Wettability and Superhydrophilic TiO_2 Film Formed by Chemical Vapor Deposition

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A superhydrophilic TiO_2 film was prepared by CVD method. In this study, the thickness and roughness of TiO_2 film were increased with the increase of oxygen fraction in the inlet flow. A rough surface of TiO_2 film exhibited a better original wettability and photoinduced superhydrophilic rate than smooth one. The reasons for the original wettability and photoinduced superhydrophilicity were explained by Wenzel's law and the degree of crystallization.

Since the discovery of photoelectrochemical splitting of water on titanium dioxide electrodes,[1] the semiconductor-based photocatalysis was extensively studied. Today, the titanium dioxide is a representative photocatalyst material owing to its strong redox ability and wide applications, such as air purification, water purification, deodorization, self-cleaning, antibacterial coating, etc.[1,2]

The nanosized TiO_2 in anatase phase is widely used for photocatalystic applications. The TiO_2 film exhibits amphiphilic properties under ultraviolet (UV) light irradiation, so it can be used in the applications of antifogging and self-cleaning materials. The TiO_2 film changes its hydrophilicity under different conditions, but the practicability of superhydrophilic TiO_2 films is limited because of the long induced period of UV light irradiation.

Factors, such as the surface roughness and chemical composition of surface material, play an important role of the wettability on the film surface. Researches found that rough surface and patterned microstructured pillar arrays can greatly alter the surface tension, depending on the wettability of the original substrate.[3,4] In this work, a proper metal organic chemical vapor deposition method (MOCVD) was developed to prepare a hydrophilic TiO_2 film which process a short induced time while activated. Furthermore, the examinations of prepared TiO_2 films were carried out to understand the surface roughness, thickness, original wettability, and photoinduced rate of hydrophilicity.

The TiO_2 film was deposited on a $10 \times 10\,\mathrm{mm}^2$ glass substrate by MOCVD method. The glass substrate was cleaned by ethanol and ultrasonic treatment before coating. The flow rates of carrier gas, N_2, and reaction gas, O_2, were controlled by mass flow controllers. A mechanical pump was used for a low pressure operation at 1 Torr and the reaction temperature was at 600 °C. Nitrogen was firstly introduced to the reaction tube during the initial heating step for purge purpose. While the desired reaction temperature is reached, 100 sccm of nitrogen gas passed through a bubbler containing the precursor, $Ti(OCH(CH_3)_2)_4$ (TTIP), at 80 °C. The oxygen gas flows of 900, 500, and 0 sccm were individually mixed with the above gas before inletting into the CVD reactor. After 5 min of deposition, the TiO_2 film was obtained and stored at 23 °C with 55% of RH in the dark for three days. The wettability of films was measured via water contact angle on the surface using a contact angle meter (First Ten Angstroms, FTA-125). Identification of photocatalyst layer was analyzed by X-ray diffraction (Shimadzu, XRD6000). The surface morphology was observed by field emission microscopy electron microscopy (Hitachi, S4800), and atomic force microscopy (Digital Instruments DI 3100).

The X-ray diffraction patterns of TiO_2 samples were shown in Figure 1. The anatase phase of TiO_2, characteristic peaks at (101), (004), (200), (105), and (211), began to appear when TiO_2 was formed over the reaction temperature of 600 °C. The peaks became sharper with increasing oxygen fraction. Not only the intensity of (101) peak increases obviously, but also (004), (200), (105), and (211) peaks do. It shows the obvious polycrystallization structure of TiO_2 film prepared in a plenty oxygen atmosphere. TTIP was thermally decomposed and react with oxygen to become TiO_2. Sun and co-workers reported the different nucleation rate and mechanism in the oxygen free and oxygen contained atmospheres in the MOCVD process.[5] This is because that the thermal decomposition and nucleation rates without oxygen gas are much lower than that with oxygen. The concentration of titania monomer vapor is increased owing to the by-product of thermal decomposition, isopropane, is converted to CO_2 in the present of O_2.

