Title	Immobilization of highly active titanium(IV) oxide particles A novel strategy of preparation of transparent photocatalytic coatings
Author(s)	Kominami, Hiroshi; Kumamoto, Hisayuki; Kera, Yoshiya et al.
Citation	Applied Catalysis B Environmental, 30(3-4), 329-335 https://doi.org/10.1016/S0926-3373(00)00245-9
Issue Date	2001-03-12
Doc URL	https://hdl.handle.net/2115/17130
Type	journal article
File Information	ACBE30-3-4.pdf

Immobilization of Highly Active Titanium(IV) Oxide Particles. A Novel Strategy of Preparation of Transparent Photocatalytic Coatings

Hiroshi Kominami,[1] Hisayuki Kumamoto,[1] Yoshiya Kera,[1] and Bunsho Ohtani[2]

[1]*Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka, Osaka 577-8502, Japan*

[2]*Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan*

Abstract

Titanium(IV) oxide (TiO_2) powders synthesized by HyCOM (hydrothermal crystallization in organic media) method, which had been proved to exhibit ultra-high photocatalytic activity in several reaction systems, were used as starting material for fabrication of transparent TiO_2 thin films. HyCOM-TiO_2 powders were dispersed in aqueous solution of nitric acid to yield a TiO_2 sol stable for more than 90 days. Transparent TiO_2 thin films were successfully produced by dip-coating from the TiO_2 sol and used for photocatalytic decomposition of malachite green (MG) in an aqueous solution under aerated conditions. These films exhibited much higher rate of MG decomposition compared with those prepared from a commercially available TiO_2 sol developed for photocatalytic use (Ishihara STS-01), indicating that the excellent photocatalytic activity of original HyCOM-TiO_2 particles was preserved after immobilization on glass substrates by the present method.

Keywords: Titanium oxide; Photocatalyst; Thin film; Photodecomposition

1. Introduction

One of the most significant environmental applications of semiconductor photocatalysis is photoinduced removal of pollutants from air and water [1-4], as well as deodorization, prevention of stains, and sterilization [5], under ambient conditions. The most potent and almost sole candidate of the photocatalyst is titanium(IV) oxide (TiO_2) because of its high activity, photostability, and availability. A key technology for realization of the practical application is preparation of immobilized-TiO_2 coatings, e.g., fabrication of transparent TiO_2 thin film on a glass substrate. Chemical and physical vapor deposition technique has been widely applied for the preparation of such thin films. Since these vapor methods need instrumental setup which enables to control temperature and pressure, their initial and running costs are generally high and the size of substrate is limited. As an alternative, sol-gel processes including dip or spin-coating as a final step of preparation have been also used to prepare various kinds of metal oxide thin films, mainly due to relatively low cost and flexible applicability to wide ranges of size and shape of substrates. Through this technique, TiO_2 films of high photocatalytic activity were produced [6-8]. Preparation of TiO_2 films from crystalline colloidal TiO_2 solution were also reported [9-11] and recently TiO_2 thin films of high photocatalytic activity were obtained from a TiO_2 sol prepared by hydrothermal treatment of peroxotitanic acid solution [12, 13] or an alkoxide-derived TiO_2 gel [14]. It is well known that the photocatalytic activity of these coatings strongly depends on the preparation and post-deposition treatments, since they give decisive influence on the chemical and physical properties of TiO_2 included in the coatings. Therefore, it is necessary to choose adequate processing conditions to yield highly active photocatalytic coatings.

Alternative promising strategy for making highly active photocatalytic coatings is attachment of stable TiO_2 particles of high photocatalytic activity onto substrate without reduction of their activity during the processing. If the size of the particles is enough small, transparent photocatalytic films are, in principle, available. Recently, we found that anatase TiO_2 powders having both high crystallinity and large surface area could be directly synthesized by hydrolysis of titanium alkoxides in organic solvents with a small amount of water that was dissolved in the solvents at high temperatures (>423 K) [15, 16]. Thus-produced TiO_2 powders (HyCOM, Hydrothermal Crystallization in Organic Media) exhibited photocatalytic activity much higher than representative active photocatalysts, P-25 (Degussa) and ST-01 (Ishihara) for dehydrogenation of 2-propanol [17], silver metal deposition [17, 18], and N-cyclization of (S)-lysine [19]. In addition to these reactions under deaerated conditions, photocatalytic mineralization of acetic acid in aerated aqueous solutions was also examined and the HyCOM-TiO_2 nanoparticles exhibited much higher rate of CO_2 formation from acetic acid [20]. Since HyCOM-TiO_2 powders satisfied the basic requirements for active TiO_2 photocatalyst which have been proposed based on the kinetic investigations [21], i.e., high crystallinity and large surface area, these superior activities can be reasonably interpreted. Therefore, the HyCOM-TiO_2 nanoparticles should be a most promising candidate as a source of active photocatalytic coatings.

