The enhancement of TiO_2 photocatalytic activity by hydrogen thermal treatment

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Abstract In this study, conventional TiO_2 powder was heated in hydrogen (H_2) gas at a high temperature as pretreatment. The photoactivity of the treated TiO_2 samples was evaluated in the photodegradation of sulfosalicylic acid (SSA) in aqueous suspension. The experimental results demonstrated that the photodegradation rates of SSA were significantly enhanced by using the H_2-treated TiO_2 catalysts and an optimum temperature for the H_2 treatment was found to be of 500 – 600 °C. The *in situ* Electron Paramagnetic Resonance signal intensity of oxygen vacancies (OV) and trivalent titanium (Ti^{3+}) associated with the photocatalytic activity was studied. The results proved the presence of OV and Ti^{3+} in the lattice of the H_2-treated TiO_2 and indicated that both were contributed to the enhancement of photocatalytic activity. Moreover, the experimental results presented that the EPR signal intensity of OV and Ti^{3+} in the H_2-treated TiO_2 samples after 10 months storage was still significant higher than that in the untreated TiO_2 catalyst. The experiment also demonstrated that the significant enhancement occurred in the photodegradation of phenol using the H_2-treated TiO_2.

Keywords: Photocatalysis, Titanium dioxide, Hydrogen treatment, Photodegradation

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1. Introduction

In recent years, great attention has been paid to the titanium dioxide (TiO_2) photocatalytic oxidation of organic pollutants in aqueous and gaseous systems (Hoffmann et al., 1995; Rajeshwar, 1995). TiO_2, when working as a photocatalyst, depends on the electron-hole (e-h) pairs generated upon illumination by light in which the energy is not less than that of the TiO_2 band gap (3.2 ev). Thus, the separation of the e-h pairs plays a predominant role in photocatalytic reaction. On the other hand, simple recombination of the e-h pairs is the major hindrance leading to a low quantum yield (<5 %). Some recent research confirmed that a number of metal islands (Heller and Miller, 1980; Allongue et al., 1989, Li and Li, 2001) or metal oxides (Gopidas et al., 1990; Bedja et al., 1994; Anderson and Bard, 1995) were introduced into the TiO_2 lattice for accelerating the e-h separation. Alternatively, the thermal hydrogen (H_2) treatment of TiO_2 was also found to be capable to prolong the holes' lifetime by reducing the number of bulk recombination centers (Harris and Schumacher, 1980; Heller et al., 1987). In the meantime, the photoactivity of the TiO_2 pigment can be enhanced by this reduction reaction in a H_2 atmosphere at a thermal condition (Heller et al., 1987). The H_2 treatment was a usual method to improve the surface and photoelectrochemical properties of TiO_2 (Chen et al., 1983; Howe and Gratzel, 1987; Qin et al., 1993; Rekoske and Barteau, 1997). More recently, some researchers have investigated the reduction mechanism in the temperature range of 300-500 ^{o}C (Khader et al., 1993) and the surface stoichiometry (Haerudin et al., 1998) of the TiO_2 with H_2 treatment by means of electrical conductivity (Khader et al., 1993) or Fourier transform infrared (FTIR) spectroscopy (Haerudin et al., 1998). Based on the results reported in the above literature, it seems that oxygen vacancies (OV) and trivalent titanium (Ti^{3+}) may be present in the modified TiO_2. In the field of photocatalysis, Okamoto et al. (1985) adopted H_2 reduction as a simple pretreatment of TiO_2 in photocatalytic degradation of phenol. However, the wide use of the H_2-treated TiO_2 has not been available. Heller and co-workers (1987) reported the enhanced photocatlaytic activity of

the TiO_2 catalyst by a thermal reduction treatment using hydrogen gas at 550 ^oC. Furthermore, they proposed that the reduction of the TiO_2 particles raised their Fermi level and increased the height of the barrier that repels electrons from the particles surface because of more Ti^{3+} available in the TiO_2 particles. Harris and Schumacher (1980) confirmed the presence and effect of OV in the H_2-reduced TiO_2 besides Ti^{3+} species. In addition, they also proved the presence of hydroxyl group in the treated TiO_2, but it has not been clear whether the improvement in the photoactivity of the TiO_2 catalysts after the H_2 reduction treatment results from all the species (i.e. OV, Ti^{3+} and hydroxyl group) or only some of them.

