JOURNAL OF Materials CHEMISTRY

Anatase nanocrystal-dispersed thin films *via* sol–gel process with hot water treatment: effects of poly(ethylene glycol) addition on photocatalytic activities of the films

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Received 4th April 2001, Accepted 23rd May 2001

Anatase nanocrystals were formed throughout the whole of poly(ethylene glycol) (PEG)-containing silica–titania films after a hot water treatment of the films, whereas in the films without PEG, anatase nanocrystals were formed only on the surface of the films. The photocatalytic activities of the anatase nanocrystal-dispersed silica films obtained with and without PEG were examined from the decomposition of methylene blue, MB. Both anatase nanocrystal-dispersed silica films with and without PEG showed slightly higher photocatalytic activities than pure anatase films in spite of their lower titania contents. The amounts of MB photocatalytically decomposed by the films with PEG increased with an increase in the film thickness. On the other hand, the amounts of MB decomposed by the films without PEG were almost independent of the film thickness. These results indicate that the effective photocatalytic decomposition of MB occurs not only at the surface but also in the inside of the films obtained with PEG, and that it occurs mainly at the surface of the films obtained without PEG.

1 Introduction

Titania has been extensively employed in photocatalysts for envirionmental purification applications such as the decomposition of harmful compounds (*e.g.* acetaldehyde, halogenated compounds, *etc.*).[1,2] When semiconductors like titania particles are illuminated using light of energy greater than the bandgap energy, electron–hole pairs are generated and then separated by the electric field within the space charge region near the surface. The photogenerated electrons and holes migrate to the surface and are then captured by reductants and oxidants, producing active species like radicals. These active species can react with, for example, harmful compounds adsorbed on the surface, resulting in their decomposition. The effectiveness of photocatalytic reactions depends upon characteristics of the semiconducting particles such as the size and specific surface area. It is reported that nanosized titania particles, which have a large surface area per unit mass and volume and facilitate the diffusion of excited electrons and holes toward the surface before their recombination, show higher photocatalytic activity than the bulk.[3] In addition, nanocomposites made up of the titania particles and silica matrices also show higher photocatalytic activities than pure titania because of easier contact between the reactants and titania due to the high dispersion of the titania particles.[4] The control of physical properties such as the particle size, surface area and dispersity of titania is essential for the improvement of photocatalytic activity. Crystalline phases also have a great influence on the photocatalytic activity of titania. Among the several crystalline phases of titania, anatase is well known to exhibit the highest activity.[5] Thus, the composites in which anatase nanoparticles are highly dispersed are expected to show high photocatalytic activity.

We have recently succeeded in the preparation of transparent anatase nanocrystal-dispersed silica films by treating the silica–titania gel films with hot water.[6–8] The processing temperature is lower than 100 °C under ambient pressure, and thus the procedure can be applied to various substrates including those with poor heat resistance such as organic polymers and organisms. The formation of anatase nanocrystals with hot water treatment is a unique phenomenon to the silica–titania system; the formation of anatase nanocrystals was not observed in pure titania gel films with the same hot water treatment. The dispersity of anatase nanocrystals formed by treating with hot water is different between the films obtained with and without poly(ethylene glycol), PEG; anatase nanocrystals are highly dispersed in the films with PEG after the hot water treatment.[8]

In a previous paper, we demonstrated the photocatalytic decomposition of acetaldehyde in the gas–solid system with the anatase nanocrystal-dispersed silica films which were obtained by hot water treatment.[9] The anatase nanocrystal-dispersed films showed high photocatalytic activities. However, the photocatalytic activities of the anatase nanocrystal-dispersed silica films in the liquid–solid system have not so far been evaluated. In addition, the effect of the addition of PEG upon the photocatalytic activities of the resultant films has not been examined.

Here, we investigate the photocatalytic activities of the anatase nanocrystal-dispersed silica films in a liquid–solid system using methylene blue, MB, as a photocatalytic reactant. MB has often been used as a reactant in semiconductor photocatalysis because it is a common dye and because it has strong adsorption characteristics on many surfaces, good resistance to light degradation and a well defined optical absorption maximum in the visible region.[10,11] Moreover, the effects of the addition of PEG to the silica–titania films upon the photocatalytic activity of the films obtained by the hot water treatment are examined in detail.