In this paper, we prepared a stable TiO_2 sol (HyCOM-sol) from HyCOM-TiO_2 powders and produced transparent TiO_2 thin film (HyCOM-film) by dip-coating from the HyCOM-sol. The excellent photocatalytic activities of HyCOM-sol and HyCOM-film are reported.

2. Experimental

2.1 Synthesis of HyCOM-TiO_2 powders and preparation of sol and transparent thin film from HyCOM-TiO_2 powders

HyCOM-TiO_2 powders were synthesized according to the procedure previously reported [15-20]. Titanium n-butoxide (Kanto Chemical, Tokyo, Japan) was dissolved in toluene (70 cm^3) in a test tube that was then set in a 200 cm^3 autoclave. In the gap between the test tube and the autoclave wall, 5 cm^3 of water was placed. The autoclave was thoroughly purged with nitrogen, heated to 573 K at a rate of 2.5 K min^{-1} and kept at that temperature for 2h. After the autoclave treatment, resulting powder was washed repeatedly with acetone under sonication to remove organic species. The thus-obtained HyCOM-TiO_2 powder (ca. 6 g) was added to diluted nitric acid (80 cm^3; 10^{-2} mol dm^{-3}, pH 2) to obtain HyCOM-sol-A and then centrifuged at 3000 rpm for 1 h. HyCOM-TiO_2 thin film was obtained by dipping a slide glass in the sol and subsequent annealing; a glass substrate was pulled up at a constant speed (2 mm min^{-1}) and then dried at room temperature. The dried TiO_2 film was heated to 723 K at a rate of 10 K min^{-1} in air in a box furnace and kept at that temperature for 30 min. This procedure of dip-coating followed by thermal treatment was repeated several times to obtain thicker films.

2.2 Characterization

Powder X-ray diffraction (XRD) (RINT 2500, Rigaku) was measured using Cu$K\alpha$ radiation with a carbon monochromater. Crystallite size was calculated from the half-height width of the 101 diffraction peak of anatase using the Scherrer equation. The value of the shape factor, K, was taken to be 0.9. Morphology of the TiO_2 was observed on a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV in the Joint Research Center, Kinki University. Particle size distribution of TiO_2 in the prepared sol was measured by a Shimadzu laser diffraction particle analyzer, SALD-2000B. The thickness of TiO_2 thin film was determined from the difference in the height between the TiO_2 coating and the substrate glass using a Nihon Shinku surface profile measuring system, Dektak 3. Absorption spectrum of TiO_2 thin film was measured by a Shimadzu UV-120 spectrometer.

2.3 Photocatalytic activity of HyCOM-sol for mineralization of acetic acid in aqueous solution under aerated conditions

Photocatalytic activity of HyCOM-sol for mineralization of acetic acid in aerated aqueous suspension was determined according to the previous papers [20, 22, 23]. Prior to the photocatalytic reaction, decomposition of contaminated organic moieties on the TiO_2 surface was carried out; HyCOM-sol 5 cm^3 (TiO_2 content: 30 mg) was photoirradiated at wavelength >300 nm by a high-pressure mercury arc (400 W) under oxygen with magnetic stirring until carbon dioxide (CO_2) was not liberated any more. After the pretreatment, air was bubbled into the sol for 30 min, and then acetic acid (175 µmol) was injected through a rubber septum. The resulting aerated sol was irradiated again at room temperature. Amount of CO_2 in the gas phase was measured at every 1 h by a Shimadzu GC-8A gas chromatograph equipped with a Porapak QS column.

2.4 Photocatalytic activity of HyCOM-films for decomposition of malachite green in aqueous solution under aerated conditions

Photocatalytic decomposition of malachite green (MG) in aqueous solution under aerated conditions was chosen to evaluate photocatalytic activity of TiO_2 thin films. HyCOM-film (20 cm^2), the surface of which was hydrophobic before irradiation, was photoirradiated at wavelength >300 nm by the high-pressure mercury arc under air for more than 1 h until it showed hydrophilicity [24]. Then the film was laid on the bottom of a dish (9.7 cm in diameter) filled with an aqueous solution (5 µmol dm^{-3}, 20 cm^3) of oxalate salt of MG $(C_{23}H_{24}N_2)_2(C_2H_2O_4)_3$). Photoirradiation was performed through the aerated MG solution under magnetic stirring by a 10 W black light (distance: 10 cm). The MG concentration was measured from its absorbance at 611 nm.

