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Preparation of photoactive anatase-type TiO_2/silica gel by direct loading anatase-type TiO_2 nanoparticles in acidic aqueous solutions by thermal hydrolysis

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Titanium (IV) oxide (titania, TiO_2) is currently of considerable interest as a means of removing harmful organic impurities from water and air by photocatalytic purification and a great deal of work has been done in this area [1, 2]. A metastable phase of anatase-type TiO_2 exhibits the most excellent photoactivity among three polymorphs: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). It is required to improve the efficiency of the TiO_2-based photocatalysts. Since pure TiO_2 has little ability of adsorption of material, combination of the photoactive TiO_2 with an adsorbent (e.g., silica (SiO_2) gel having excellent adsorptivity), is effective for improvement of its efficiency. Not only does this provide preconcentration of the material near the photoactive sites, it also allows the possibility of adsorbing the material in the dark followed by later irradiation to decompose the material and restore the original photocatalyst. The addition of SiO_2 into TiO_2 was shown to be also effective for enhancement of the phase stability [3–5] and its own photocatalytic activity [6, 7]. Most mixed oxides and composites of TiO_2 and SiO_2 were produced by a sol-gel [4, 5, 7] and impregnation method. TiO_2-loaded silica gel was reported to be prepared via impregnation of titanium alkoxide solution into silica gel and heat treatment at 600 °C [8]. We have synthesized nanometer-sized crystalline metal oxide particles [9–15] , anatase-type TiO_2 [2], and ZrO_2-doped anatase-type TiO_2 [16, 17] using soft solution routes, e.g., hydrothermal technique.

The present study was concerned with applying thermal hydrolysis of acidic aqueous $TiOSO_4$ solution in order to directly load nanometer-sized anatase-type TiO_2 on the silica gel particles under mild hydrothermal condition, and their photoactivity was investigated.

Aqueous solutions of reagent-grade $TiOSO_4$ with Ti concentrations of 0.01–1.0 mol/dm^3 were prepared, and 90 cm^3 of each solution and 20 g of spherical silica gel before drying was taken into a Teflon container held in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 120 °C for 10 h under rotation at 20 rpm. After hydrothermal treatment, the silica gel were separated from the solution, washed with distilled water until the pH value of the rinsed water was 7.0, and maintained in distilled water at room temperature. A part of the samples after the hydrothermal treatment was dried in an oven at 65 °C for measurement of specific surface area, and pulverized for chemical analysis and X-ray diffraction.

The as-prepared samples were examined by X-ray diffractometry (XRD; model RINT-2000, Rigaku, Tokyo, Japan) with Cu K_α radiation. The crystallite size of anatase was estimated from the line broadening of 200 diffraction peak, according to the Scherrer equation. The specific surface area of the samples was measured from adsorption isotherm of nitrogen at 77 K based on the Brunauer-Emmett-Teller (BET) method (model Nova-1200, Yuasa Ionics, Japan). Photocatalytic activity and adsorptivity of these prepared samples were estimated separately from the change in the concentration of methylen blue (guaranteed reagent grade, $C_{16}H_{18}N_3S$, MB) in the dark and also under ultraviolet ray irradiation from black light (10 W). The sample of 0.5 g was maintained on a stainless-steel net in an aqueous 5 ppm MB solution of 100 cm^3 and then either irradiated by ultraviolet ray (UV) with an intensity of 24 mW/cm^2 for 1–8 h under stirring or maintained in the dark for 1–8 h with stirring. The photocatalytic activity and adsorptivity was measured from the absorbance change with a spectrophotometer (V-560, Nihon Bunko, Tokyo, Japan). The photocatalytic activity was also estimated using 10 ppm MB solution of 100 cm^3 under the UV irradiation for 1–24 h by means of the similar method as mentioned above.

