Superhydrophilicity of Rutile TiO_2 Prepared by Anodic Oxidation in High Concentration Sulfuric Acid Electrolyte

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The contact angles of rutile TiO_2 prepared by anodic oxidation in an electrolyte with a high concentration of sulfuric acid is almost zero without UV illumination. The water droplet spread across the surface within 1 ms because of the strong interaction with the hydroxy groups.

The photoinduced superhydrophilicity of TiO_2 allows water to spread completely across its surface under ultraviolet (UV) light illumination.[1,2] In this study, we have used an anodic oxidation method to fabricate superhydrophilic TiO_2 since by using this method, the microstructure and chemical composition of the oxide can be controlled by selecting the electrolyte composition.[3]

Ti plates (cp-Ti, grade I) with dimensions of 1.0 × 2.0 × 0.1 cm^3 were prepared for use as an anode in the anodic oxidation method. The plates were chemically polished using a 40-nm colloidal silica suspension, following which they were thoroughly rinsed in ethanol using an ultrasonic cleaner. A constant current of 50 mA/cm^2 was applied to the Ti plate in a sulfuric acid electrolyte ranging from 0.002 to 1.6 M, and a Pt mesh electrode was used as the cathode. The anodic oxidation was controlled galvanostatically until the conversion voltage reached 210 V, and the time duration of oxidation was fixed at 0.5 h. The anodized electrode was rinsed with distilled water and dried at room temperature, following which it was annealed at 723 K for 5 h in air. The contact angle of distilled water (0.1 mL) is the average of three measurements taken for each sample by using a goniometer system (CA-X, Kyowa Interface Science Co., Ltd., Japan). Ultraviolet light of $\approx$0.1 mW/cm^2 intensity was radiated by a beam lamp (SOLAX XC-100B, Seric Co., Ltd., Japan), and the contact angle was measured every half hour during illumination.

Figure 1a shows the microstructure of the annealed oxide anodized in 0.1 M sulfuric acid; the oxide contains homogeneously distributed nanosized pores. The relationship between the pore size and the sulfuric acid concentration in the electrolyte is shown in Figure 1b; with an increase in the concentration of sulfuric acid, the average pore size varies from approximately 170 to 950 nm. Concurrently, the primary phase of the anodic oxide is converted from anatase to rutile, as revealed by X-ray diffraction analysis with a thin-film geometry arrangement.[4] This implies that the rutile-structured phase is stabilized as the sulfuric acid concentration in the electrolyte is increased. The surface roughness of the anodic oxide was measured by using AFM, and it varies from approximately 260 to 800 nm with an increase in the concentration of sulfuric acid.

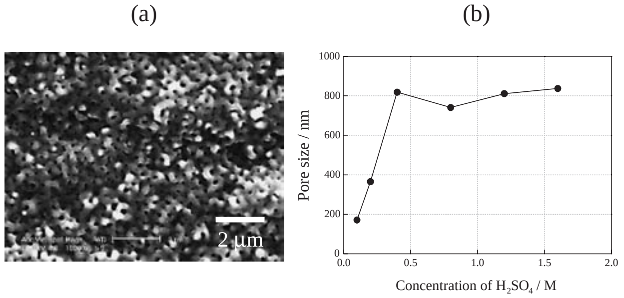

Figure 1. (a) Micrograph of the oxide anodized in 0.1 M sulfuric acid and (b) the variation in the pore size with the sulfuric acid concentration in the electrolyte.

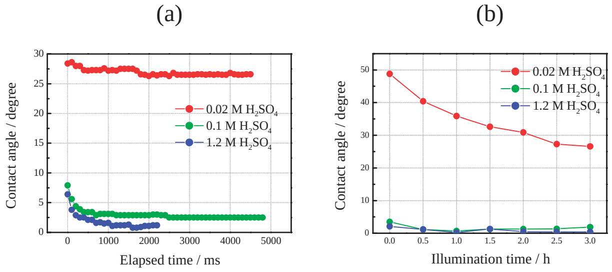

Figure 2. (a) Plot of the contact angle against the time at which the water droplet falls on the oxide after UV illumination for 3 h and (b) plot of the contact angle against the duration of UV illumination for the oxide anodized in sulfuric acid with concentrations of 0.02, 0.1, and 1.2 M.

Figure 2a shows the plot of the contact angle against the time at which the water droplet falls on the oxide after UV illumination for 3 h, while the plot of the contact angle against the duration of UV light illumination is shown in Figure 2b. The contact angle approaches a specific value with elapsed time, as shown in Figure 2a, suggesting that the low contact angle is not due to capillary effect. The specific value obtained from Figure 2a is used for the contact angle in Figure 2b. The contact angle of the oxide prepared in 1.2 M sulfuric acid is low regardless of UV illumination, whereas the contact angle of the oxide prepared in 0.02 M sulfuric acid decreases with the duration of UV illumination, as shown in Figure 2b. The contact angle of the oxide prepared in an electrolyte with a high sulfuric acid concentration is lower than that of the oxide prepared in an electrolyte with a low sulfuric acid concentration, regardless of the duration of UV light illumination. Further, it should be noted that in the absence of UV light illumination, the contact angle of the oxide prepared in an electrolyte with a high sulfuric acid concentration is quite low. In order to explore the effect of the pores on the hydrophilicity, a water droplet on the surface of an Al_2O_3