3. Results and Discussion

3.1 Sol and films prepared from HyCOM-TiO_2 particles

Figure 1 shows an XRD pattern of the starting HyCOM-TiO_2 powder consisting of anatase crystallites without any contamination of rutile or brookite. The size of anatase crystallites was calculated to be 11 nm from the broadening of its 101 diffraction peak and was consistent with their large specific surface area (156 m^2g^{-1}).

In a preliminary experiment, it was found that a diluted nitric acid solution (pH 2) was one of the best medium to make stable suspension of HyCOM-TiO_2 particles, as suggested in a previous report for TiO_2 powders [25]. In this study, HyCOM-sol at pH 2 was used. As Fig. 2 shows, an as-dispersed sol (HyCOM-sol-A) showed wide particle-size distribution with median size of 0.926 μm, suggesting the presence of large aggregated secondary particles. Centrifugation of HyCOM-sol-A at 3000 rpm for 1 h gave a sol (HyCOM-sol-B), which showed narrower particle-size distribution (30-200 nm, Fig. 2) with smaller median size of 88 nm. TEM observation (Fig. 3) revealed that HyCOM-sol-B consisted of agglomerates, corresponding to the median size shown above, of primary particles of average diameter 11 nm, which agreed with the crystallite size estimated by XRD, indicating that each particle observed in TEM is a single crystal of anatase. The HyCOM-sol-B was stable for more than 90 days.

Thickness of HyCOM-TiO_2 thin film obtained by a single dip-anneal cycle (HyCOM-film-A) was ca. 50 nm and increased to ca. 110 nm after three cycles (HyCOM-film-B). Figure 4 shows an XRD pattern of HyCOM-film-A. An intense 101 diffraction peak of anatase indicated the orientation of TiO_2 crystallites included in this thin film. Similar orientation of anatase crystallites has been also reported by Negishi et al., [6, 7, 8] who prepared thick TiO_2 films (1 μm) by dip-coating of a TiO_2 sol. Figure 5 shows absorption spectra of HyCOM-film-A and B as well as the glass substrate. Clearly the TiO_2 coating absorbs light of ultraviolet region while negligible absorption was seen in the visible region. Thus, the present method enables us to immobilize the HyCOM TiO_2 particles without losing transparency in visible region. The photoabsorption of the film, estimated by subtraction of substrate part from the transmission spectrum shown in Fig.5, was almost proportional to the thickness for each TiO_2 (Table 1). For comparison, another TiO_2 film was also prepared from commercial TiO_2 sol, STS-01 (Ishihara) for photocatalytic use by dip-coating. Apparently no morphological difference in HyCOM and STS films was observed in scanning electron spectroscopy. However, STS film exhibits higher photoabsorption than HyCOM film with almost same thickness, which indicates that the former contains larger amount of TiO_2 than the latter because photoabsorption is proportional to the amount of TiO_2 and that density of TiO_2 in STS film is larger than that in HyCOM film. This suggests that porosity of TiO_2 in the latter film is larger than that in the former film although the amount of nitrogen adsorbed on these TiO_2 films was too small to evaluate to the pore structure and surface area. More porous structure of HyCOM film may be pointed out as one of the characteristic properties of HyCOM film.

3.2 Photocatalytic activity of HyCOM-sol for mineralization of acetic acid in aqueous solution

The previous reports [20, 22, 23] have revealed that stoichiometric decomposition ($CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$) proceeds by TiO_2 photocatalysts with fairly good reproducibility and its rate is less sensitive to the conditions, e.g., concentration of acetic acid. HyCOM-sol-B, source of the film, led to linear increase of CO_2 (Fig.6). The rate of CO_2 liberation (59 µmol h^{-1}) was almost twice larger than that by a sol of STS-01 (31 µmol h^{-1}) (Ishihara), which was developed for photocatalytic coatings. Photocatalytic decomposition of acetic acid in suspensions of representative active TiO_2 powders (Degussa P-25 and Ishihara ST-01) was also examined under the similar conditions of TiO_2 content and pH to result in inferior activity (20 and 16 µmol h^{-1} CO_2 formation, respectively). From these results, it is confirmed that HyCOM-sol-B possesses excellent photocatalytic activity for the mineralization of acetic acid, as a typical photocatalytic reaction under aerated conditions. It should be noted that in these photocatalytic reactions the thickness of light path is enough large and thereby almost complete photoabsorption can be expected. The difference in photocatalytic activity should depend solely on the efficiency of utilization of electron-hole pairs in each TiO_2 particle.