Figure 2 shows the surface morphology and photograph of TiO_2 film prepared under different oxygen atmosphere. Figure 2a shows the TiO_2 film without oxygen gas and aggregated particle size is in the range of 80–120 nm. The TiO_2 particles were arranged in good order on the glass substrate, resulting a smooth surface of TiO_2 film. As oxygen flow rate increased to 500 sccm in Figure 2b, TiO_2 cluster was overlapped and aggregated so that the TiO_2 film surface became rough. At 900 sccm of oxygen flow rate shown in Figure 2c, the TiO_2 particles were aggregated seriously. The secondary particles of 300–500 nm were easily observed, and the aggregated particles were made of tiny TiO_2 particles with the particles size smaller than 50 nm. The roughness was clearly examined by AFM. The average roughness Ra of these samples was 17, 41, and 150 nm. The photograph shows that the transparence of TiO_2 film is decreas-

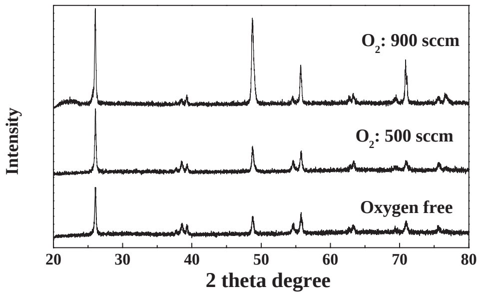

Figure 1. XRD patterns of prepared TiO_2 film.

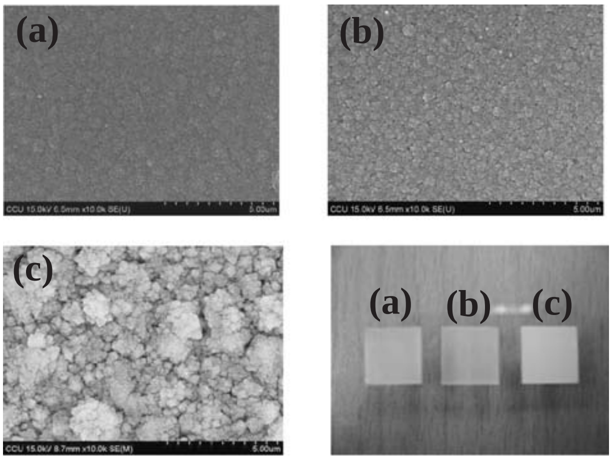

Figure 2. Surface morphology and photograph of prepared TiO_2 films at oxygen flow rate (a) 0, (b) 500, (c) 900 sccm.

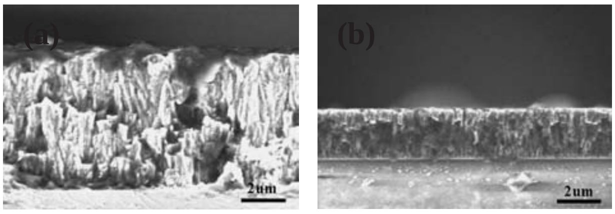

Figure 3. Cross-section of prepared TiO_2 film at O_2 flow rate of (a) 900 and (b) 0 sccm.

ed with thickness.

Figure 3 shows the cross section of film under 900 sccm of oxygen flow and pure nitrogen flow, where the film thicknesses were 5 and 2.3 µm, respectively. The small-sized columnar structure was also observed and similar to the results from Jung and co-workers.[6] The results of both AFM and FESEM showed the film roughness decreased by decreasing deposition rate.

