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Superhydrophobic−Superhydrophilic Micropatterning on Flowerlike Alumina Coating Film by the Sol−Gel Method

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Wettability of solid surfaces with liquids is governed by the chemical properties and the microstructure of the surfaces. As far as the microstructure of a surface is concerned, fine roughness is well-known to enhance the hydrophobic and hydrophilic properties.[1,2] A hydrophobic surface, in which the contact angle for water is enhanced by small roughness and is larger than about 150°, is called "superhydrophobic," and a hydrophilic surface, in which the contact angle is similarly enhanced by small roughness and is less than 5°, is called "superhydrophilic." Very recently, we have succeeded in forming transparent, superhydrophobic coating films on glass plates through the sol−gel method by the combination of microstructural and chemical approaches.[3,4] Alumina thin films with roughnesses of less than 50 nm were formed by immersing the porous alumina gel films in boiling water, and we named this the "flowerlike structure." Coating of hydrolyzed fluoroalkylsilane (FAS) on this flowerlike Al_2O_3 produced the superhydrophobic surface; the contact angle for water was about 165°. The roughness led to the extremely high water repellency. We also reported that the contact angle for water of the surface was drastically decreased with heat treatment at temperatures higher than 500 °C because of thermal decomposition of the fluoroalkyl chain in FAS.[5]

On the other hand, patterning of a surface into regions of different surface free energies using self-assembled monolayers has been reported.[6−11] This pattern is, for example, applied to selective deposition of tantalum oxide thin film.[10] However, these studies have focused on the control of the chemical properties of surfaces with self-assembled monolayers, and the difference of the contact angle for water is smaller than 90°; this may limit practical applications of the hydrophobic−hydrophilic patterns. It has also been reported that hydrophobic character of a super-water-repellent surface can be changed by UV irradiation through photoisomerization of an organic compound; however, the difference of contact angle for water is around 80°.[12,13] UV irradiation on TiO_2 surfaces has been also reported to induce the change in contact angle from 72° to 0°.[14] However, the hydrophilic surface becomes hydrophobic again with storage.

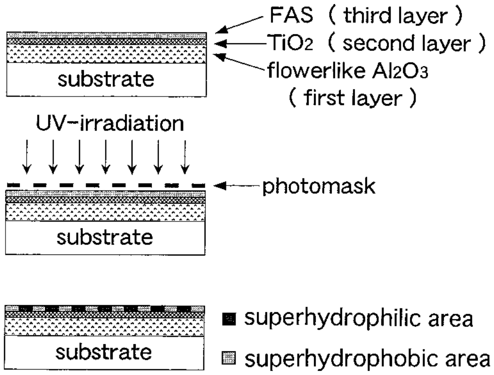

Figure 1. Schematic representation of preparation procedure of superhydrophobic−superhydrophilic patterned surface.

In the present paper, we demonstrate the conversion of a superhydrophobic into a superhydrophilic surface by UV irradiation, where the hydrophobic and hydrophilic properties are enhanced by a fine roughness. The formation of superhydrophobic−superhydrophilic micropatterns is also reported by the application of this conversion technique.

Schematic representation for the formation of superhydrophobic−superhydrophilic patterns is shown in Figure 1. First, the alumina thin films (about 200 nm thick) with roughness of less than 50 nm were prepared using aluminum tri-*sec*-butoxide, isopropyl alcohol, ethyl acetoacetate, and water, as reported previously.[3−5] The coating was carried out on soda lime glass plates in a dipping−withdrawing manner. The coating films obtained were heat-treated at 400 °C for 10 min to get porous Al_2O_3 gel films. Then, the porous Al_2O_3 gel films were immersed in boiling water for 10 min and, after being dried, heat-treated again at 400 °C for 10 min. The flowerlike Al_2O_3 films were thus obtained.

Second, very thin TiO_2 gel layers of about 5−10 nm thick were formed using titanium *n*-butoxide, ethanol (EtOH), acetyl acetone (AcAc), and water. Titanium *n*-butoxide and EtOH were mixed, and this solution was stirred at room temperature for 1 h. Acetyl acetone (AcAc) was added to the solution as a chelating agent, and the solution was stirred for 3 h. Water diluted with EtOH was then carefully added to the solution for hydrolysis, and this solution was used for coating. The molar ratios of EtOH, AcAc, and H_2O to $Ti(O\text{-}n\text{-}Bu)_4$ were 160, 1, and 2, respectively. The TiO_2 gel layer was

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[1] Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley & Sons: New York, 1990.

