalytic reaction. The photo-generated holes may be trapped by hydroxyl groups attached on the surface to form hydroxyl radicals (Eq. (3)). The electrons may be trapped by oxygen to form oxygen species (Eq. (4)). The holes, together with hydroxyl radicals and oxygen species, oxidize the RB in aqueous solution to carbon dioxide, water and some simple mineral acids (Eq. (5)).



The photosensitization pathway of RB under visible light has been well characterized [5,14,16]: RB adsorbed to the titania surface is excited by the visible light (Eq. (6)) and

injects electrons into the conduction band of titania particles to form RB cationic radicals (Eq. (7)). The electrons in the conduction band of titania undergo the similar transformation to Eq. (4). Finally, RB is photodegraded to end products (Eq. (8)). The *N*-de-ethylation process, mainly a surface reaction, occurs when the ethyl groups of RB are attacked by one of the active oxygen species such as  $\bullet\text{OH}$  [14]. This photosensitization process also functions under the ultraviolet irradiation [5].



In the present experiment, for the first cycle, RB degraded directly to colorless end products (Figs. 4a and 5a); on the contrary, after several cycles, the existence of the *N*-de-ethylated compound, rhodamine, was evident (Figs. 4b and 5b). Since the *N*-de-ethylation process occurs mainly on the titania surface, Ma and Yao [5] has attributed the absence of the process to the poor adsorption ability of the Degussa P-25 coated films. Fig. 2 indicates that for over night about  $4 \times 10^{-9}$  mol RB molecules were adsorbed on  $1 \text{ cm}^2$  of the anatase film, about ten times as large as the value of  $4.2 \times 10^{-10}$  mol on the anatase film prepared by Ma and Yao [5] (calculated from the values provided, i.e. 4.2% RB adsorbed on  $10 \text{ cm}^2$  film, 10 ml of the RB solution with initial concentration of 0.01 mM was used), which induced the *N*-de-ethylation process under a 500 W mercury high-pressure resonance lamp. The high adsorption ability of the present anatase films can be ascribed to the high surface area resulted from the low processing temperatures encountered. Therefore, the absence of rhodamine for the first cycle does not necessarily mean the absence of the *N*-de-ethylation process; otherwise one cannot explain the existence of rhodamine after certain cycles. We would like to ascribe the absence of the rhodamine intermediate to the fast subsequent destruction of the rhodamine, once it was produced, to other organic intermediates (see Fig. 6a) or end products.

Interactions between titanium and hydrogen peroxide resulted in abundant superoxide and hydroxyl radicals in the amorphous titania gel [21]. As this titania gel was only subjected to a hot water treatment, we suppose that many of the radicals would remain in the crystallized anatase films. The role of the hydroxyl radical on the photocatalytic degradation of organics has been stressed as it can adsorb a photo-generated hole to form the highly oxidative  $\bullet\text{OH}$  in a simple step [20]. Superoxide radicals such as  $\text{O}_2^-$  and  $\text{HO}_3^-$  also contribute positively to the photodegradation of organics [14,22]. Except for the photo-separated electrons (Eq. (2)), the excited RB molecules also inject electrons to the conduction band of the titania (Eq. (7)). We suppose this photosensitization process enhanced the beneficial effect of the superoxide species incorporated in the anatase films. Thus, the abundance of the superoxide and hydroxyl

radicals in the anatase films helped in the fast decomposition of both rhodamine and RB. The *N*-de-ethylation process failed to be detected by the UV-Vis spectrophotometer.

With repetitive cycles, the gradual loss of such beneficial radicals can be discerned, which resulted in gradual decrease in the photocatalytic activity. As suggested by Ma and Yao [5], the *N*-de-ethylation process was significant due to the high adsorption ability of the anatase films. The produced intermediate rhodamine was photodegraded gradually with prolonged irradiation, as shown in Fig. 4b.

The decrease in the photodegradation rate with the increasing RB initial concentration agreed well with Daneshvar et al. [13]. The large amount of the adsorbed dye is thought to affect negatively the reaction between the dye molecules and the holes or the hydroxyl radicals. The adsorption or scattering of the light by the dyes in the solution also decreased the photons reaching the titania surface, thus decreasing the photodegradation rate of RB.

In the view of practical use, the photocatalytic activity is another important point to be considered in addition to the preparation procedure of the catalysts. Unfortunately, direct comparison of the present anatase films to those known titania such as Degussa P-25 is difficult due to the fact that the photocatalytic activity of titania is sensitive to the film thickness as well as the amounts of the titania coated on the substrates. However, a rough comparison can be made based on Ma and Yao [4], who reported an apparent reaction rate of  $0.01255 \text{ min}^{-1}$  when 10 ml of 0.01 mM RB aqueous solution was photocatalytically decomposed under the illumination of a 500 W high-pressure mercury lamp, using a 19 mm × 26 mm glass slide coated with the commercial Degussa P-25.

Assuming that the photocatalytic reaction fits the pseudo first-order expression, the photodegradation rate of RB molecules  $dn/dt$  on  $1 \text{ cm}^2$  of titania films can be expressed as

$$\frac{dn}{dt} = -\frac{1}{S} \cdot \frac{d(cV)}{dt} = \frac{kc_0V}{S} \exp(-kt) \quad (9)$$

where  $k$  is the apparent reaction rate,  $c_0$  the initial concentration of RB,  $V$  the solution volume, and  $S$  the surface area of the titania films.