3.3 Photocatalytic activity of HyCOM-films for degradation of MG in aqueous solution

Figure 7 shows time course of absorbance of MG solution in the presence and absence of HyCOM-film-A. Practically no decrease in absorbance by immersing HyCOM-film-A or by keeping in the dark for 10 min indicated that adsorption of MG onto the film and thermal catalytic decomposition of MG can be neglected. In the absence of TiO_2 film, the UV irradiation reduced the absorbance negligibly, showing little direct photolysis of MG. On the other hand, the absorbance, i.e., the MG concentration was reduced in the presence of HyCOM-film-A along with irradiation time. These results clearly show that MG was photocatalytically decomposed by TiO_2 under UV irradiation, though at present we have no mechanistic details in the molecular level. Photocatalytic oxidation of MG with participation of molecular oxygen (O_2) is most probable. The rate of MG decomposition by several TiO_2 films immersed in its aqueous solution is summarized in Table 1. For each TiO_2 film, HyCOM and STS, the rate was increased with the film thickness, but not linearly; the rate of each thicker film (film-B) was less than that expected from the rate of each thinner film (film-A). This could not be attributed to non-linear photoabsorption property, since the photoabsorption of the film was almost proportional to the thickness for each TiO_2 (Table 1). Therefore, one of the reasons for non-linearity is that only the outer part of the TiO_2 could be exposed to the MG solution, i.e., penetration depth of the solution into the film is limited. Along with the thickness of TiO_2 film, the total number of absorbed photons, which produce electron-hole pairs, should be increased, but the number of adsorbed MG molecules can not be increased proportionally to result in the non-linearity of photocatalytic reaction rate. On the basis of these considerations, we can compare the photocatalytic activity of HyCOM and STS TiO_2 films depending on the film thickness, i.e., photoabsorption (Table 1). For each of thinner (film-A) and thicker (film-B) cases, the HyCOM films showed the higher rate but smaller photoabsorption while their thickness was even larger than the STS films. This fact unambiguously shows the higher efficiency of utilization of electron-hole pairs in HyCOM TiO_2 compared with STS-TiO_2; the ratio of efficiency should be larger than that of apparent rate of MG decomposition (1.3 and 1.4 for films-A and films-B, respectively). Careful inspection of the activity of the sol and the film shows that difference in the activity of HyCOM and STS films is relatively smaller compared with the sol. Immobilization of HyCOM (and also STS) TiO_2 and post thermal treatment of films might decrease the intrinsic activity in the sol state. However, if one compares the activity of two films of the same photoabsorption, it is clear that the HyCOM films are more active than the STS films (Fig. 8). Moreover, it should be noted that the rate of STS film almost was saturated at ca. 40 % absorption whereas the rate of HyCOM film was not saturated at the same absorption. This result can be explained by the porosity of TiO_2 in films as discussed previously, i.e., larger amount of

MG is adsorbed on the HyCOM films of higher porosity. Therefore, porosity of TiO_2 in films is also an important factor controlling the activity of TiO_2 films as well as the probability of electron-hole recombination. In the present stage, we can not determine which of two significant factors of photocatalytic activity, larger amount of adsorbed substrate and smaller probability of electron-hole recombination, predominates these results. It has been clearly demonstrated that superior photocatalytic activity of source HyCOM-TiO_2 particles is preserved after immobilization on the glass substrate.