XRD patterns of TiO_2-loaded silica gel samples that were prepared from the $TiOSO_4$ solutions having Ti concentration of 0.01–1.0 mol/dm^3 by thermal hydrolysis at 120 °C for 10 h are shown in Fig. 1. Table I shows analyzed content of TiO_2 loaded on the silica gels in the as-prepared samples. The amount of loaded

TABLE I Characterization of samples

Sample	Concentration of $TiOSO_4$ solution (mol/dm^3)	Analytical value of TiO_2 (mol%)	Specific surface area (m^2/g)	Crystallite size (nm)
(0)	Without treatment	0.0	666	–
(i)	0.01	0.2	703	–
(ii)	0.1	3.8	659	–
(iii)	1.0	21.4	533	10

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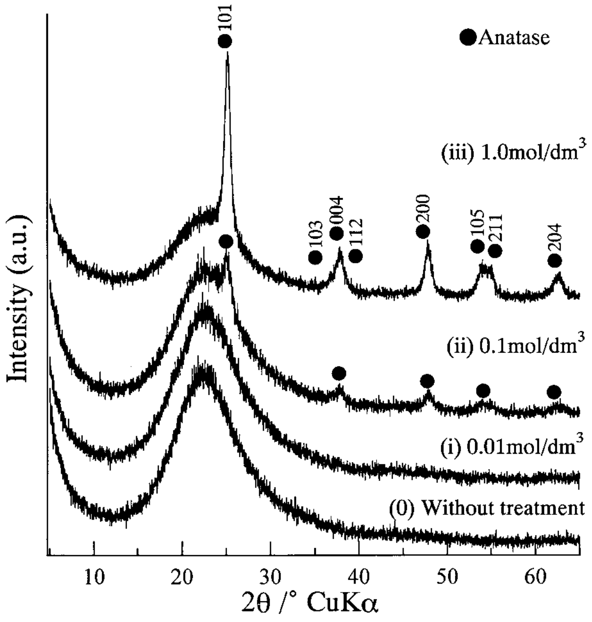

Figure 1 XRD patterns of silica gel samples (0) without treatment and after hydrothermal treatment in an aqueous solution of $TiOSO_4$ with Ti concentration of (i) 0.01, (ii) 0.1, and (iii) 1.0 mol/dm^3 at 120 °C for 10 h.

TiO_2 is found to closely depend on the concentration of $TiOSO_4$ solution from the result of analyzed content of TiO_2 listed in Table I, since the amount of TiO_2 loaded on the silica gels in the 1.0 mol/dm^3 $TiOSO_4$ solution was nearly 100 times as much as that loaded in the 0.01 mol/dm^3 solution. Anatase as crystalline phase was only detected in all of the as-prepared samples, no trace of diffraction peaks due to another crystalline phase being detected, although the diffraction peaks of anatase were hardly observed in the sample prepared from 0.01 mol/dm^3 $TiOSO_4$ solution. The XRD intensity of anatase in the samples increased with increasing the concentration of $TiOSO_4$ solution, corresponding to increase in the loaded TiO_2 content in the samples listed in Table I. The crystallite size of the anatase-type precipitates on the silica gels prepared from 1.0 mol/dm^3 $TiOSO_4$ solution determined from 200 XRD peak was 10 nm as shown in Table I.

Fig. 2 shows photographs of the appearance of the as-prepared TiO_2-loaded silica gel samples. The translucency of the samples is clearly observed to decrease with increasing the concentration of the $TiOSO_4$ solution i.e., the content of loaded TiO_2. The specific surface area of the as-prepared anatase type TiO_2/silica