The value of  $dn/dt$  as a function of the illumination time  $t$  for the present low-temperature prepared anatase film ( $c_0 = 0.01 \text{ mM}$ ,  $k = 0.01173 \text{ min}^{-1}$ , see Fig. 3b), the Degussa P-25 coated film ( $k = 0.01255 \text{ min}^{-1}$ ) and the sol-gel prepared film (at the initial stage,  $k = 0.01993 \text{ min}^{-1}$ ) [4] was illustrated in Fig. 7. As the photodegradation conditions for the two experiments were similar, for a rough estimate, it is safe to say that the present anatase film exhibits higher photocatalytic activity during the illumination time for up to 4 h.

It is generally accepted that bleaching dyes is easy; whilst complete mineralization of dyes is somewhat difficult. The present prepared anatase films were able to induce thorough photodegradation of RB in water, without any detectable organic species (Fig. 6b). This exhibits great potential for them

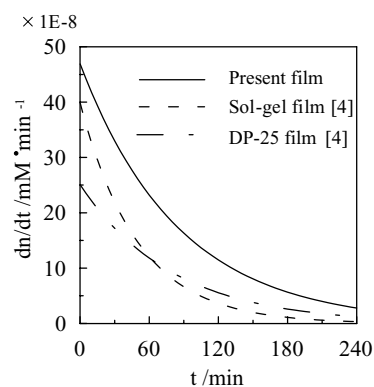


Fig. 7. The photodegradation rate of RB molecules  $dn/dt$  on  $1 \text{ cm}^2$  of titania films derived by different methods, as a function of the illumination time  $t$ .

to be used widely for wastewater purification, especially for treatments of the dye effluents.

## 5. Conclusions

A novel procedure suitable for scaled-up production, i.e. oxidizing metallic titanium with 30 mass% hydrogen peroxide at  $80^\circ\text{C}$  for 5 h followed by treatment in hot water at  $80^\circ\text{C}$  for 3 days, was developed to prepare anatase films. Assisted by such prepared anatase films, the rhodamine B in water was photodegraded directly to end products due to the high photocatalytic activity. After several cycles, the photocatalytic activity decreased, and hence the production and further decomposition of the intermediate rhodamine was evident during the complete mineralization process of the rhodamine B in water.

## References

- [1] M. Penpolcharoen, R. Amal, M.J. Brungs, *Nanopart. Res.* 3 (2001) 289.
- [2] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipse, J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, *Appl. Catal. B: Environ.* 7 (1995) 49.
- [3] H. Liu, S.A. Cheng, J.Q. Zhang, C.N. Cao, *Chemosphere* 38 (1999) 283.
- [4] Y. Ma, J.N. Yao, *Chemosphere* 38 (1999) 2407.
- [5] Y. Ma, J.N. Yao, *J. Photochem. Photobiol. A: Chem.* 116 (1998) 167.
- [6] E.C. Bulter, A.P. Davis, *J. Photochem. Photobiol. A: Chem.* 70 (1993) 273.
- [7] A. Scalfani, M.N. Mozzanega, P. Pichat, *J. Photochem. Photobiol. A: Chem.* 59 (1991) 181.
- [8] M. Burgos, M. Langlet, *J. Sol-Gel Sci. Technol.* 16 (1999) 267.
- [9] S. Yamabi, H. Imai, *Chem. Mater.* 14 (2002) 609.
- [10] K. Shimizu, H. Imai, H. Hirashima, K. Tsukuma, *Thin solid films* 351 (1999) 220.
- [11] S. Baskaran, L. Song, J. Liu, Y.L. Chen, G.L. Graff, *J. Am. Ceram. Soc.* 81 (1998) 401.
- [12] V. Petkov, G. Holzhtuter, U. Troge, Th. Gerber, B. Himmel, *J. Non-Cryst. Solids* 231 (1998) 17.

- [13] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A: Chem. 157 (2003) 111.
- [14] T.X. Wu, G.M. Liu, J.C. Zhao, H. Hidaka, N. Serpone, J. Phys. Chem. B 102 (1998) 5845.
- [15] F.L. Zhang, J.C. Zhao, L. Zang, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, J. Mol. Catal. A: Chem. 120 (1997) 173.
- [16] T. Watanabe, T. Takizawa, K. Honda, J. Phys. Chem. 81 (1977) 1845.
- [17] C.G. Hatchard, C.A. Parker, Proc. R. Soc. Lond., Ser. A 235 (1956) 518.
- [18] J. Yang, S. Mei, J.M.F. Ferreira, J. Am. Ceram. Soc. 83 (2000) 1361.
- [19] J.M. Wu, H. Satoshi, K. Tsuru, A. Osaka, J. Ceram. Soc. Jpn. 110 (2002) 78.
- [20] A.E.H. Machado, A.M. Furuyama, S.Z. Falone, R. Ruggiero, D.daS. Perez, A. Castellan, Chemosphere 40 (2000) 115.
- [21] P. Tengvall, I. Lundstrom, Clin. Mater. 9 (1992) 115.
- [22] M. Klare, G. Waldner, R. Bauer, H. Jacobs, J.A.C. Broekaert, Chemosphere 38 (1999) 2013.