This work aimed at studying the TiO_2 photocatalytic oxidation affected by the H_2 treatment and also the correlation between the photocatalytic activity and the change of TiO_2 structure, in which sulfosalicylic acid (SSA) and phenol were used as model chemicals.

2. Materials and methods

Photooxidation experiments were conducted in a cylindrical photoreactor surrounded with a circulating water jacket as described in our previous work (Leng et al., 2000). A 6W UV lamp with a maximum emission at 365 nm was used as a light source. The intensity of the UV irradiation was detected to be 2 mW cm^{-2} by a Black-ray ultraviolet meter (Model No. J221, Upland, CA, USA). TiO_2 (anatase, 30 nm in size) sample was provided by the Taixing Nano-Materials Plant in China, while SSA and phenol were supplied by the Shanghai Chemical Reagent Factory in China and used as model chemicals. TiO_2 suspension was prepared by adding 0.165 g of TiO_2 powder into 165 ml of SSA solution. An initial SSA concentration of 1.2×10^{-4} M was used in the experiments. The initial pH in the suspension was adjusted to 7.5 using solutions of 0.01 M $HClO_4$ and 0.01 M NaOH. To eliminate the adsorption effect, the SSA or phenol solution after adding TiO_2 powder was magnetically stirred in the dark for 60 min to establish an adsorption/desorption equilibrium condition prier

to the photoreaction. During the photoreaction, temperature was kept at 22±1 ^{o}C by a thermostat and samples were collected at different time intervals. The collected samples after filtration and centrifugation were measured by a UV-VIS spectrosphotometer (Hitachi, Model 200-10) to determine the absorbance of SSA in the wavelength range of 190-350 nm. In this analysis, the molar extinction coefficient at the wavelength of 208 nm was determined to be 2.94×10^{4} l (mol cm)$^{-1}$.

A thermal reduction process was performed to prepare the H_2-treated TiO_2 samples for the photooxidtion reaction. In this process, the conventional TiO_2 powder was put in a homemade quartz tube and together with the tube was placed into an oven. Hydrogen gas with general grade was then introduced into the tube at a flow rate of 30 ml min^{-1} continuously. The temperature in the process was increased from 20 ^{o}C to a designated level at an increasing rate of 10 ^{o}C min^{-1} first, and then was kept for 2 hrs. After that, the samples were cooled down to the room temperature naturally.

The *in situ* Electron Paramagnetic Resonance (EPR) measurement was performed using an Endor spectrometer (JEOL ES-ED3X) at the liquid nitrogen temperature of 77 K. A microwave with the frequency of 9.42 GHz was used and its power was set at 1 mW. The g factor was obtained by taking the signal of manganese as an internal standard. A specially designed cell in the *in situ* EPR measurement under H_2 environment was used. After being thermally treated, the TiO_2 samples were gradually cooled to the room temperature, and then transferred together with the reactor into the resonance cavity of the EPR spectrometer while still under the H_2 environment.

The temperature-programmed reduction (TPR) measurement using H_2 gas was also performed in a specially designed quartz tube with 0.5 g of TiO_2 samples. The tube was put

in a cylindrical electric furnace. The temperature of the furnace was controlled by a programmable regulator with the thermocouple attached to the outside of the quartz tube. Gas chromatography (Shimadzu, GC-8A) with a thermal conductivity detector was used to detect H_2 consumption during the H_2 treatment. The TiO_2 sample was pretreated by Ar gas from room temperature to 300 ^oC at a gradient rate of 10 ^oC min^{-1} for 30 min, then cooled to the room temperature again. Thereafter, 5 % H_2/Ar mixture gas was introduced into the TiO_2 bed at a flow rate of 18 ml min^{-1} concomitant with the temperature increase to 1,000 ^oC. The H_2/Ar mixture gas was dewatered using dry ice (solid CO_2) mixed with alcohol before it passed through the GC.

