Preparation and photocatalytic activity of Cu-deposited TiO_2 film with high transparency

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ABSTRACT

Cu-deposited TiO_2 films were prepared by photoreduction of Cu(II) in the presence of sodium formate. With the initial Cu(II) concentrations more than $100\,mg\,L^{-1}$, induction periods were observed before the transmittance decreased. Scanning electron microscopy indicated that Cu particles of $2.6 \pm 0.5\,\mu m$ were deposited isolatedly with much open space in the induction periods. The films prepared by changing the irradiation time within the induction periods showed a higher photocatalytic activity than a pure TiO_2 for the degradation of methylene blue under the reaction condition without purging air.

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1. Introduction

The use of TiO_2 photocatalysts in environmental cleanup has received much attention since TiO_2 is stable, harmless, inexpensive and potentially activated by solar energy [1]. As an effort to increase the photocatalytic efficiency on pollutant degradation, an enhancement of the activity was observed when metal particles were deposited on TiO_2 [2–5]. The metal can act as charge carrier traps, effectively enhancing charge separation of the electrons and holes and resulting in an increase in the quantum yield of surface photoreactions [5]. It has also been reported that the trapped electrons on the Cu which was loaded by TiO_2 reduced carbon dioxide to methanol [6–8]. Not only acting as electron traps but also changing reaction pathways by providing catalytic sites where intermediates can be stabilized have been reported as functions of the deposited metals [9–11].

Most of the studies have been conducted by using TiO_2 powders, where an optimum amount for the metal was given by a unit of wt% which was calculated by the mixing ratio in the preparation. Transmission electron micrographs were often provided to show morphology and size of the metal particles. Apart from catalysts for thermal reactions, an excess metal loading results a decrease in photocatalytic activities because of screening the surface of the photocatalyst. However, in the powder form, it is difficult to elucidate the effect of the size and coverage of the metals on

the photocatalytic performance. We have reported kinetic studies of the photocatalytic removal of Cu^{2+} ion from the viewpoint of the remediation of the contaminated water and the resulting change in transmittance of the TiO_2 film which was fabricated on an indium–tin oxide (ITO) glass [12,13]. We have found that the TiO_2 film kept transparent at a certain reaction condition although it was deposited by Cu particles. This finding suggests that Cu-deposited TiO_2 films can be fabricated with minimizing the screening effect on TiO_2 surface by loading of Cu. However, the ITO glass is not an appropriate support because its conducting property may affect the photocatalytic activity of the TiO_2 films. In this paper, we describe a novel preparation method to change the size and coverage of Cu on the TiO_2 films supported on the glass and examine the photocatalytic activity for the degradation of methylene blue (MB).

2. Experimental

Glasses (Micro slides glass, Muto Pure Chemicals Co., cut into $40\,mm \times 8\,mm$) as substrates for TiO_2 films were washed in water containing detergents under sonication for 30 min followed by washing with water thoroughly. Then the glasses were sonicated for 30 min in water. After washing with water thoroughly, the glasses were sonicated in acetone for 30 min and dried. Then the glass was coated with a commercially available precursor solution, T-199 B (Nagase ChemteX Co.), by spin-coating (2000 rpm for 30 s after 1000 rpm for 15 s) and sintered at $500\,^{\circ}C$ for 4 h with a rising rate of $3\,^{\circ}C\,min^{-1}$. This precursor solution is an ethanol solution containing titanium complexes of aminopolycarboxylic acids [14]. Laboratory grade water was prepared with a Milli-Q water system.