4. Conclusion

Stable TiO_2 sol could be prepared by adding HyCOM-TiO_2 powders into dilute nitric acid (pH 2) and subsequent centrifugation to remove undispersed agglomerates, and was used for photocatalytic mineralization of acetic acid in aqueous solution under aerated conditions. This HyCOM-TiO_2 sol exhibited much higher rate of CO_2 formation than a commercial TiO_2 sol for photocatalytic use (STS-01) and suspensions of commercial active TiO_2 powders under similar conditions. Transparent TiO_2 thin film was successfully prepared from the HyCOM-TiO_2 sol by dip-coating and exhibited much higher rate of MG decomposition compared with the STS-01 films, indicating that use of TiO_2 powders of high activity is effective for fabrication of transparent TiO_2 thin films of excellent activity. Our recent studies on several photocatalytic reactions in the HyCOM-TiO_2 suspension system have shown that property of TiO_2 suitable for each reaction system depends on the type of reaction [18, 20, 22, 23]. For example, larger surface is preferable for mineralization of acetic acid in aqueous solution under aerated conditions and decrease in surface area by the calcination of TiO_2 results in the reduction of photocatalytic activity [20, 22, 23]. On the other hand, higher crystallinity rather than the surface area was needed for the photocatalytic O_2 formation

[18]. Thus, the design and control of the TiO_2 properties matching to the desired photocatalytic reaction system are required. As shown in this paper, the fabrication of films through immobilization of TiO_2 particles without losing their original photocatalytic activity is one of the most significant strategies.

Acknowledgment

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan (09750861, 09218202, and 09044114). B.O. thanks financial support of Grand-in-Aid for Scientific Research on Priority Area of “Electrochemistry of Ordered Interfaces.” Dr. K. Hashimoto (Osaka Municipal Technical Research Institute) is acknowledged for his help to measure particle size distribution.

References

[1] M. A. Fox, M. T. Dulay, Chem. Rev., 93 (1993) 341.

[2] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Chem. Rev., 95 (1995) 69.

[3] T. Ibusuki, K. Takeuchi, J. Mol. Catal., 88 (1994) 93.

[4] N. Serpone, E. Pelizzetti, Eds., Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989.

[5] T. Watanabe, A. Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, A. Fujishima, p. 747, in: Photocatalytic Purification and Treatment of Water and Air, D. E. Olis and H. Al-Ekabi Eds., Elsevier, 1993.

[6] N. Negishi, T. Iyoda, H. Hashimoto, A Fujishima, Chem. Lett., (1995) 841.

[7] N. Negishi, K. Takeuchi, T. Ibusuki, Appl. Surf. Sci., 121/122 (1997) 417.

[8] N. Negishi, K. Takeuchi, T. Ibusuki, J. Mater. Sci., 33 (1998) 5789.

[9] I. M. Thomas, Appl. Opt., 26 (1987) 4688

[10] H. G. Floch, J. Priotton, J. M. Thomas, Thin Solid Films, 175 (1989) 173.

[11] J. L. Keddie, P. V. Brawn, E. P. Giannelis, J. Am. Ceram. Soc., 76 (1993) 2529.

[12] H. Ichinose, M. Terasaki, H. Katsuki, J. Ceram. Soc. Jpn., 104 (1996) 715.

[13] H. Ichinose, H. Katsuki, J. Ceram. Soc. Jpn., 106 (1998) 344.

[14] Y. Tanaka, J. Ceram. Soc. Jpn., 107 (1999) 47.

[15] H. Kominami, Y. Takada, H. Yamagiwa, Y. Kera, M. Inoue, T. Inui, J. Mater. Sci. Lett., 15 (1996) 197.

[16] H. Kominami, M. Kohno, Y. Takada, M. Inoue, T. Inui, Y. Kera, Ind. Eng. Chem. Res., 38 (1999) 3925.

[17] H. Kominami, T. Matsuura, K. Iwai, B. Ohtani, S.-i. Nishimoto, Y. Kera, Chem. Lett., 1995, 693.

[18] H. Kominami, S.-y. Murakami, Y. Kera, B. Ohtani, Catal. Lett., 56 (1998) 125.

[19] B. Ohtani, K. Iwai, H. Kominami, T. Matsuura, Y. Kera, S.-i. Nishimoto, Chem. Phys. Lett., 242 (1995) 315.

[20] H. Kominami, J.-i. Kato, M. Kohno, Y. Kera, B. Ohtani, Chem. Lett., 1051 (1996).

[21] B. Ohtani, S.-i. Nishimoto, J. Phys. Chem., 97 (1993) 920.

[22] H. Kominami, J.-i. Kato, Y. Takada, Y. Doushi, B. Ohtani, S.-i. Nishimoto, M. Inoue, T. Inui, Y. Kera, Catal. Lett., 46 (1997) 235.

[23] H. Kominami, J.-i. Kato, S. Murakami, Y. Kera, M. Inoue, T. Inui, B. Ohtani, J. Mol. Catal. A, 144 (1999) 165

[24] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigashi, T. Watanabe, Nature, 388 (1997) 431.