3. Results and discussion

3.1 The evaluation of the photocatalytic activity

The first set of tests was carried out to evaluate the photocatalytic activity of the modified TiO_2 sample in the SSA photodegradation experiment against that of the TiO_2 sample without H_2 treatment. In which two reactions lasted for 120 min and samples were collected at different time intervals for determination of light absorption spectra. The experimental results are shown in Fig. 1. It can be seen that the UV absorption peak of the SSA by using the H_2-treated TiO_2 disappeared more rapidly than using the bare TiO_2. The peak at 208 nm disappeared almost completely after 60 min reaction when the H_2-treated TiO_2 was used. However, the peak at 208 nm by using the bare TiO_2 was still partially remained after 120 min reaction. Moreover, the disappearance (or decrease) of the SSA absorption peaks in the UV region showed that the molecular decomposition of the organic substrate, because an aromatic molecular has an absorption peak in the region. Therefore the H_2-treated TiO_2 catalyst behaved a higher photocatalytic activity in the SSA photodegradation at the same reaction time, compared to that of the TiO_2 catalyst without H_2 treatment.

[Fig. 1]

The second set of tests was then carried out to photodegrade SSA in the TiO_2 suspensions, in which the TiO_2 catalysts were treated at different temperatures from 20 to 700 °C. Several studies (Pruden and Ollis, 1983; Ollis *et al*., 1984; Matthews, 1988) indicated that the rate of photocatalytic degradation of various organic contaminants over illuminated TiO_2 could be explained with the Langmuir-Hinshelwood (L-H) kinetic expression. When the initial concentration of organic contaminants was low, the L-H rate form reduced to an apparent first-order kinetics form. In this study, if we assume that the SSA photodegradation follows the first order reaction, the kinetic constant (k) for each reaction can be simply calculated based on the experimental data. Therefore, a relationship between the kinetic constant and the temperature of H_2 treatment is shown in Fig. 2. The results demonstrated that the photocatalytic activity increased with the increase of H_2 treatment temperature firstly and reached a maximal value at 560 ^{o}C. However, when the temperature was further increased beyond 560 ^{o}C, the photocatalytic activity decreased rapidly. The falling of photocatalytic activity may be resulted from the phase transition from anatase to rutile at around 700 ^{o}C, which is generally considered to be not favorable to TiO_2 photocatalytic activity (Rekoske and Barteau, 1997). However, it seems that there was an optimal temperature for the H_2 treatment between 500 and 600 ^{o}C.

[Fig. 2]

3.2 Reason causing the enhancement of photocatalytic activity by H_2 treatment

To determine the change of the TiO_2 structure affected by the H_2 treatment, Brunauer-Emmett-Teller, X-ray diffraction and diffuse reflection spectrum analyses were performed in our previous work (Liu et al., 2001) and the results suggested that the H_2 treatment of TiO_2 did not change the surface area, particle size and absorption edge of TiO_2 very much and also did not result in any significant phase transfer if the temperature was controlled below 700 ^{o}C. This founding was in agreement with that by Heller et al. (1987). On the other hand, it has been indicated that the thermal H_2 treatment of TiO_2 at 550 ^{o}C may produce OV and Ti^{3+} species (Harris and Schumacher, 1980), which exist even on the TiO_2 surface as it is prepared originally (Qin et al., 1993).

In this study, the H_2 consumption during the treatment was monitored by the TPR measurement in order to further investigate the H_2 treatment process. The analytical results are shown in Fig. 3. The TPR spectrum demonstrated that when the temperature was lower

than 400 ^{o}C (A), the H_2 consumption was insignificant. However, when the temperature was further increased beyond 400 °C, the H_2 consumption became much faster and reached its maximum value at 520 °C (C). It can be noted that a turning point at 450 °C (B) may indicate some changes in the TiO_2 structure undergo a chemical reaction. As the temperature reached 600 ^{o}C, the H_2 consumption fell to a low value. Beyond the turning point at 600 °C (D), the H_2 consumption increased again and reached the second peak value at 710 ^{o}C (E). It may indicate that a phase transfer from anatase to rutile took place around this temperature. It should also be pointed out that some of the H_2 introduced into the TiO_2 bulk flooded out when the temperature was higher than 850 ^{o}C. However, it is not a main concern in this study.