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The glass covered with TiO$_2$ was stood against the wall of a glass standard cell (1.25 cm × 1.25 cm × 4.5 cm, optical length: 1 cm) which contained 5–150 mg L^{-1} Cu^{2+} (as Cu(NO$_3$)$_2$) and 0.1 mol dm^{-3} HCOONa at pH 3.6. The cell was capped with a silicone rubber and two needles were used as inlet and outlet for nitrogen (99.999%, Sumitomo Seika Chemicals Co.) which was purged through the solution for 30 min before irradiation and in the upper gas phase during the irradiation. A 15 W black light (Toshiba EFD15BLB) was used as the light source and the intensity on the surface of the cell was measured to be 6.3 mW cm^{-2} at 365 nm by radio meter (UVR-400, Iuchi). The reaction temperature was maintained at 26.8 ± 0.2 °C. The transmittance of the cell was measured at the wavelength of 420 nm (Shimadzu UV-1600) although it did not depend on the wavelength in the region of 400–500 nm. The Cu^{2+} concentration in the solution was analyzed by inductively coupled plasma spectroscopy (Varian, ICP-AES Liberty Series II). The surface morphology of the films was observed using a scanning electron microscope (SEM, JSM-820, JEOL) operating at 15 kV. X-ray diffraction (XRD, RINT-2500, Rikagaku) analysis was performed with Cu Kα radiation (40 kV, 100 mA) at 2θ angles from 10° to 70° with a scan speed of 4° min^{-1}. Since Cu particles are oxidized in air, the glass covered with Cu-deposited TiO$_2$ films was removed from the reaction solution and stored under nitrogen atmosphere before the SEM and XRD measurements.

Photocatalytic degradation of 1 × 10^{-5} mol dm^{-3} MB was performed in a glass standard cell (1.25 cm × 1.25 cm × 4.5 cm, optical length: 1 cm), all of whose surfaces were transparent. Reaction apparatus and the light source were the same as described above, except for purging with air or exposing to air without capping instead of purging with nitrogen. Concentrations of MB were determined from absorbance at 664 nm. The TiO$_2$ film was located parallel to the light pass during the measurement in the spectrophotometer.

3. Results and discussion

When the experiments were performed with the initial Cu(II) concentration of 5–50 mg L^{-1}, the transmittance of the TiO$_2$ films decreased with an increase in irradiation time and approached a limiting value as shown in Fig. 1. These decreases in the transmittance were due to the deposition of Cu on the TiO$_2$ films by
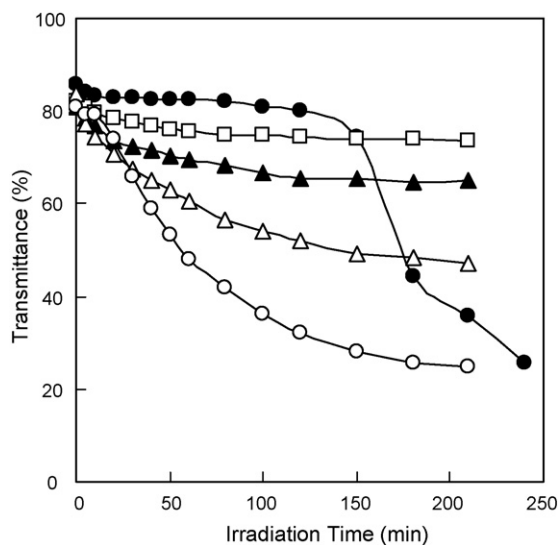

Fig. 1. Transmittance change against irradiation time. Conditions: 0.1 mol dm^{-3} HCOONa aqueous solution containing 5 mg L^{-1} (□), 10 mg L^{-1} (▲), 30 mg L^{-1} (△), 50 mg L^{-1} (○), and 100 mg L^{-1} (●) Cu(II).
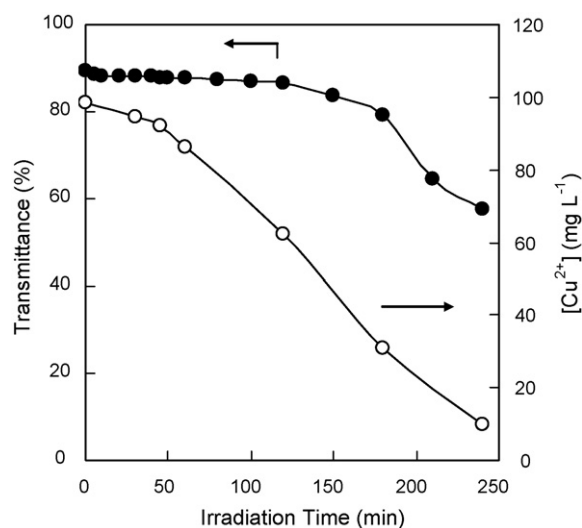