[2] Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. *Langmuir* **1996**, *12*, 2125.

[3] Tadanaga, K.; Katata, N.; Minami, T. *J. Am. Ceram. Soc.* **1997**, *80*, 1040.

[4] Tadanaga, K.; Katata, N.; Minami, T. *J. Am. Ceram. Soc.* **1997**, *80*, 3213.

[5] Minami, T.; Katata, N.; Tadanaga, K. *Proc. SPIE (Sol−Gel Optics IV)* **1997**, *3136*, 168.

[6] Dressick, W. J.; Calvert, J. M. *Jpn. J. Appl. Phys. Part 1* **1993**, *32*, 5829.

[7] Kumar, A.; Whitesides, G. M. *Science* **1994,** *263,* 60.

[8] Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.

[9] Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550.

[10] Clem, P. G.; Jeon, N. L.; Nuzzo, R. G.; Payne, D. A. *J. Am. Ceram. Soc.* **1997**, *80*, 2821.

[11] Lee, B. E.; Clark, N. A. *Langmuir* **1998**, *14*, 5495.

[12] Sasaki, H.; Shoji, M. *Hyomengijutsu* **1998**, *49*, 944 (in Japanese).

[13] Sasaki, H.; Shoji, M. *Chem. Lett.* **1998**, 293.

[14] Wang, R.; Hashimoto, K.; Fujishima, A. *Nature* **1997**, *388*, 431.

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Table 1. Contact Angle for Water of Thin Films on Flowerlike Al_2O_3 before and after UV Irradiation

coating film	flowerlike Al_2O_3 substrate before	flowerlike Al_2O_3 substrate after
FAS	165°	165°
Ti(AcAc)[a] + FAS	150°	<5°
a-TiO_2[b] + FAS	160°	<5°
TiO_2 (anatase)[c] + FAS	160°	<5°

[a] At room temperature. [b] At 350 °C. [c] At 500 °C.

coated on the flowerlike Al_2O_3 layer and dried only at room temperature or heat-treated at 350 or 500 °C. In the samples in which the TiO_2 gel film was only dried at room temperature for several days, the chelating bonds between Ti and acetyl acetone were still present in the gel films, and the samples are denoted as Ti(AcAc)[a] in Table 1 as explained later. When TiO_2 gel layer was heat-treated at 350 °C to decompose the chelating bonds, the X-ray diffraction measurement showed that TiO_2 was not crystallized; i.e., amorphous TiO_2 was obtained, and the samples are referred to as a-TiO_2[b] in Table 1. TiO_2 heat-treated at 500 °C was crystallized to the anatase phase, which is indicated as TiO_2 (anatase)[c].

Heptadecafluorodecyltrimethoxysilane, which is one of the fluoroalkyltrimethoxysilanes (FAS), was used as a water repellent agent. Partially hydrolyzed FAS was coated as the top layer on the TiO_2 gel layer with an underlayer of flowerlike Al_2O_3 and then dried at room temperature for 1 h. The thickness of the FAS layer was estimated to be less than 10 nm.

UV light from a high-pressure mercury lamp (about 150 mW cm^{-2}) was irradiated on the films with or without a photomask for 10 min in the ambient atmosphere.

Static contact angles were measured with a horizontal microscope with a protractor eyepiece at room temperature (Kyowa Interface Science, CA-X). Water droplets were placed at five positions for one sample, and the averaged value was adopted as the contact angle.

