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Synthesis of Structured Macroporous TiO\textsubscript{2} Thin Films and Investigation on Their Photocatalytic Activities

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Abstract. Synthesis of structured macroporous TiO\textsubscript{2} thin films on quartz substrate (macro-TiO\textsubscript{2}/Q) was performed by a dip-coating method using poly(methyl methacrylate) (PMMA) microspheres as template. Obtained TiO\textsubscript{2} thin films kept high transparency and had anatase crystalline structure. SEM observations revealed that the macropores were uniformly formed on the film surface. The size of macropores was quite similar to the diameter of PMMA microspheres as template. In comparison to the nonporous TiO\textsubscript{2} thin films (TiO\textsubscript{2}/Q), macro-TiO\textsubscript{2}/Q exhibited twice higher photocatalytic activity for decolorization of methylene blue in water. Decomposition of acetaldehyde in gas phase also proceeded efficiently on macro-TiO\textsubscript{2}/Q. Moreover, the surface of macro-TiO\textsubscript{2}/Q was easily hydrophilized after a short period of UV light irradiation and maintained lower water contact angle in the dark for a long period as compared to those of TiO\textsubscript{2}/Q.

1. Introduction

It is well known that the TiO\textsubscript{2} thin films exhibit two fascinating photofunctional properties such as photocatalytic activity and photoinduced superhydrophilicity [1-3]. Under irradiation of UV light using various light sources, TiO\textsubscript{2} thin films show photocatalytic activities for complete decomposition of undesired compounds. In addition, the wettability of film surface gradually changes from hydrophobic to hydrophilic under irradiation of UV light. On this film surface, water droplets evenly spread and therefore it appears the self-cleaning and anti-fogging effect. These phenomena have already been applied for various commercial products. Thin film types of TiO\textsubscript{2} photocatalyst have also advantages in their easy handle from a practical viewpoint. Moreover, TiO\textsubscript{2} thin films have technological importance for variety of applications, i.e. fabrication of dye-sensitized solar cells and optical devices.

On the other hand, recently, designs of nanostructured materials have attracted much attention for their applications in the research fields of photonic materials, sensor devices and catalysts. The preparations of these materials are often performed using microspheres such as oxides and polymer particles as template by bottom-up processes [4]. These microspheres used as template are easily removed by heat treatment or solvent extraction. Several attempts have been made to design of unique structured materials by using different precursor solutions as well as changing the size or number of microspheres as template. In the preparation of TiO\textsubscript{2} thin films, controlling the surface morphology as well as the design of a unique architecture is important for enhancement of their photofunctional properties.

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In the present study, aiming at the design of unique surface morphology as well as the enhancement of photofunctional properties, macroporous TiO$_2$ thin films on quartz substrate (macro-TiO$_2$/Q) were prepared by using PMMA microspheres as template. In particular, the effects of the construction of macropores on photofunctional properties of TiO$_2$ thin films have been examined in detail.

2. Experimental

The precursor solution of TiO$_2$ was prepared using tetrabutyl orthotitanate (TBOT), diethanolamine (DEA), H$_2$O and ethanol. 4.1 g of TBOT was dissolved in the mixture of 1.3 g of DEA and 24 g of ethanol with stirring at 298 K [5]. After stirring for 2 h, 0.9 g of H$_2$O was slowly added, and then solution was continuously stirred for another 2 h. Non-cross-linked PMMA microspheres (Soken Chem. & Eng. Co. Ltd., ca. 200 nm in radius) as template of macropores were firstly assembled on quartz substrate (10 × 10 × 1 mm), and then precursor solution of TiO$_2$ was filled into the interstices of aligned microspheres during the dip-coating process. The drawing rate was 1.0 cm/min. After drying at 298 K for 12 h, samples were calcined at 723 K for 5 h in air. Scheme 1 presents the typical procedure for the preparation of macro-TiO$_2$/Q on quartz substrate. Nonporous TiO$_2$ thin films (TiO$_2$/Q) were prepared by the direct coating of same precursor solution of TiO$_2$ on quartz substrate.

![Scheme 1. A schematic illustration of the synthetic procedure of macro-TiO$_2$/Q.](image)

X-ray diffraction (XRD) of prepared thin films was measured by Shimadzu XRD-6100 diffractometer with Cu K$_\alpha$ radiation ($\lambda =$ 1.5406 Å). Scanning electron microscope (SEM) investigations were carried out using a JSM-6500 field emission microscope (JEOL). Prior to SEM analyses, sample surfaces were coated with gold/palladium using ion-sputtering device (JEOL JFC-1100) for improvement of electrical conductivity. Krypton adsorption isotherms were recorded by using a BELSORP TCV (BEL Japan, Inc.) at 77 K.

The photocatalytic activities of thin films were evaluated by the decolorization of methylene blue (MB) diluted in water. One piece of thin films (10 × 10 × 1 mm) was used in each reaction test. An aqueous MB (1 ml; 0.01 mmol/l) was charged into a quartz reaction vessel, and UV light irradiation (Intensity: 5 mW/cm$^2$) was carried out at 298 K by a high-pressure mercury lamp (Toshiba, SHL-100UVQ-2). The changes of solution color were monitored by UV-vis absorption measurement using a Shimadzu UV-2450A spectrometer at certain time intervals.