DOI: 10.1039/b103043b

2 Experimental

2.1 Preparation of films

Silica–titania coating films were prepared from silicon tetraethoxide and titanium tetra-*n*-butoxide. The silica : titania mol ratio was 5 : 1, *i.e.* 16.5 mol% titania. Silicon tetraethoxide in ethanol was hydrolyzed with hydrochloric acid (3.6 wt%) at room temperature for 30 min; the mol ratios of ethanol and water to silicon tetraethoxide were 5 and 4, respectively. The hydrolyzed solution was then mixed with titanium tetra-*n*-butoxide diluted with ethanol, the mol ratio of ethanol to titanium tetra-*n*-butoxide being 20, and was stirred continuously for 30 min. In the case of the preparation of films with the addition of PEG, an average molecular weight of 600 was added to the solution, this resulting solution serving as a coating solution. The weight ratio of PEG added to the silica–titania oxides was fixed to be unity.

One side of the substrate was covered with a Scotch™ tape mask so that only the other side of the substrate was coated. The coating was carried out by a dipping–withdrawing manner in a dry atmosphere of about 20% relative humidity at room temperature. Silica–titania films were coated on several kinds of substrates such as non-alkaline glass and silicon single crystals. After coating, the Scotch™ tape was removed. The substrates coated with the films were dried at 90 °C for 60 min in air using an oven and were then immersed in boiling water for different periods.

2.2 Characterization of films

Changes in the texture of the films were examined using a field-emission type transmission electron microscope (TEM) (Model HF-2000, Hitachi) and a field-emission type scanning electron microscope (FE-SEM) (Model S-4500, Hitachi). Crystallinity of the films was examined from the X-ray diffraction (XRD) patterns using a diffractometer equipped with a sample holder for thin films (MAC M18XHF22-SRA, Mac Science) with CuKα radiation. Specific surface area measurements of the films were performed by nitrogen adsorption at 77 K using the BET method on a specific surface area apparatus (TriStar 3000, Micromeritics). Films coated on aluminum foils were used as samples for specific surface area measurements. The thickness of the films was *ca.* 200 nm.

Photocatalytic decomposition of MB with sol–gel-derived silica–titania films before and after a hot water treatment was examined. The non-alkaline glass substrates coated with silica–titania films before and after boiling water treatment were placed in a Pyrex® spectrophotometer cell containing 1×10^{-5} mol dm^{-3} MB aqueous solution (2.0 g const.) before the cell was sealed with a silicone rubber stopper. The area of silica–titania films on the substrates was fixed to be 1.0 cm^2. Each substrate was irradiated with UV light from the uncoated side using a super high pressure Hg lamp (USH-250BY; Ushio Denki) for several periods of time. The light of wavelength <350 nm was cut off using a color glass filter (UV-33; Toshiba Glass) in order to prevent the direct degradation of MB during UV irradiation. The light power was *ca.* 6.5×10^2 W m^{-2}. The changes in concentrations of MB in the aqueous solution were examined from absorption spectra measured on a UV spectrophotometer (V-560; JASCO).

3 Results and discussion

Fig. 1 shows bright field TEM images of cross-sections of the silica–titania films obtained (a) with the addition of PEG and (b) without PEG after the hot water treatment for 1 h, and (c) pure titania film prepared from titania gel film by heat treatment at 500 °C for 1 h. In the film with PEG [Fig. 1(a)], nanocrystals are observed not only on the surface but also inside the film. The precipitates were identified as anatase nanocrystals from the corresponding selected-area electron diffraction pattern. On the other hand, anatase nanocrystals are observed only on the surface of the film without PEG in Fig. 1(b); none are observed inside the film. It is thus noted that the addition of PEG to the silica–titania films is indispensable to obtain homogeneously dispersed anatase nanocrystals inside the films. PEG within the films can be readily leached out with hot water, indicating that the resultant films therefore have a porous structure. As the pores in obtained films should accelerate the nucleation and growth of anatase nanocrystals, results are consistent with the presence of anatase nanocrystals inside the films. In the pure titania film heated at 500 °C, anatase crystals are homogeneously observed inside the films [Fig. 1(c)].