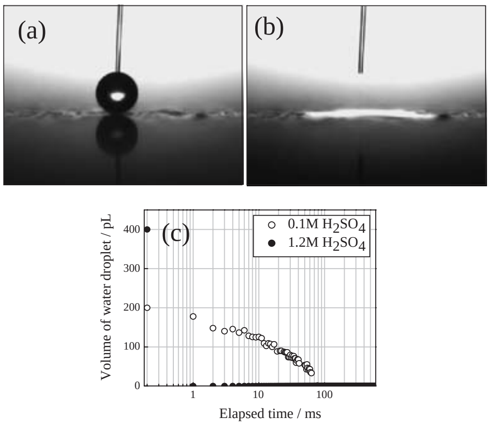

Figure 3. Images of the 400-pL water droplet before (a) and 5 ms after (b) being dropped on the surface of the oxide prepared in 1.2 M sulfuric acid, and the change in the volume of the droplet against the elapsed time (c).

membrane filter with a pore diameter of 20 or 200 nm (Anodisc, Whatman Plc., U.K.) was investigated. The result shows that the contact angles of the 20 and 200 nm membrane filter are 11.6 and 9.8°, respectively. This proves that the low contact angle observed in the anodic TiO_2 is not due to the nanosized pores but due to the intrinsic superhydrophilicity of anodic oxide.

The hydrophilic behavior of the anodic oxides was reexamined without UV light illumination by using a goniometer system equipped with a high-speed CCD camera capable of monitoring a water droplet at 1-ms intervals. Figure 3 shows the images of a water droplet with a drop size of 400 pL before (a) and 5 ms after (b) being dropped on the surface of the oxide prepared in 1.2 M sulfuric acid (average pore size is 820 nm). The change in the volume of the water droplet is plotted against the elapsed time, as shown in Figure 3c; the change in the volume of a 180-pL water droplet dropped on the surface of the oxide prepared in 0.1 M sulfuric acid (average pore size is 170 nm) is used as the reference. The 400-pL water droplet is perfectly spread across the surface within 1 ms, and the water contact angle becomes zero. This is an extremely interesting phenomenon because it occurs in the absence of UV light illumination and the water droplet is spread across the surface at a rather high speed. As a reference, in the case of an inkjet printer, it takes 5 ms for a 10-pL water droplet to be absorbed by the hygroscopic paper. On the other hand, the change in the volume of the water droplet on the oxide anodized in 0.1 M sulfuric acid is reduced monotonously, as shown in Figure 3c. The contact angles of the droplet on the surface of the oxides anodized in 0.1 and 1.2 M sulfuric acid are 10.1 and 0°, respectively, 5 ms after being dropped on the surface. Further study focusing on the photocatalytic activity under visible light is in progress to elucidate the mechanism of this result.

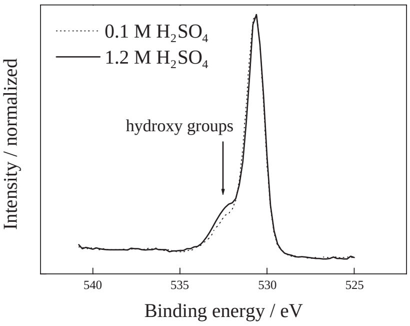

Figure 4. O 1s XPS spectra of the oxides anodized in an electrolyte with a sulfuric acid concentration of 0.1 and 1.2 M.

Figure 4 shows the O 1s XPS (X-ray photoelectron spectroscopy) spectra of the oxides anodized in 0.1 and 1.2 M sulfuric acid. The XPS spectra were obtained by monochromatized Al Kα radiation (ESCA1600, Ulvac-Phi Co., Ltd., Japan). It is noteworthy that S 2p XPS spectra appear in the profiles and that the intensity of the spectra increases with an increase in the concentration of sulfuric acid. A shoulder band on the higher-binding-energy side of the main peak originating from the adsorption of hydroxy groups can be observed.[5,6] This is verified by the spectral profiles obtained for different take-off angles, since the intensity of the hydroxy groups at low take-off angles is higher than that at high take-off angles. The intensity of the shoulder peak for the oxide anodized in 1.2 M sulfuric acid is higher than that in the case of 0.1 M sulfuric acid. This implies that the surface of the oxide anodized in 1.2 M sulfuric acid interacts strongly with the hydroxy groups as compared to the oxide anodized in 0.1 M sulfuric acid. Although the mechanism of the variation of the interaction with hydroxy groups depending on the sulfuric acid concentration in the electrolyte has not been elucidated, this result is quite important when considering the superhydrophilicity of anodic oxide.

In conclusion, TiO_2 prepared by anodic oxidation in an electrolyte with a high sulfuric acid concentration possesses excellent superhydrophilicity without UV illumination.

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