[25] T. Imae, K. Muto, S. Ikeda, Colloid Polym. Sci., 269 (1991) 43.

Figure captions

Fig. 1 A part of XRD pattern of a source HyCOM-TiO_2 powder.

Fig. 2 Particle-size distribution (cumulative transmittance curves) of HyCOM-TiO_2 sols before (HyCOM-sol-A, broken line) and after (HyCOM-sol-B, solid line) centrifugation.

Fig. 3 A TEM photograph of the HyCOM-sol-B

Fig. 4 A part of XRD pattern of TiO_2 thin film (HyCOM-film-A) prepared from HyCOM-sol-B

Fig. 5 Transmission spectra of TiO_2 thin films with different thickness (50 nm for HyCOM-film-A and 110 nm for HyCOM-film-B)

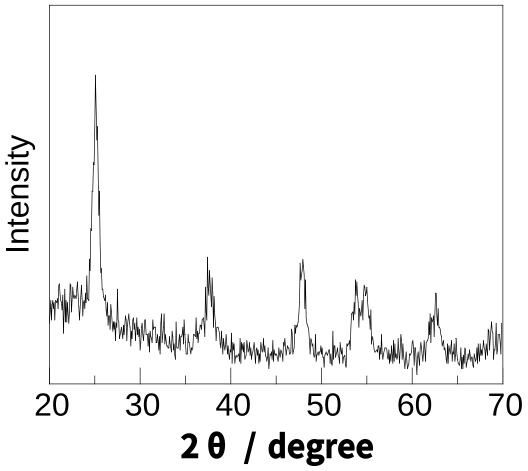
Fig. 6 Time course of the photocatalytic CO_2 formation from aqueous solution of acetic acid by HyCOM-sol-B (circle) and a commercial sol STS-01 (triangle)

Fig. 7 Time course of absorbance of MG solution in the presence of slide glass (triangle) or HyCOM-film-A (circle)

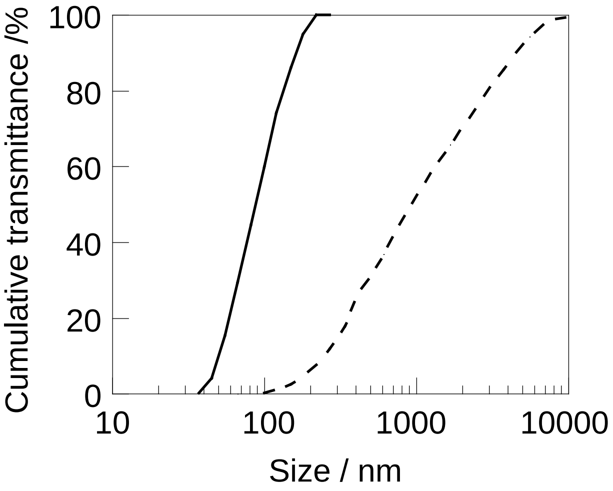
Fig. 8 Correlation between photoabsorption of HyCOM and STS films at 320 nm and rate for photocatalytic decomposition of MG

Table 1 Rate of photocatalytic decomposition of malachite green by TiO_2 thin films immersed in its aqueous solution (2.5×10^{-4} mol dm^{-3})