Fig. 2. Changes in transmittance of the TiO$_2$ film and in concentration of Cu(II) during irradiation. The initial concentration of Cu(II) was 100 mg L^{-1} in the presence of 0.1 mol dm^{-3} HCOONa.

photocatalytic reduction of Cu(II) ions. However, at the Cu(II) concentration above 100 mg L^{-1}, the transmittance did not change for a certain time which is referred as an induction period and then decreased. The induction period became longer as the initial Cu(II) concentration increased, i.e. it took 142 min for 100 mg L^{-1} and 300 min for 150 mg L^{-1}. The amounts of Cu deposited on the TiO$_2$ film were estimated by determining a decrease in the Cu(II) concentration in the reaction solution by the ICP measurements. Removal % of the Cu(II) ion from the reaction solution by depositing on the TiO$_2$ films were calculated to be 97.6%, 92.0%, 87.6%, 83.3% and 77.9%, respectively, for 5, 10, 30, 50, and 100 mg L^{-1} as initial concentrations.

In order to examine whether the photocatalytic reduction of Cu(II) proceeded or not during the induction period which was observed with 100 mg L^{-1} as the initial Cu(II) concentration, aliquot samples were withdrawn from the reaction solution at appropriate irradiation times, diluted with water and analyzed by the ICP measurements. Fig. 2 showed that the Cu(II) concentration decreased during the induction period where the transmittance hardly decreased. The SEM images were observed in order to clarify why the transmittance was not changed although the Cu deposited on the TiO$_2$ films. Fig. 3 showed that some particles of 2.6 ± 0.5 μm were deposited isolatedly when irradiating 100 mg L^{-1} Cu(II) solution for 30 min. After irradiating for 6 h, the film was covered with many particles of 0.83–3.6 μm. On the other hand, when irradiation was conducted in 50 mg L^{-1} Cu(II) solution for 6 h, small particles of 0.51 ± 0.04 μm were deposited closely. These observations suggest that, within the induction period, particles deposited isolatedly with much open space. This is the reason why the transmittance was not decreased so much in spite of the Cu deposition. Fig. 4(a) and (b) indicated XRD patterns of the TiO$_2$ films without and with Cu deposition, respectively. The latter was prepared by irradiating 50 mg L^{-1} Cu(II) solution for 6 h, which corresponded to the sample as shown at the right in Fig. 3. Fig. 4(a) showed a broad anatase peak, perhaps due to small TiO$_2$ nanocrystalline particle size. In Fig. 4(b), we observed (1 1 1) and (2 0 0) reflections of Cu metal near 43.3° and 50.4°. A size of 51.8 nm for the Cu metal was obtained from the observed full width at half-maximum and the Scherrer equation. This value was much smaller than that obtained by the SEM measurement (0.51 ± 0.04 μm), indicating that the nearly spherical particles observed in the SEM were aggregates of the Cu particles.