The wettability of thin film surface were examined by measuring the contact angle of pure water droplet (ca. 1 µl) using a contact angle meter (Kyowa Interface Science Co., Ltd., DropMaster 300). UV light irradiation was carried out with a 200 W mercury xenon lamp (San-ei Electric Co., Ltd., UVF-204S) under controlled light intensity (0.5 mW/cm$^2$). In each experiment, the UV light intensities at around 360 nm were measured by a UV radiometer (Topcon, UVR-2).

3. Results and Discussion

Figure 1(a) shows the SEM image of TiO$_2$/Q. TiO$_2$ layer was uniformly formed on quartz substrate without any large cracks. The thickness of this film was about 200 nm. As shown in Fig. 1(b), the formation of macropores was clearly observed in the case of TiO$_2$ thin films prepared by using PMMA microspheres as template. The thickness of film and radius of macropores was about 200 nm, which showed the good correspondence with the size of PMMA microspheres as template (ca. 200 nm in radius). The quartz substrate was also homogeneously covered by TiO$_2$ thin films with macroporous
structure. After calcined at 723 K for 5 h, the removal of PMMA microspheres as template was confirmed by FT-IR measurement. The FT-IR peaks attributed to the stretching vibration of CH$_2$ and CH$_3$ group of PMMA microspheres at around 2900 cm$^{-1}$ were completely disappeared. It was also confirmed that TiO$_2$ layer of TiO$_2$/Q and macro-TiO$_2$/Q were well fixed on quartz substrate. The peeling of TiO$_2$ layer was scarcely observed after mechanical scratching. Figure 2 shows the photographs of quartz substrate and prepared samples. By construction of macroporous structure, the color of thin films was slightly changed to white. However, macro-TiO$_2$/Q was maintained relatively high transparency (Fig. 2 (c)).

The crystalline structure of prepared samples was investigated by XRD measurement. As shown in Fig. 3, the diffraction peak due to the (101) reflection of TiO$_2$ anatase phase was observed at around 25$^\circ$. The formation of TiO$_2$ anatase phase was also confirmed by XAFS measurements (data not shown). The position and shape of pre-edge peaks was quite similar to the anatase TiO$_2$ powder as reference, indicating that prepared samples were mainly composed of TiO$_2$ anatase phase. The absorption edge of UV-vis spectra was located at around 380 nm, showing the good correspondences with the results of XRD and XAFS measurements. The surface area of TiO$_2$/Q and macro-TiO$_2$/Q measured by krypton adsorption at 77 K was determined to be 40 cm$^2$ and 79 cm$^2$, respectively. These results indicated that the surface area of TiO$_2$ thin films was increased by the construction of macroporous structure.

The photocatalytic performances of TiO$_2$/Q and macro-TiO$_2$/Q were evaluated by the decolorization of MB diluted in water. The water purification such as complete removal of organic pollutants in water as well as the decolorization of waste water is important issues concerning the environmental remediation. TiO$_2$ thin films have advantages in the recovery of catalyst from reaction solutions. MB was used as a model contaminant and the absorption peak changes of MB in water at around 665 nm (Inset of Fig. 4) were monitored at certain time intervals. The changes of absorption were corrected by blank test in the absence of samples. Figure 4 shows the time profiles of the decolorization of MB. The relative intensity of absorption of MB ($I/I_0$) in a natural logarithm scale is plotted against reaction time. Decolorization of MB was occurred in proportion to the UV light irradiation time. The disappearance of solution color (blue) was observed with increases in the UV irradiation time. In this reaction system, macro-TiO$_2$/Q exhibited two times higher photocatalytic performances compared with that on TiO$_2$/Q, which might be attribute to the larger surface area of thin films by the construction of macroporous structure. Moreover, macroporous structure was effective for enhancement of the
decomposition of acetaldehyde in gas phase as a model substance of volatile organic compounds (VOCs).

The surface wettabilities of TiO$_2$/Q and macro-TiO$_2$/Q were investigated by measurement of water contact angles. Water contact angle on both thin films was ca. 60° before UV light irradiation. Under irradiation of UV light, water contact angle of these films gradually decreased and reached to the photoinduced superhydrophilic state (water contact angle below 5°). The conversion of surface hydrophilicity from hydrophobic to hydrophilic state on macro-TiO$_2$/Q was faster than that on TiO$_2$/Q. Moreover, macro-TiO$_2$/Q maintained lower water contact angle in the dark for a long period. These results suggested that the macroporous structure was effective for enhancement of surface hydrophilicity.

4. Conclusions

TiO$_2$ thin films with uniform macroporous structure were successfully prepared on quartz substrate using PMMA microspheres as template by a dip-coating method. Macroporous structure was effective for enhancement of photofunctional properties of TiO$_2$ thin films. The decolorization of MB in water and decomposition of acetaldehyde in gas phase smoothly proceeded on macro-TiO$_2$/Q under irradiation of UV light. In comparison to the TiO$_2$/Q, macro-TiO$_2$/Q showed good surface hydrophilicity, which may attributed to the formation of rough surface by construction of macropores.

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References