[Fig. 3]

Considering the fact that there are unpaired electrons in the structure of either Ti^{3+} or OV, the TiO_2 samples treated at different temperatures were measured by the *in situ* EPR to determine their presence and alteration during the H_2 reduction. The analytical results as shown in Fig. 4 indicated that the peak with a g factor of 1.955 could be assigned to Ti^{3+}, since it was very close to 1.946 (140K) (Torimoto et al., 1996) and 1.989 (Howe and Gratzel, 1985) reported by other researchers. The peak with a g factor of 2.002 might be assigned to adsorbed oxygen when the H_2 treatment temperature was lower than 400 ^{o}C, which was similar to those of the superoxide radical anions (O^{-}_{2}) formed on the TiO_2 anatase surface (Howe and Grätzel, 1987). As the H_2 treatment temperature was above 400 ^{o}C, the peak with a g factor of 2.003 could be assigned to the OV, which was similar to the OV observed in ZrO_2 during the thermal treatment by air (Torralvo et al., 1984). It is also noted that the peaks with a g factor of 2.003 at the temperatures below 300 ^{o}C became more negative and could be assigned to the O_2^{-}, since the O_2^{-} species came from the adsorbed oxygen on the TiO_2 surface (Yu et al., 2000). However, it was found that some peaks appeared again in the EPR spectra due to oxidation reaction, after the H_2-treated TiO_2 samples were exposed to air for a while. This will be further discussed in the later part of this paper.

[Fig. 4]

To view a full picture of the OV and Ti^{3+} intensity affected by the temperature of H_2 treatment, an evolution profile of OV and Ti^{3+} intensity vs. the temperature is summarized in Fig. 5. It can be seen that the adsorbed oxygen and a small amount of OV had already presented in the TiO_2 at the lower temperature as it was obtained. With an increase of temperature, the signals of the adsorbed oxygen weakened and the OV species were produced simultaneously. It is noted that there are some changes in the peak shapes for the g factor of 2.002. Furthermore, when the H_2 treatment temperature increased up to 450 ^oC, the signal of Ti^{3+} turned up although it was weak. When the H_2 temperature was further increased, the signal intensity of Ti^{3+} increased and reached to a maximum value at 600 ^oC. Meanwhile, the signal intensity of OV was maintained almost constant, till the temperature reached 520 ^oC, and declined at above 560 ^oC. At this temperature, the OV reached a saturated status and the electrons in the OV were transferred out to form Ti^{3+} due to more energy was supplied by hydrogen. At 700 ^oC, the signal intensity of both OV and Ti^{3+} became very weak, due to the phase transition reaction from anatase to rutile.

[Fig. 5]

Consequently, it is worth to discuss the interaction between H_2 and TiO_2 during the H_2 treatment. We propose that the interaction fell into three types: Firstly, hydrogen interacted physically with the adsorbed oxygen at a temperature below 300 ^oC. This phenomenon was proved by the disappearance of the EPR signals of adsorbed oxygen as shown in Fig. 4 and the insignificant H_2 consumption as shown in Fig. 3; Secondly, when the temperature was higher than 300 ^oC, electrons were transferred from the H atoms to the O atoms in the lattice of TiO_2. Then the OV was formed, when the O atom left with the H atom in the form of H_2O. Accordingly, the H_2 consumption became faster as shown in Fig. 4; Thirdly, the interaction between H_2 and TiO_2 proceeded more drastically, in which the

electrons transferred to Ti^{4+} and Ti^{3+} were formed, when the temperature was up to 450 ^{o}C, and the H_2 consumption rate appeared to be even higher. It seems that the electrons arrived at Ti^{4+} via OV due to a little change of the EPR signal intensity of OV at 400–520 ^{o}C, while the signal intensity of Ti^{3+} continued increasing. Furthermore, when the temperature increased to 560 ^{o}C, more energy was supplied and the electrons already in the OV were driven away and transferred to Ti^{4+}. This resulted in that the EPR signal intensity of OV decreased and that of Ti^{3+} increased till the temperature reached 600 ^{o}C. Unfortunately, the presence of any hydroxyl (OH) group could not be identified by the EPR analysis in this study, even though Harris and Schumacher (1980) reported the presence in their work with the aid of infrared spectrum.