These findings proposed two methods to fabricate the TiO$_2$ films deposited with Cu. The Cu amounts loaded on the film can be veri-
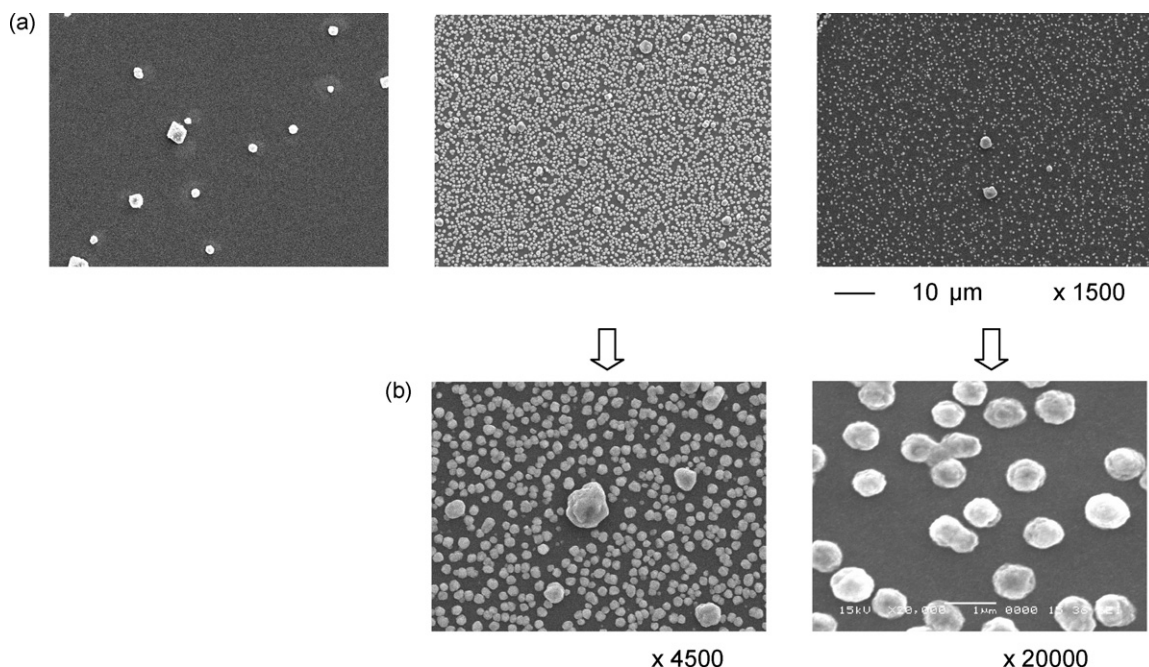
Fig. 3. SEM images of the TiO_2 films deposited with Cu. Conditions: $100 \, mg \, L^{-1}$ Cu(II) with the irradiation of 30 min (left) or 6 h (middle) and $50 \, mg \, L^{-1}$ Cu(II) with 6 h (right). (a) Magnification for all images was 1500. (b) Higher magnification was used to show Cu particles.

fied by changing the initial Cu(II) concentration in the region up to $50 \, mg \, L^{-1}$ (method A), or changing the irradiation time within the induction period under the Cu(II) concentration above $100 \, mg \, L^{-1}$ (method B). Fig. 5 illustrated the dependence of the transmittance of the film on the amounts of Cu loaded by these two methods. The amounts of Cu were varied in method A by changing the initial Cu(II) concentration (5, 10, 30, and $50 \, mg \, L^{-1}$) under irradiation of 210 min while, in method B, changing the irradiation time (45, 60, 120, 180, 240 min) under the initial Cu(II) concentration of $100 \, mg \, L^{-1}$. As the amount of Cu increased, the transmittance of