According to the classic theory, the apparent contact angle, θ^*, for the rough surface obeys Wenzel's law:[7] $\cos\theta^* = r\cos\theta$, where θ is the contact angle of a flat substrate and r is the roughness ratio of the surface which is always greater than unity. Hence, the wettability increased for a rough surface with θ smaller than 90°, but it decreased with θ larger than 90°. The titanium dioxide is a hydrophilic material, and the contact angle of the flat dense TiO_2 layer (θ) is about 52°.[8] The water contact angle of the various TiO_2 film with the UV light irradiation time is shown in Figure 4. Before UV light irradiation, the original contact angles of TiO_2 film (θ^*) were 46, 32, and 13° for the oxygen flow rate of 0, 500, and 900 sccm, respectively. The original wettability of prepared films was obviously related to the amount of reacted oxygen gas.[9] Therefore, it is reasonable to obtain a good hydrophilic TiO_2 film with a CVD process in a plenty oxygen atmosphere.[10] The Wenzel relation r value of the TiO_2 films can be calculated as were 1.58, 1.37, and 1.13 for oxygen flow rate of 900, 500, and 0 sccm, respectively. After 1 h of UV light irradiation at 1 mW/cm^2, all prepared TiO_2 films were photoinduced to become superhydrophilic. The contact angles were below 5° that revealed a good photocatalytic wettable property. Moreover, the rate of photoinduced superhydrophilicity was proportion to the oxygen fraction. The induced time of superhydrophilicity were 10, 40, and 60 min for the films prepared at oxygen flow rate of 900, 500, and 0 sccm, respectively. There are two plausible mechanisms for the photoinduced superhydrophilicity of TiO_2. One is the increase of number of hydroxy groups of the TiO_2 surfaces during UV light irradiation.[11] The number of hydroxy groups increase with the increase of TiO_2 thickness because of the amount of absorbed photons. However, Anpo and co-workers reports this phenomenon is originated by the desorption of water molecules from the TiO_2 surfaces by the heating from the light sources and the partial elimination of hydrocarbons by photocatalytic decomposition under UV light irradiation.[12] The reason for this better photoinduced hydrophilic film is the well-crystallized, rough, and thick structure on the surface.

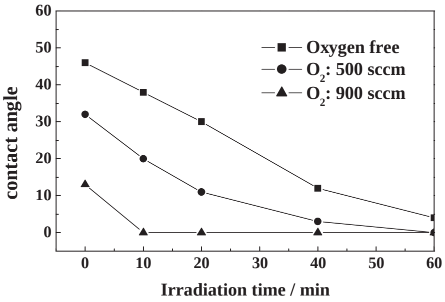

Figure 4. Effect of UV light irradiation on the water contact angle on TiO_2 films.

In conclusion, a simple method to prepare well-crystallized TiO_2 films was developed in this study. A thick and rough TiO_2 film can be coated on the glass substrate by a CVD process with large oxygen fraction. The smooth and thin TiO_2 film was obtained in the contrary condition. The rough TiO_2 film exhibited a good original wettability and it was easily excited to be superhydrophilic after short period of UV light irradiation. This coating technology is more practicable for the use in the self-cleaning and antifogging applications.

References

1 A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.
2 A. Fujishima, N. R. Tata, A. T. Donald, *J. Photochem. Photobiol., C* **2000**, *1*, 1.
3 A. Kawai, H. Nagata, *Jpn. J. Appl. Phys.* **1994**, *33*, 1283.
4 D. Oner, T. J. Mcarthy, *Langmuir* **2000**, *16*, 7777.
5 Y. Sun, A. Li, M. Qi, L. Zhang, X. Yao, *Mater. Sci. Eng.* **2001**, *86*, 185.
6 S. C. Jung, S. J. Kim, N. Imaishi, Y. I. Cho, *Appl. Catal., B* **2005**, *55*, 253.
7 R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.
8 S. Dohshi, M. Anpo, S. Okuda, T. Kojima, *Top. Catal.* **2005**, *35*, 327.
9 T. Uelzen, J. Muller, *Thin Solid Films* **2003**, *434*, 311.
10 J. G. Fan, X. J. Tang, Y. P. Zhao, *Nanotechnology* **2004**, *15*, 501.
11 R. Wang, N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Phys. Chem. B* **1999**, *103*, 2188.
12 M. Takeuchi, K. Sakamoto, G. Martra, S. Coluccia, M. Anpo, *J. Phys. Chem. B* **2005**, *109*, 15422.

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