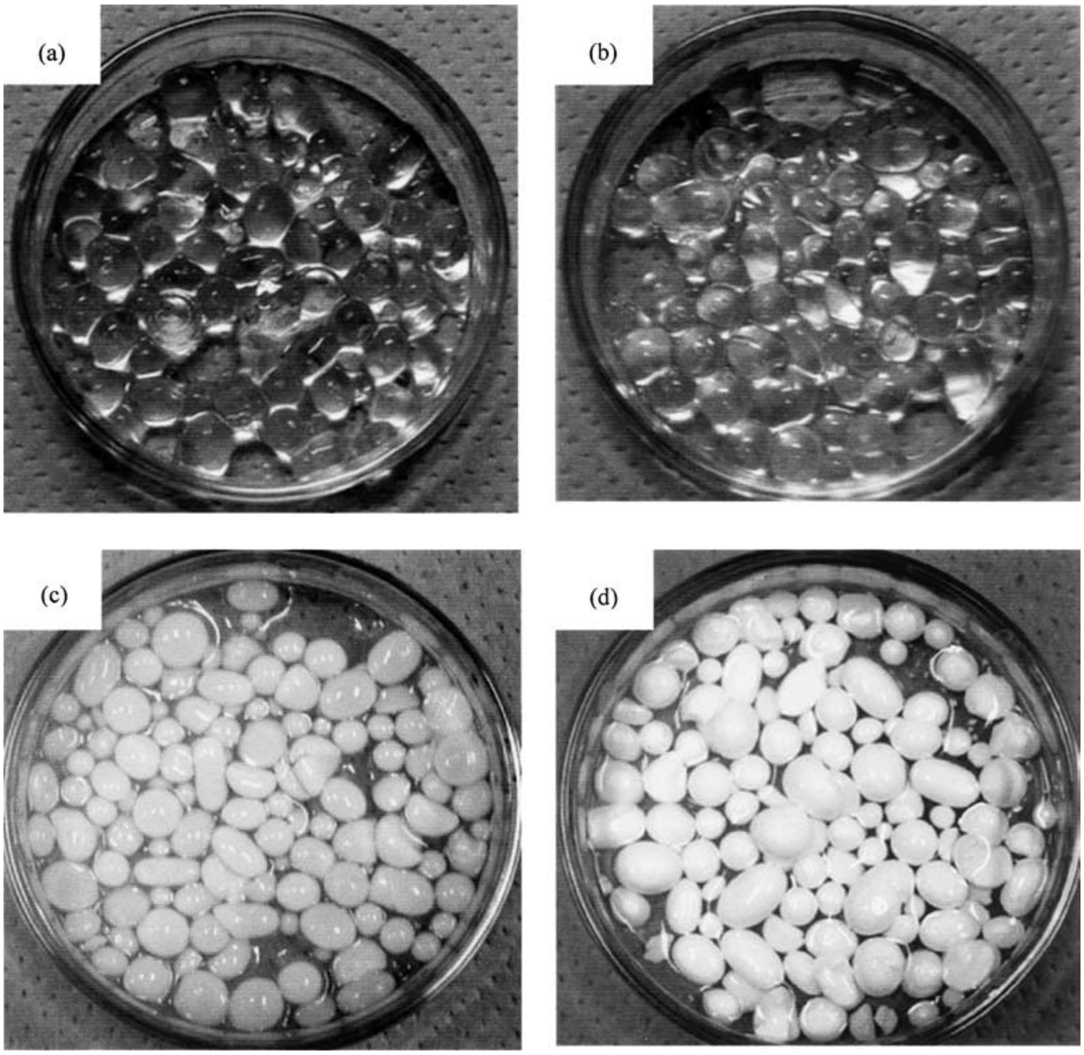

Figure 2 Photographs of appearance of silica gel samples: (a) without treatment and after hydrothermal treatment in an aqueous solution of $TiOSO_4$ with Ti concentration of (b) 0.01, (c) 0.1, and (d) 1.0 mol/dm^3 at 120 °C for 10 h.

gel samples decreased with increasing SiO_2 content as shown in Table I. Fine anatase particles covered most of the surface of the silica gel as shown in Fig. 2d and the specific surface area of the silica gel prepared from 1.0 mol/dm^3 $TiOSO_4$ solution became the least value (Table I). In the present study, direct loading nanometer-sized anatase-type TiO_2 on the silica gel using hydrolysis of $TiOSO_4$ solution was confirmed to be practically possible.