the film decreased. However, the transmittance of the film fabricated by method B did not decrease in the region of the deposited Cu less than 0.14 mg. The Cu-deposited TiO_2 film without a decrease in transmittance is expected to have a higher photocatalytic activity because no interference with the light energy reached on the TiO_2 surface. This prompted us to investigate the photocatalytic activity of the Cu-deposited TiO_2 films. However, when the film deposited by Cu was immersed into water, the dissolution of Cu(II) ion was observed due to the oxidation by the dissolved oxygen. Thus, the Cu-deposited film was sintered at 500 °C before conducting the photocatalytic experiments. Fig. 6 indicated the SEM images of the films which were sintered at 500 °C after deposition of 0.14 mg Cu by methods A and B. The film obtained by method A showed many small Cu particles of $0.97 \pm 0.06 \, \mu m$ and the transmittance of the film was 24.9%. On the other hand, the transmittance of the film fabricated by method B was 81.8% because of the much open space
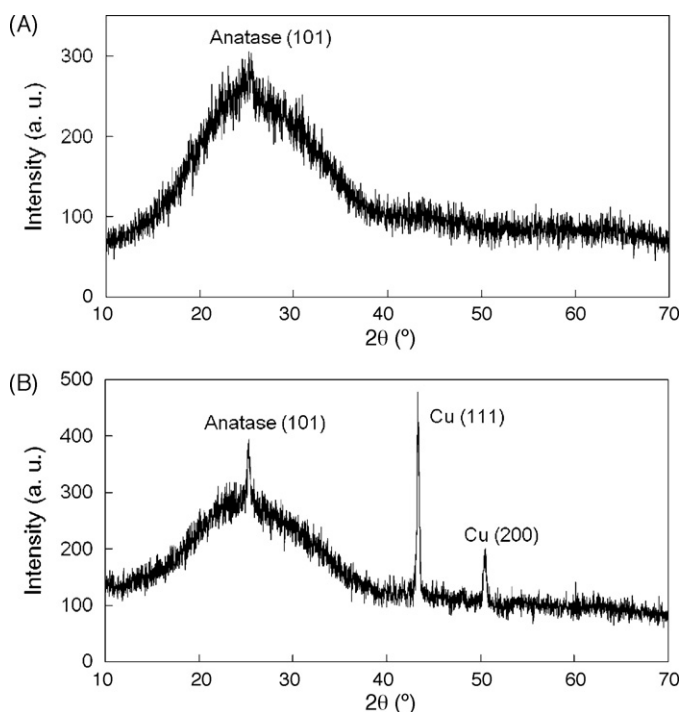

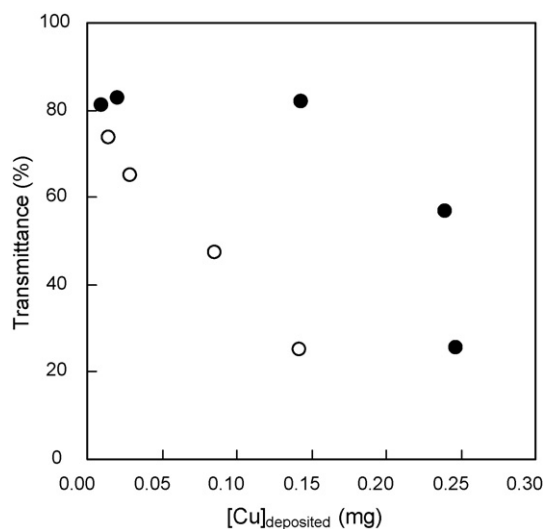**Fig. 4.** XRD patterns of (a) naked TiO_2 and (b) TiO_2 with Cu deposition.

Fig. 5. Effect of the amount of Cu-deposited on the transmittance of the TiO_2 films fabricated by method A (○) and method B (●).
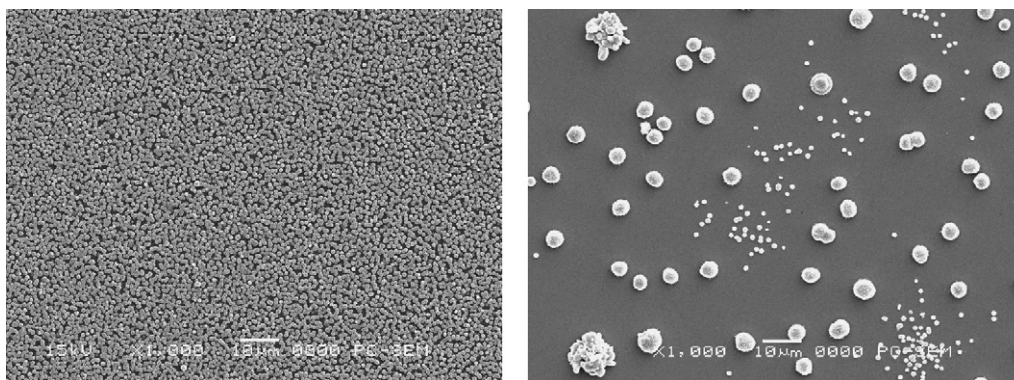
Fig. 6. SEM images of the TiO$_2$ films which were sintered at 500 °C after deposition of 0.14 mg Cu by method A (left) and method B (right).