Table 1 shows the contact angles for water before and after UV irradiation on the coating films. All of the samples were transparent in the visible-light region. The contact angle for water on only FAS-coated flowerlike Al_2O_3 is about 165°; this surface is superhydrophobic. When one of the TiO_2 layers was the second layer and FAS was the top layer, the contact angles are larger than 150°, indicating that these surfaces are also superhydrophobic. FE-SEM observation of the surface of the FAS−TiO_2-flowerlike Al_2O_3 showed that the flowerlike structure was preserved even after the coating of TiO_2 and FAS. After UV irradiation, the contact angle on only FAS-coated Al_2O_3 is not changed. On the other hand, for the FAS−TiO_2-coated samples, the contact angles for water are drastically decreased by the UV irradiation and become smaller than 5°; the surface becomes superhydrophilic. In the XPS measurements, fluorine was not observed in the UV-irradiated region but was observed in the UV-unirradiated region. These results indicate that the fluoroalkyl chain of FAS was cleaved by the irradiation of UV light through the photocatalytic reaction on TiO_2 layer. With the cleavage of the fluoroalkyl chain, the FAS layer became a silica layer, and the fine roughness in flowerlike Al_2O_3 enhances the hydrophilic property of silica to superhydrophilicity. In this way, the difference of the contact angle before and after UV-irradiation in this surface becomes greater than 150°.

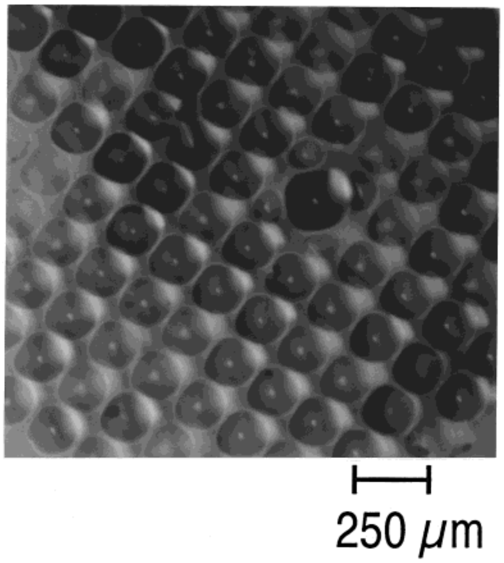

Figure 2. Optical microscope photograph of water droplet on the superhydrophobic−superhydrophilic surface prepared by the irradiation of UV light through a photomask.

As to the photocleavage of the fluoroalkyl chain in FAS, the anatase form of TiO_2 is well-known to have a high photocatalytic activity. The results in Table 1 and the XPS measurements showed that amorphous TiO_2 and TiO_2 gel containing chelating bonds also have a photocatalytic activity that cleaves the organic chain on the surface, although these types of TiO_2 are assumed to have very small activities for photocatalytic reactions. This indicates that the fluoroalkyl chain in FAS is easily cleaved through the photocatalytic reaction.

The conversion of the superhydrophobic surface into superhydrophilic was applied to formation of superhydrophobic−superhydrophilic micropattern. Figure 2 shows the optical microscope photograph of water droplets on the superhydrophobic−superhydrophilic surface prepared by the irradiation of UV light through a photomask. When water was put on this surface, water droplets are preferentially present in the hydrophilic areas. Since the difference of the contact angle is larger than 150°, a large volume of water can be present only on the superhydrophilic regions without bridging the other superhydrophilic regions. In addition, the size and shape of this pattern is adjustable for use with a wide variety of applications since this superhydrophobic−superhydrophilic pattern was formed with irradiation of UV light. These results suggest that one can use this kind of pattern as a new type of stamper for printing or a substrate for micropatterning and micro-optical components, where several types of ‘ink’, such as water-soluble polymers, monomers for polymerization by UV irradiation, sol−gel derived coating solutions, and so on, may be used instead of water in Figure 2.

In conclusion, a novel route to form superhydrophobic−superhydrophilic micropatterned coating film has been developed. UV light was irradiated on the superhydrophobic coating film which consists of three layers, a flowerlike Al_2O_3 gel film, a very thin TiO_2 gel layer, and a FAS layer, to cleave the fluoroalkyl chain in FAS selectively, and well-defined superhydrophobic and superhydrophilic regions were formed. Amorphous TiO_2 and TiO_2 gel films containing chelating bonds, as well as anatase, were effective for cleavage of the fluoroalkyl chain, indicating that the fluoroalkyl chain in FAS is easily cleaved through the photocatalytic reaction. Since this superhydrophobic−superhydrophilic pattern was formed through UV irradiation and showed a large difference in the contact angle, this pattern must have a wide variety of applications, such as fabrication of micro-optical components, micropatterned oxide thin films, and stampers for printing.

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