Based on the results shown in Figs. 2, 3 and 5, it may be summarized that if the H_2 treatment occurred at a low temperature (below 450 °C), OV species was produced alone and the photocatalytic activity of TiO_2 samples was only improved slightly. When the H_2 treatment was conducted at a higher temperature up to 520 ^{o}C, both the OV and Ti^{3+} species were generated and resulted in the significant enhancement of photocatalytic activity. Furthermore, the H_2 treatment at 560 ^{o}C led TiO_2 have a maximal photocatalytic activity, where the H_2 consumption rate also reached the highest value as shown in the TPR spectrum. At this temperature, the best photocatalytic activity achieved might be resulted from a proper ratio of OV and Ti^{3+} in the modified TiO_2 structure. When the H_2 temperature was beyond 600 ^{o}C, the OV declined rapidly and the photocatalytic activity decreased simultaneously. Therefore, both the OV and Ti^{3+} in the H_2-treated TiO_2 samples played a role in the enhancement of photocatalytic activity. Since the optimum temperatures to produce OV and Ti^{3+} were not exactly same, we herein state that the optimal temperature for the H_2 reduction treatment would fall between 500 and 600 ^{o}C. This conclusion may support the work done by Okamoto et al. (1985), in which they pretreated TiO_2 catalyst by H_2 at 550 ^{o}C.

3.3 The proposed mechanism of OV and Ti^{3+} in the photocatalytic reaction

A limited amount of OV and Ti^{3+} species generated during the H_2 reduction appears as defects in the TiO_2 structure. While the electrons and holes are generated in the initial stage of UV illumination, the defects on the TiO_2 surface or in the bulk can suppress the recombination of electron-hole pairs and hence extend their lifetime (Linsebiger et al., 1995). The OV and Ti^{3+} species act as hole traps (Liu et al., 2001). Once the OV and Ti^{3+} are combined with the holes, they become charged species. At the same time, oxygen acts as electron traps during the reaction. Thereafter, the trapped holes transfer to the organic substrate leading to a degradation reaction and the charged defects recover to their original states of OV and Ti^{3+}. In our previous work (Liu et al., 2000a), we employed electrochemical impedance spectroscopy to investigate the photocatalytic reaction, and found that the reaction impedance of the H_2-treated TiO_2 was much smaller than that of the TiO_2 without H_2 treatment. This may indicate the existence of a more effective separation of the electron-holes (Liu et al., 2000b).

3.4 The stability of the enhanced photocatalytic activity

If the H_2-treated TiO_2 were employed in photooxidation applications as a photocatalyst, the lifetime of its enhanced photocatalytic activity would be concerned. The freshly generated OV and Ti^{3+} on the TiO_2 surface by the H_2 reduction could be thermodynamically oxidized when exposed to air. However, the rate of this reversed reaction depends on temperature. Thus kinetically, it may take a much longer period to be oxidized back under a mild condition, i.e., at a room temperature, than it was reduced at a much higher temperature. Torimoto et al. (1996) thought that the lifetime of the Ti^{3+} species would be as long as several months, judged by the duration of the blue color on the H_2-treated TiO_2 surface. In this study, it was observed that the blue color of the TiO_2 treated at over 520 ^{o}C still remained after 10 months storage. To determine the efficiency of the H_2-treated TiO_2 catalysts in photocatalytic activity, two TiO_2 samples of freshly treated and stored at a room

temperature after 10 months were examined by the EPR analysis and both the results are shown in Fig. 6. It can be seen that the intensity of OV in the TiO_2 sample after 10 months storage decreased to a limited degree, while the signal of Ti^{3+} declined more significantly.

[Fig. 6]

The above two TiO_2 samples were also tested in the SSA photodegradation and the experimental results are shown in Fig. 7. Fortunately, the results demonstrated there was only a slight difference between their photodegradation rates ($k = 0.029\ min^{-1}$ for the freshly treated TiO_2 sample and $k = 0.022\ min^{-1}$ for the treated TiO_2 sample after 10 months storage).

[Fig. 7]

To determine the disappearance of OV and Ti^{3+} affected by the storage temperature, the H_2-treated TiO_2 samples were prepared at 600 °C for 60 min first and then were stored at different temperatures from 20 to 400 °C for 20 minutes under air/O_2 environment. Their EPR results are shown in Fig. 8. It was found that the oxidation of OV and Ti^{3+} species proceeded much faster at a higher storage temperature.