between large particles of 4.6 ± 0.2 μm. The XRD measurements of the films which were sintered at 500 °C showed peaks attributable to CuO (1 1 1), indicating that the Cu particles were oxidized in the sintering process.

Photocatalytic degradation of methylene blue was performed in order to examine the photocatalytic activity of the films. Fig. 7 depicted the effect of the Cu amounts deposited by both methods on the initial degradation rate (V_o) of MB under air purging, where V_o was obtained by the initial slope of the plots of the concentration of MB against the irradiation time. Fig. 7 indicated that the degradation rates on the TiO$_2$ films fabricated by method B were higher than those by method A, as expected. Higher activity for method B was attributable to higher transmittance of the films compared with for method A. However, it is noted that the highest rate (1.41×10^{-7} mol dm^{-3} min^{-1}) was observed on the film without Cu deposition. The deposition of Cu on TiO$_2$ films has a negative effect for the degradation of MB under air purging. On the other hand, when the degradation experiments were performed on the pure TiO$_2$ without air purging, the degradation rate decreased to 4.39×10^{-8} mol dm^{-3} min^{-1} as shown in Fig. 8. It is generally believed that the MB was degraded oxidatively by the photogenerated holes. In the case of air purging, the concentration of dissolved oxygen maintained and oxygen trapped the photogenerated electrons to form O$_2^-$ ion. However, without air purging, the concentration of oxygen decreased with a progression of the reaction and the photogenerated electrons recombined with holes,

leading to a decrease in the photocatalytic oxidation. Fig. 8 illustrated that the deposition of Cu less than 0.14 mg showed higher activity than the pure TiO$_2$ film in the case of no purging with air. This finding indicates that Cu deposited on the surface by method B acts as the electron trap and then suppresses the recombination between holes and electrons.

In conclusion, the Cu-deposited TiO$_2$ film fabricated by method B was the more efficient photocatalyst working even without air purging because of the high transmittance and the function of Cu as the electron trap. The reason why Cu deposited isolatedly with much open space in method B remained unclear. The HCOONa was employed as a sacrificial donor in this study to consume the photogenerated holes. When the Na$_2$C$_2$O$_4$ was used instead of HCOONa, the transmittance of the films decreased without any induction period even with the initial Cu(II) concentration more than 100 mg L^{-1}. This may indicate that HCOONa affects the deposition of Cu. Sawunyama et al. reported that the photodecomposition process of stearic acid molecules on a TiO$_2$ film was inhomogeneous, with the various reaction initiation centers or nucleation regions being randomly distributed throughout the TiO$_2$ surface [15,16]. When the initial Cu(II) concentration was more than 100 mg L^{-1} in the presence of HCOONa as in method B, the Cu particles might grow at the most active parts on the TiO$_2$ film. The research is now being conducted to clarify the mechanism for the Cu deposition and to apply the obtained films for the practical decontamination of the environment.
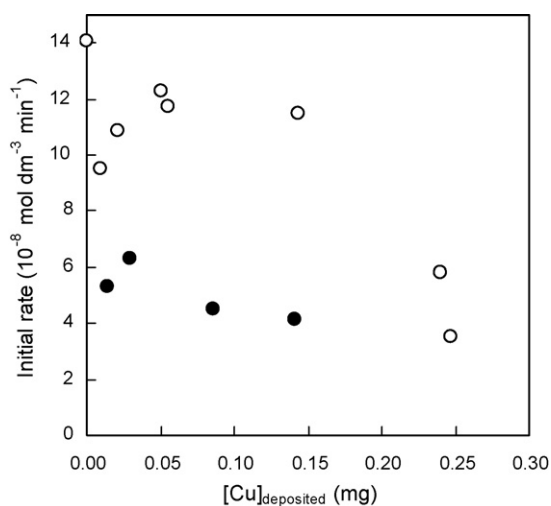

