Preparation of Thin Macroporous TiO_2 Films Using PMMA Microspheres and Their Photoinduced Hydrophilicities

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Thin macroporous TiO_2 films were successfully prepared on quartz substrate by a dip-coating method using poly(methyl methacrylate) (PMMA) microspheres as template. SEM observations as well as other spectroscopic measurements revealed that the thin TiO_2 films with uniform macropores were formed on quartz substrate with relatively high transparency and anatase crystalline structures. It was also found that the photoinduced hydrophilicity under UV light as well as the durability of hydrophilic surface in the dark was enhanced on thin macroporous TiO_2 films.

For many years, TiO_2 photocatalyts were widely investigated because of their potential applications in the fields of environmental remediation as well as clean energy production.[1–7] In addition, after the discovery of the photoinduced hydrophilicity of thin TiO_2 films in 1997,[8] commercially applicable photofunctional materials, which possess self-cleaning and antifogging properties, were intensively studied.[8–11] Even today, many researchers have been devoted to the design and development of fascinating photofunctional materials.

On the other hand, in recent years, preparation of nanostructured materials which have well defined macropores (typically a few hundred nanometers), has been achieved by using uniform microspheres such as polystyrene and poly(methyl methacrylate) (PMMA) as templates.[12–16] These nanostructured materials have been of importance in a range of applications such as photonic materials as well as sensor devices.[13,17] Close-packed microspheres were used as template, with the interstices of the microspheres being filled by precursor solutions of objective functional materials due to the capillary force. Finally, macroporous structure was obtained after the complete removal of the microspheres through calcination or solvent extraction. Following this process, various fascinating nanostructured materials can be designed by using different precursor solutions as well as controlling the number or size of microspheres.

In the present study, based on the above method, thin TiO_2 films with varying numbers of macropores were prepared on quartz substrate by a dip-coating using PMMA microspheres as template, aimed at the design of unique surface morphology as well as the enhancement of their photofunctional properties.

Thin macroporous TiO_2 films were prepared using non-cross-linked PMMA microspheres (400 nm in diameter, Soken Chem. & Eng. Co., Ltd.) as template. The PMMA template was assembled on clean quartz substrate ($10 \times 10 \times 1\,mm^3$) by spin coating using aqueous dispersions (concentrations: 10 and 20 wt %). The precursor solution of TiO_2 was filled into the PMMA template during the dip-coating process (drawing rate 10 mm/min). The molar ratio of precursor solution was as follows: $Ti(OC_4H_9)_4$:$NH(CH_2CH_2OH)_2$:H_2O:C_2H_5OH = 1:1:8:43. Thin nonporous TiO_2 films (denoted as TiO_2/Q) were also prepared under the same conditions except for the PMMA pre-coated process. After drying at room temperature, all samples were calcined at 723 K for 6 h. Hereafter, the prepared macroporous TiO_2 thin films are denoted as m_x-TiO_2/Q, where x described the PMMA concentration of pre-coated aqueous dispersions. The prepared samples were characterized by XRD (Shimadzu, XRD-6100), FE-SEM (JEOL, JSM-6500), and UV–vis (Shimadzu, UV-2450) measurements.

As shown in Figure 1a, the SEM image of TiO_2/Q prepared by the direct coating of precursor solution on quartz substrate showed a smooth surface without any cracks, indicating that the uniform and dense thin TiO_2 films were formed on the substrate. The formation of macropores was clearly observed on the surface of m_{10}-TiO_2/Q and m_{20}-TiO_2/Q (thickness ca. 200 nm), while the number of macropores depended on the PMMA concentration of pre-coated aqueous dispersions (Figures 1b and 1c). In the case of m_{20}-TiO_2/Q, macropores were formed homogeneously on the entire surface of substrate. The magnified SEM image of m_{20}-TiO_2/Q (Figure 1d) revealed that the pore diameter of m_{20}-TiO_2/Q (ca. 400 nm) shows good correspondence with the size of PMMA microspheres as template.

Figure 2 shows photographic images of prepared samples. TiO_2/Q was colorless and completely transparent, while the color of thin films gradually changed to white with increasing number of macropores. However, in spite of the existence of macropores, m_{20}-TiO_2/Q retained relatively high transparency. The absorption band of samples was located in the UV light region below 380 nm. Moreover, no peeling of these thin films was observed after mechanical scratching, showing that the thin TiO_2 films were well fixed on quartz substrate.