[Fig. 8]

It should be mentioned that the response of OV and Ti^{3+} species detected in the EPR analysis came from both the surface and bulk of TiO_2. It is really unfortunate that we were unable to differentiate the species on the surface and those in the bulk. Haerudin et al. (1998) assumed that the OV were mainly located on the surface of TiO_2 due to their fast saturation, and the Ti^{3+} were confined into the surface layer of TiO_2 due to an electrostatic repulsion of

net charges. Oppositely, Torimoto et al. (1996) claimed that the Ti^{3+} sites must be deep within the crystal lattice because the blue color caused by the Ti^{3+} could retain for few months. Apparently, the oxidation rate affected by the surface defects is different from that in the bulk. In the present work, when exposed to air, the OV and Ti^{3+} species on the TiO_2 surface might be oxidized only partially after a 10 months time, since the blue color on the H_2-treated TiO_2 was still observed. Alternatively, if the OV and Ti^{3+} species on the TiO_2 surface was mostly oxidized, the defects in the bulk might also improve the photocatalytic activity by separating the electrons and holes, because the photogenerated charge carriers can be trapped in both bulk and on the surface (Linsebiger et al., 1995), although the photocatalytic oxidation reaction occurred on the surface of TiO_2 catalyst only.

3.5 The photodegradation of phenol in the H_2-treated TiO_2 suspensions

To confirm the enhancement of the photocatalytic activity of TiO_2 by the H_2 thermal treatment in general, one set of tests was conducted to photodegrade phenol in aqueous suspensions containing either the TiO_2 sample treated at 550-560 ^oC or the conventional TiO_2 sample without H_2 treatment. The experimental results are shown in Fig. 9. Based on the experimental data, the first order kinetic constants (k) were figured out to be 0.0012 min^{-1} and 0.0041 min^{-1} for the reaction using the TiO_2 before and after the H_2 treatment respectively.

[Fig. 9]

Then another set of tests was followed, but using the TiO_2 catalysts treated at different temperatures in the range of 25-800 °C. Based on the experimental data, the kinetic constants (k) were calculated and a relationship between the kinetic constant and the temperature used in the H_2 treatment is shown in Fig. 10. It can be clearly seen that the photodegradation rate increased significantly, while the heating temperature increased. A maximum value of k

occurred at the temperature of 500-600 °C. This result confirmed the enhanced photocatalytic activity of the H_2-treated TiO_2 catalysts again.

[Fig. 10]

4. Conclusion

The conventional TiO_2 power thermally treated with hydrogen gas demonstrated a significant improvement in the photocatalytic degradation of SSA and phenol in its aqueous suspensions. An optimal temperature of the H_2 treatment was found to be between 500 and 600 ^{o}C. The EPR results showed that during the hydrogen treatment, OV were first produced and Ti^{3+} was then generated. Both the OV and Ti^{3+} were attributed to the enhancement of photocatalytic activity. The modified TiO_2 catalyst containing OV and Ti^{3+} was quite stable at a mild temperature. It has a good potential to be used in photodegradation for water and wastewater treatment as a more efficient photocatalyst.

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Fig. 1. The SSA photocatalytic degradation on the TiO_2 catalysts before and after the H_2 reduction treatment at 550 ^oC.

Fig. 2. The effect of the H_2 treatment temperature on the rate of SSA photocatalytic degradation.

Fig. 3. The TPR spectrum of H_2 consumption vs. H_2 treatment temperature during the H_2 treatment.

Fig. 4. The EPR spectra of oxygen vacancies (OV) and trivalent titanium (Ti^{3+}) during the H_2 treatment.

Fig. 5. The EPR intensity of Ti^{3+} and OV vs. H_2 treatment temperature during the H_2 treatment.

Fig. 6. The EPR spectra of OV and Ti^{3+} in the TiO_2 catalyst after 10 months storage.

Fig. 7. The photocatalytic activity of the H_2-treated TiO_2 catalyst after 10-month storage in SSA photodegradation.

Fig. 8. Stability of OV and Ti^{3+} in the TiO_2 catalysts under different conditions.

Fig. 9. The photocatalytic degradation of phenol in the TiO_2 suspensions (Hydrogen treatment temperature: 560 ^oC, light source: 6W UV lamp, wavelength: 365 nm).

Fig. 10. The rate of phenol photodegradation affected by the H_2 treatment temperature (Light source: 125 W high pressure mercury lamp, wavelength: <320 nm).