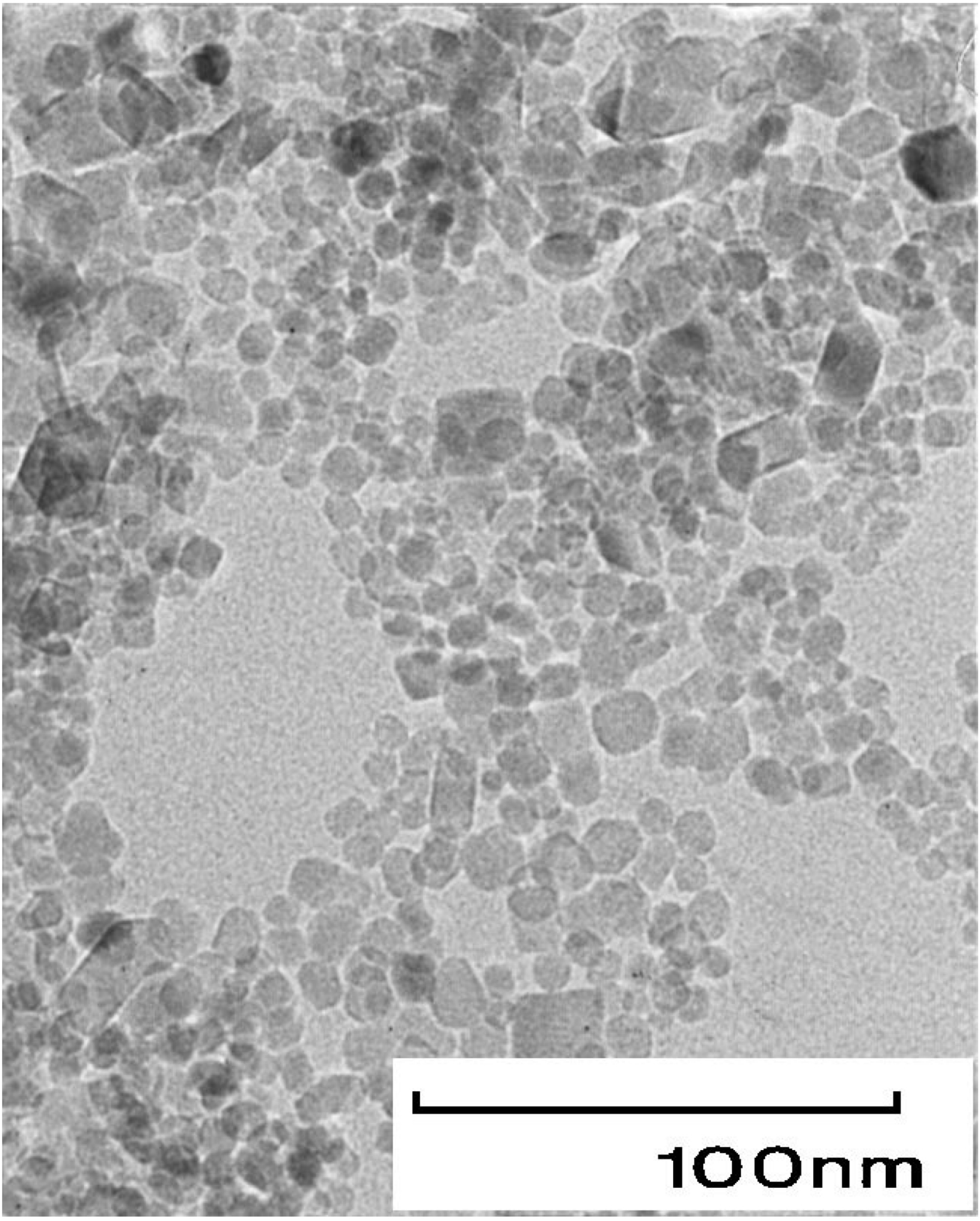
film	thickness / nm	% absorption at 320 nm	rate / % h^{-1}
HyCOM-film-A	50	20	52
HyCOM-film-B	110	38	73
STS-film-A	40	25	41
STS-film-B	100	52	52