Figure 3 shows the XRD patterns of TiO_2/Q and m_x-TiO_2/Q. The diffraction peaks were observed at around 25 and 48° due to (101) and (200) reflections of TiO_2 anatase phase,

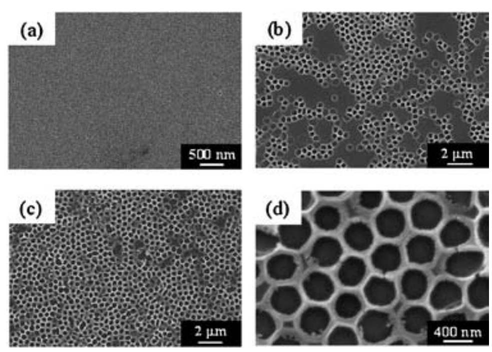

Figure 1. SEM images of (a) TiO_2/Q, (b) m_{10}-TiO_2/Q, and (c), (d) m_{20}-TiO_2/Q.

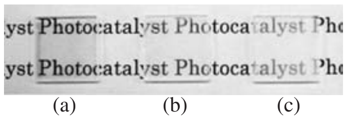

Figure 2. Photographic images of (a) TiO_2/Q, (b) m_{10}-TiO_2/Q, and (c) m_{20}-TiO_2/Q.

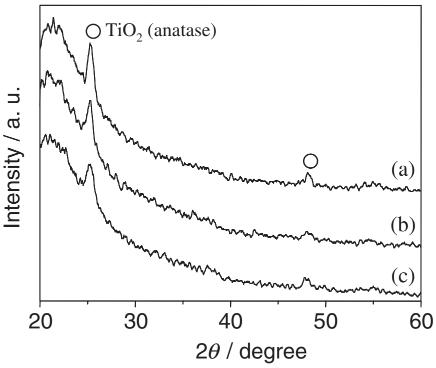

Figure 3. XRD patterns of (a) TiO_2/Q, (b) m_{10}-TiO_2/Q, and (c) m_{20}-TiO_2/Q.

indicating that the thin crystalline TiO_2 films with macropores were successfully prepared on substrate. The intensity of diffraction peaks also slightly decreased with increases in the number of macropores since the surface density of thin TiO_2 films on quartz substrate was decreased by the presence of macropores.

In order to investigate the surface properties of TiO_2/Q and m_x-TiO_2/Q, water contact angle measurement were carried out under UV light irradiation (intensity: $0.5\,mW\,cm^{-2}$). The water contact angle was measured at three different points on the film surface and an average value was adopted. As shown in Figure 4A, the water contact angle on TiO_2/Q and m_x-TiO_2/Q gradually decreased under UV light irradiation and then became lower than 5° (photoinduced superhydrophilic state). m_{20}-TiO_2/Q was easily hydrophilized compared to TiO_2/Q and m_{10}-TiO_2/Q. The water contact angle on m_{20}-TiO_2/Q finally became almost 0° within ca. 30 min, suggesting the positive roles of macropores for the enhancement of hydrophilicity. Moreover, as shown in Figure 4B, after the UV light irradiation was ceased, the water contact angle on TiO_2/Q gradually increased and finally reached to almost initial angles, while m_x-TiO_2/Q exhibited a slow recovery and maintained lower water contact angles. Especially, m_{20}-TiO_2/Q showed good durability of the hydrophilic surface in the dark. These results clearly indicated that the photoinduced hydrophilicity as well as the durability of hydrophilic surface was improved by the construction of macropores, which may attribute to the formation of rough surface as well as the effect of the capillary phenomenon of macropores.

In conclusion, thin macroporous TiO_2 films, which not only have uniform macropores and relatively high transparency but as also well fixed on substrate, were successfully prepared by a dip-coating method using PMMA microspheres as template. These thin films exhibited good photoinduced hydrophilicity after a short period of UV light irradiation and maintained lower water contact angle compared to those on thin nonporous TiO_2 films. These results clearly showed that macropores play an important role in enhancement of their photofunctional properties.

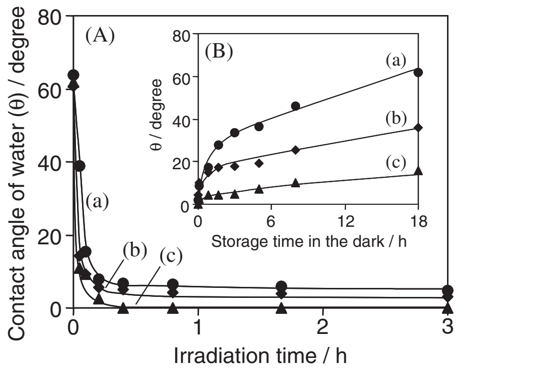

Figure 4. (A) The changes in the contact angle of water (θ) under UV light irradiation and (B) the recovery profiles of θ in the dark. Samples: (a) TiO_2/Q, (b) m_{10}-TiO_2/Q, and (c) m_{20}-TiO_2/Q.

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