Fig. 7. Dependence of the initial degradation rate of MB under air purging on the amount of Cu deposited on TiO$_2$ films which were fabricated by method A (●) or method B (○).
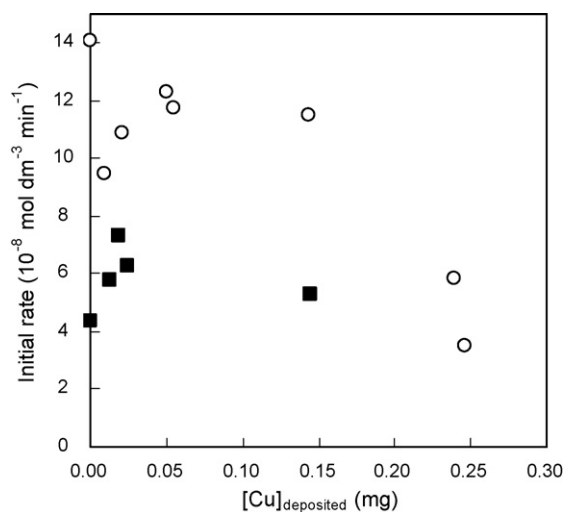

Fig. 8. Dependence of the initial degradation rate of MB without purging with air (■) on the amount of Cu deposited on TiO$_2$ films prepared by method B. The data (○) were the same as in Fig. 7, which were obtained with air purging.

Acknowledgment

References

[1] A. Fujishima, T. Rao, D.A. Tryk, J. Photochem. Photobiol. C: Rev. 1 (2000) 1.
[2] V. Subramanian, E. Wolf, P.V. Kamat, J. Phys. Chem. B 105 (2001) 11439.
[3] T. Ohsawa, Y. Yamamoto, M. Sumiya, Y. Matsumoto, H. Koinuma, Langmuir 20 (2004) 3018.
[4] B. Wen, C. Liu, Y. Liu, J. Phys. Chem. B 109 (2005) 12372.
[5] H. Einaga, T. Ibusuki, S. Futamura, Environ. Sci. Technol. 38 (2004) 285.
[6] I.H. Tseng, W.-C. Chang, J.C.S. Wu, Appl. Catal. B: Environ. 37 (2002) 37.
[7] I.H. Tseng, J.C.S. Wu, H.-Y. Chou, J. Catal. 221 (2004) 432.
[8] P. Ushbharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, Ind. Eng. Chem. Res. 45 (2006) 2558.
[9] S. Kim, W. Choi, J. Phys. Chem. B 106 (2002) 13311.
[10] J. Lee, W. Choi, Environ. Sci. Technol. 38 (2004) 4026.
[11] J. Lee, W. Choi, J. Phys. Chem. B 109 (2005) 7399.
[12] S. Yamazaki, S. Iwai, J. Yano, H. Taniguchi, J. Phys. Chem. A 105 (2001) 11285.
[13] S. Yamazaki, N. Takemura, Y. Yoshinaga, A. Yoshida, J. Photochem. Photobiol. A: Chem. 161 (2003) 57.
[14] T. Otsuki, T. Yanagihara, Y. Sakashita, M. Sato, T. Nishide, Key Eng. Mater. 206–213 (2002) 539.
[15] P. Sawunyama, L. Jiang, A. Fujishima, K. Hashimoto, J. Phys. Chem. B 101 (1997) 11000.
[16] P. Sawunyama, A. Fujishima, K. Hashimoto, Langmuir 15 (1999) 3551.