Surface and cross-sectional morphologies of the silica–titania films treated with hot water and those of the pure titania film heated at 500 °C are compared in Fig. 2. Figs. 2(a) and 2(b) show SEM images of the films with and without PEG after the hot water treatment for 1 h, respectively. The SEM image of the pure titania film prepared from a titania gel film by heat treatment at 500 °C for 1 h is shown in Fig. 2(c). A number of roundish anatase particles of *ca.* 50 nm in diameter are observed for the silica–titania film with PEG in Fig. 2(a). In addition, it can be seen from SEM observation that the cross-section of the film is rough due to the formation of anatase precipitates as shown in Fig. 1(a). The anatase particles on the surface of the film without PEG are rock-like and their diameters are *ca.* 50–200 nm [Fig. 2(b)]: these particles are larger than those precipitated by treating the PEG-containing films with hot water. The cross-section of the film without PEG in Fig. 2(b) is smoother than that of the film with PEG addition. These results correspond to the fact that anatase

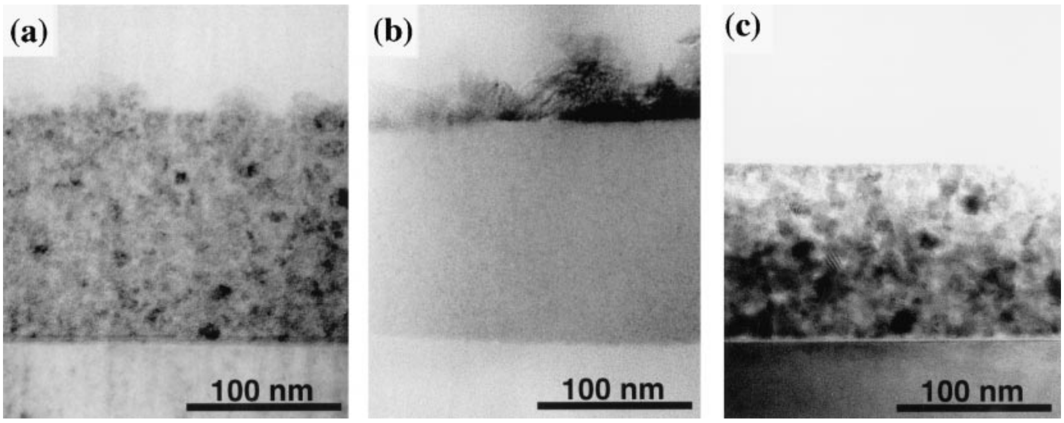

Fig. 1 Bright field TEM images of the cross-sections of silica–titania films obtained (a) with the addition of PEG and (b) without PEG after the hot water treatment for 1 h, and (c) pure titania film prepared from titania gel film by heat treatment at 500 °C for 1 h.

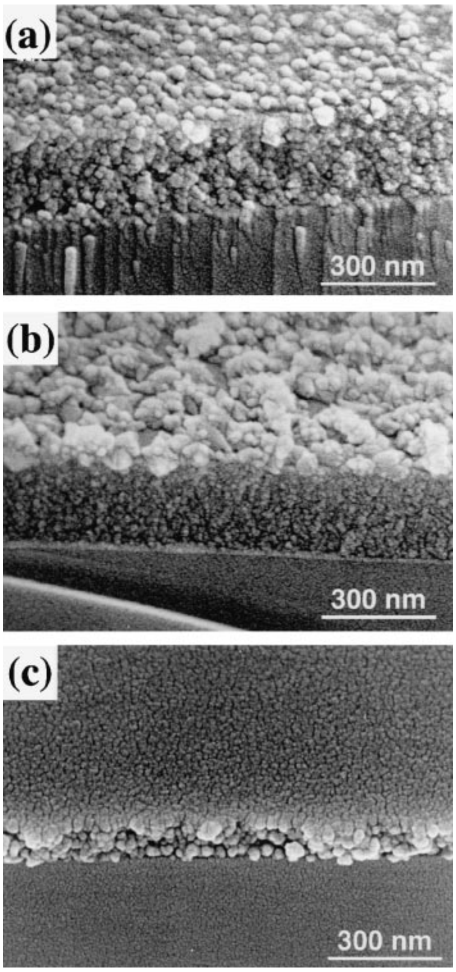

Fig. 2 SEM images of silica–titania films obtained (a) with the addition of PEG and (b) without PEG after the hot water treatment for 1 h, and (c) pure titania film prepared from a titania gel film by heat treatment at 500 °C for 1 h.

nanocrystals are not formed inside the film without PEG, as shown in Fig. 1(b). As can be seen in Fig. 2(c), the cross-section of the titania film is rough due to the formation of anatase precipitates of *ca.* 30 nm in diameter whereas the surface of the film is relatively smooth.