The effects of the presence and the amount of loaded TiO_2 on the MB adsorption for the silica gel and on the photodecomposition of MB for the TiO_2-loaded sample were investigated. The change in MB concentration of 5 ppm MB solution after maintaining the sample in the dark without UV irradiation with stirring or maintaining it under UV irradiation with stirring are shown in Fig. 3a and b as a function of time. The MB adsorption in the dark via the silica gel decreased with increasing the amount of loaded TiO_2. Loading a small amount (0.2 mol%) of TiO_2 on the silica gel fairly affected its adsorption as shown in the sample prepared from 0.01 mol/dm^3 dilute $TiOSO_4$ solution, and the MB adsorption still more decreased with increasing loaded-TiO_2 content, i.e., concentration of $TiOSO_4$. The sample loaded 21.4 mol% TiO_2 that was prepared from 1.0 mol/dm^3 $TiOSO_4$ solution scarcely showed MB adsorption. Saturation time for MB adsorption in the samples also decreased with increasing the amount of TiO_2 loaded. The MB adsorption of the TiO_2-loaded samples saturated within nearly 2 h as shown in Fig. 3.

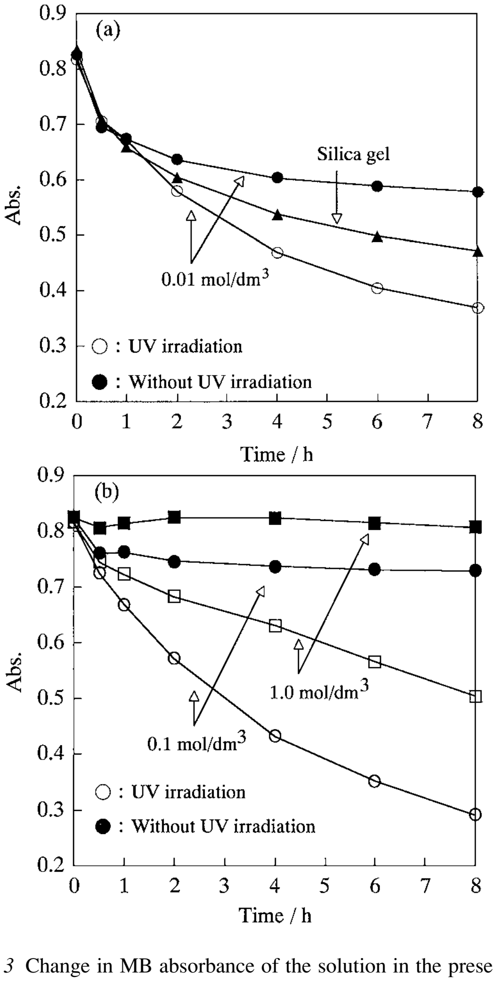

Figure 3 Change in MB absorbance of the solution in the presence of silica gel and TiO_2-loaded one in the dark and under UV irradiation with time (condition: 5 ppm MB solution of 100 cm^3 in the presence of 0.5 g sample): (a) silica gel and TiO_2-loaded one prepared from 0.01 mol/dm^3 $TiOSO_4$ solution and (b) TiO_2-loaded one prepared from 0.1, and 1.0 mol/dm^3 $TiOSO_4$ solution.

The difference between relative MB concentration in the solution after maintaining the sample under UV irradiation and that after maintaining it in the dark without UV irradiation (shown in Fig. 3) can be regarded as photocatalytic decomposition of MB by loaded TiO_2. Even in the sample containing very small amount (0.2 mol%) of loaded TiO_2 prepared from 0.01 mol/dm^3 $TiOSO_4$ solution, steady decomposition of MB was observed. Efficiency of photocatalytic MB decomposition was enhanced by combination of the photoactive nanometer-sized anatase-type TiO_2 material with silica gel adsorbent. The anatase-type TiO_2-loaded silica gel prepared from 0.1 mol/dm^3 $TiOSO_4$ solution showed the most enhanced photocatalytic activity in 5 ppm MB solution after UV irradiation for 8 h.

The rate of decrease in MB concentration in 10 ppm MB solution of 100 cm^3 in the presence of the 0.5 g sample prepared from 0.01–1.0 mol/dm^3 $TiOSO_4$ solution is shown in Fig. 4 as the change in absorbance of MB with UV irradiation time. Although the decrease rate of the sample prepared from 1.0 mol/dm^3 solution was low under 6 h of UV irradiation time due to the lowest MB adsorption, 10 ppm MB solution of 100 cm^3 was thoroughly decomposed after UV irradiation for 24 h.