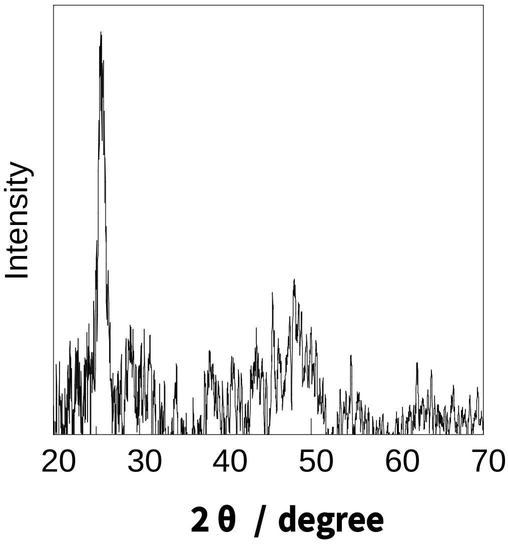


Kominami et al.,
Fig. 1

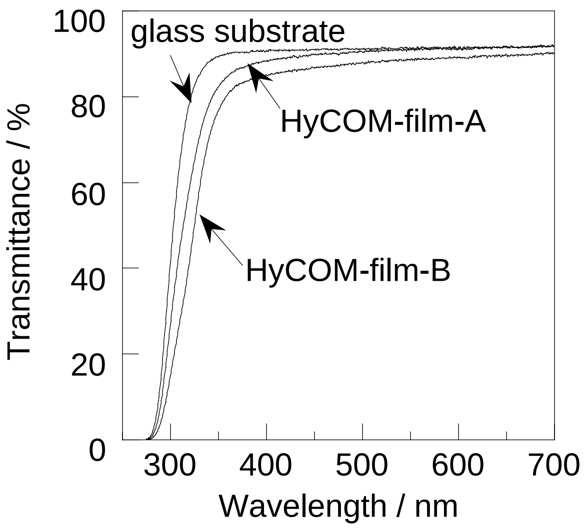


Kominami et al.,
Fig. 2

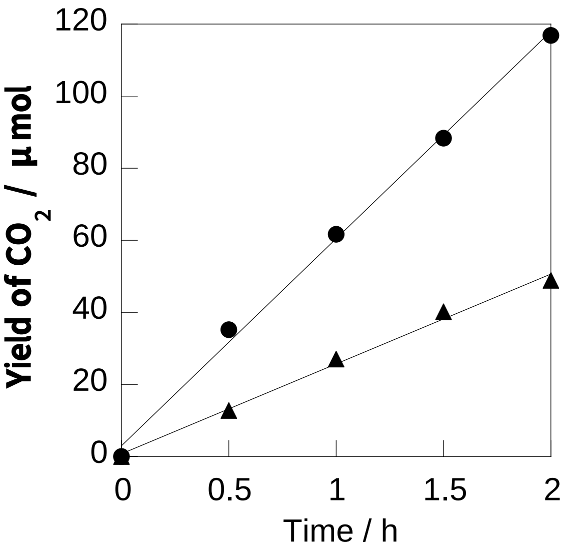

100nm



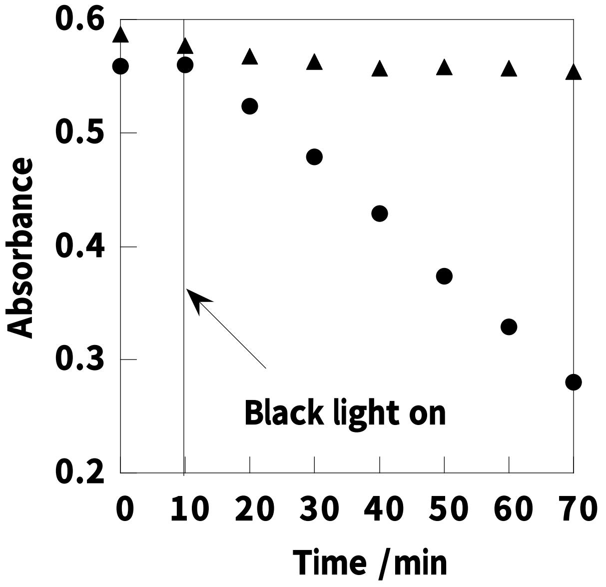
Kominami et al.,
Fig. 4



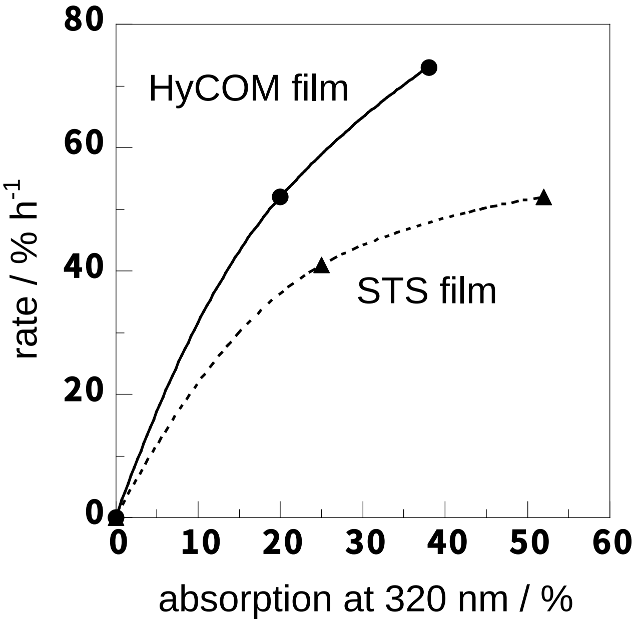
Kominami et al.,
Fig. 5



Kominami et al.,
Fig. 6



Kominami et al.,
Fig. 7



Kominami et al.,
Fig. 8