Fig. 3 shows the XRD patterns of the silica–titania films (a) with PEG and (b) without PEG after the hot water treatment for 1 h, and (c) pure titania film prepared from a titania gel film by a heat treatment at 500 °C for 1 h. Diffraction peaks characteristic of anatase, which are indicated by closed circles, are seen for all of the films. The diffraction peaks due to anatase in Figs. 3(a) and 3(b) are much broader than those in Fig. 3(c). This result indicates that the size and quantity of anatase crystals in the silica–titania films with and without addition of PEG formed by the hot water treatment are smaller than those of anatase crystals in the pure titania film formed by heat treatment.

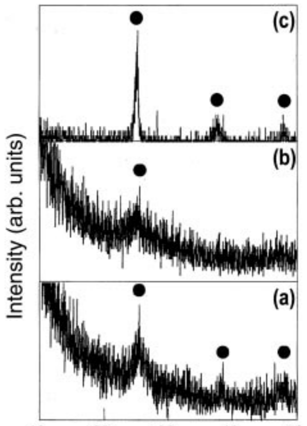

Fig. 3 XRD patterns of the silica–titania films (a) with PEG and (b) without PEG after the hot water treatment for 1 h, and (c) pure titania film prepared from a titania gel film by heat treatment at 500 °C for 1 h. ●; anatase.

The values of the specific surface area of the silica–titania films with and without PEG after the hot water treatment for 1 h are *ca.* 424 and 0.3 $m^2\ g^{-1}$, respectively, and that of the pure titania film prepared from titania gel film by a heat treatment at 500 °C for 1 h is lower than the limit of detection. The silica–titania films with PEG have a very large specific surface area due to the pores formed by leaching of PEG and thus are much more porous than the silica–titania films without PEG and than the pure titania film.

Fig. 4 shows the variation of the UV–Vis absorption spectra of MB aqueous solutions in the spectrophotometer cells containing the glass substrates coated with silica–titania films without PEG treated with hot water for 1 h before and after UV irradiation; the films without PEG treated with hot water for 1 h were used as an example. Solid and dotted curves are absorption spectra of MB aqueous solution before and after UV irradiation for 2 h, respectively. Absorption bands at *ca.* 290 and 670 nm are observed in the spectrum before UV irradiation; the absorbance of each band decreases after irradiation. This result typically indicates that MB is decomposed by the photocatalytic reactions of silica–titania films treated with hot water. The change of MB concentration can be estimated from the change in absorbance of the absorption maximum at 667 nm.

Fig. 5 shows the changes in the concentration of MB for silica–titania and pure titania films as a function of exposure time. Open circles denote the silica–titania films without PEG before hot water treatment, and closed circles and triangles represent, respectively, the films without and with PEG after the hot water treatment for 1 h. The changes for the pure titania film, which was prepared from titania gel film by heat treatment at 500 °C for 1 h, are shown by open squares for comparison. The thickness of all the films was controlled to be *ca.* 200 nm for the evaluation of photocatalytic activities. The UV irradiation was started 30 min after the glass substrates coated with the films were immersed into the optical cells filled with MB aqueous solution. Since the concentration of MB in the cell without the substrate hardly decreased during the UV irradiation as the blank test, the direct decomposition of MB due to UV light is negligible. During standing for 30 min before the UV irradiation, changes in the concentrations of MB are

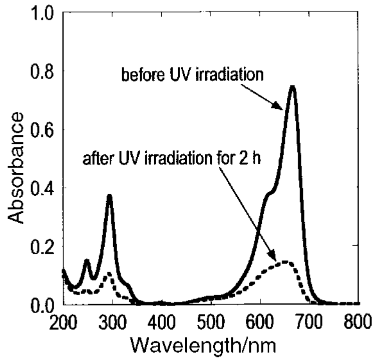

Fig. 4 Variation of the UV–Vis absorption spectra of MB aqueous solutions in the spectrophotometer cells containing the glass substrates coated with silica–titania films without PEG treated with hot water for 1 h before and after UV irradiation.