In conclusion, combination of the photoactive TiO_2 material with silica gel adsorbent was performed by direct loading nanometer-sized anatase-type TiO_2 on the silica gel using hydrolysis of $TiOSO_4$ solution under mild hydrothermal condition at 120 °C for 10 h. The amount of loaded anatase-type TiO_2 on the silica gel was increased and translucency of the silica gel samples was decreased with increasing the concentration of the $TiOSO_4$ solution. Efficiency of photocatalytic activity for the decomposition of methylene blue was enhanced by combination of the photoactive anatase-type loaded-TiO_2 material with silica gel adsorbent and by controlling the amount of loaded-TiO_2, which was

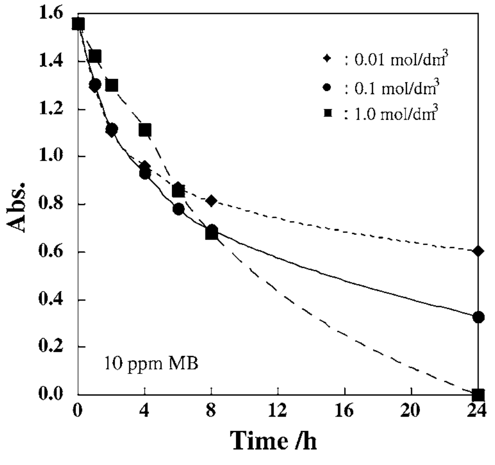

Figure 4 Change in MB absorbance of the solution in the presence of TiO_2-loaded silica gel (prepared from 0.01, 0.1, and 1.0 mol/dm^3 $TiOSO_4$ solution) under UV irradiation with time (condition: 10 ppm MB solution of 100 cm^3 in the presence of 0.5 g sample).

performed by means of controlling the concentration of $TiOSO_4$ solution.

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References

1. M. A. FOX and M. T. DULAY, *Chem. Rev.* **93** (1993) 341.
2. M. INAGAKI, Y. NAKAZAWA, M. HIRANO, Y. KOBAYASHI and M. TOYODA, *Int. J. Inorg. Mater.* **3** (2001) 809.
3. Y. SUYAMA and A. KATO, *Yogyo Kyokaishi (J. Ceram. Soc. Jpn.)* **86** (1978) 119 (in Japanese).
4. M. YOSHINAKA, K. HIROTA and O. YAMAGUCHI, *J. Amer. Ceram. Soc.* **80** (1997) 2749.
5. K. OKADA, N. YAMAMOTO, Y. KAMESHIMA, A. YASUMORI and K. J. D. MACKENZI, *ibid.* **84** (2001) 1591.
6. C. ANDERSON and A. J. BARD, *J. Phys. Chem.* B **101** (1997) 2611.
7. X. FU, L. A. CLARK, Q. YANG and M. A. ANDERSON, *Environ. Sci. Technol.* **30** (1996) 647.
8. H. TAODA and K. KATO, Japan Patent no. 2775399 (May 1, 1998).
9. M.HIRANO, H. MORIKAWA, M. INAGAKI and M. TOYODA, *J. Amer. Ceram. Soc.* **85** (2002) 1915.
10. M. HIRANO and H. MORIKAWA, *Chem. Mater.* **15** (2003) 2561.
11. M. HIRANO and N. SAKAIDA, *J. Ceram. Soc. Jpn.* **111** (2003) 176.
12. M. HIRANO, S. OKUMURA, Y. HASEGAWA and M. INAGAKI, *J. Sold State Chem.* **168** (2002) 5.
13. M. HIRANO and N. SAKAIDA, *Amer. Ceram. Soc.* **85** (2002) 1145.
14. M. HIRANO, T. MIWA and M. INAGAKI, *J. Amer. Ceram. Soc.* **84** (2001) 1728.
15. M. HIRANO and K. HIRAI, *J. Nanoparticle Res.* in press.
16. M. HIRANO, C. NAKAHARA, K. OTA and M. INAGAKI, *J. Amer. Ceram. Soc.* **85** (2002) 1333.
17. M. HIRANO, C. NAKAHARA, K. OTA, O. TANAIKE and M. INAGAKI, *J. Solid State Chem.* **170** (2003) 39.

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