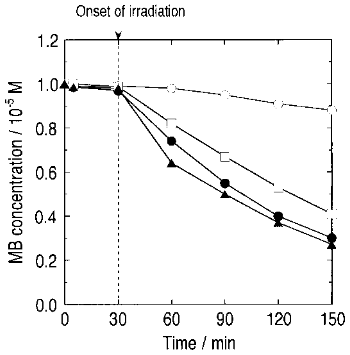

Fig. 5 Changes in the MB concentrations in aqueous solution in the optical cells containing the glass substrates coated with silica–titania and pure titania films as a function of exposure time. Silica–titania films without PEG before the hot water treatment (○), films with (▲) and without PEG (●) after the hot water treatment for 1 h. The changes for the pure titania films (□) are shown for comparison.

scarcely observed for all the solutions in which substrates coated with silica–titania or titania films were immersed. The concentration of MB for the films without hot water treatment decreases slightly with the exposure. This decrease in MB concentration should be mainly due to the adsorption of MB on the films. In the silica–titania films after hot water treatment, the concentrations of MB decrease with increasing UV irradiation time, independent of the addition of PEG, indicating that the hot water treatment of the silica–titania films is indispensable to achieve the photocatalytic activities regardless of the PEG addition. The photocatalytic activities of the silica–titania films treated with hot water are slightly higher than those for the pure titania film. This result is probably caused by the fact that the size of anatase crystals formed in the silica–titania films with and without PEG are smaller than that of the pure titania film as shown in Fig. 3.

Changes in the photocatalytic activities of the silica–titania films with increase in the film thickness are shown in Fig. 6. The films were treated with hot water for 1 h and UV-irradiated for 2 h. The closed triangles and circles represent the films with and without PEG, respectively. The amounts of MB photocatalytically decomposed by the films with PEG increase with an increase in the film thickness, whereas those without PEG are almost constant. In the silica–titania films with PEG, anatase nanocrystals are homogeneously formed throughout the whole film upon hot water treatment as shown in Fig. 1(a). The photo-decomposition reaction of MB is, thus, considered to occur not only at the surface but also inside the films. On the other hand, the formation of anatase in the films without PEG occurs only on the film surface, leading to the photo-decomposition reaction mainly at the surface of the films. Photocatalytic activities of the silica–titania films with PEG are higher than those of the films without PEG at a given film thickness. This phenomenon should be ascribed to the larger specific surface area of the films with PEG than that of the films without PEG.

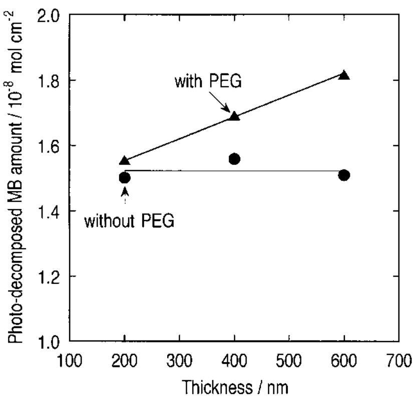

Fig. 6 Changes in photocatalytic activities with an increase in film thickness for the silica–titania films treated with hot water for 1 h. Films with (▲) and without (●) PEG, respectively.

4 Conclusions

The photocatalytic activities in the liquid–solid system of anatase nanocrystal-dispersed silica films obtained with hot water were investigated using MB as a photocatalytic reactant. The films decomposed MB under UV irradiation and showed slightly higher photocatalytic activities than pure anatase titania films. The amounts of MB photocatalytically decomposed by the films with PEG increased with an increase in the film thickness, whereas those without PEG showed no apparent dependency. The photocatalytic-decomposition reaction of MB should occur not only at the surface but also inside the films which were prepared with the addition of PEG and subsequently treated with hot water because anatase nanocrystals were formed in the whole of the films. On the other hand, the anatase nanocrystals were formed only on the surface of the films prepared without PEG and treated with hot water. Therefore, MB is supposed to be photocatalytically decomposed mainly at the surface of the films without PEG.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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