Effect of Roughness on Lipophobicity of a Surface Prepared Using Boehmite Nanoparticles and Fluoroalkylsilane

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The effect of surface roughness on lipophobicity was investigated on a surface prepared using a combination of boehmite nanoparticles and fluoroalkylsilane. The requirement of surface roughness for superlipophobicity by oleic acid is higher than 565 nm when the surface energy is approximately 14 mJ/m^2. This roughness value is around ten times of that for superhydrophobicity.

Surfaces with a water contact angle greater than 150° (superhydrophobic surface) have attracted much interest. The small contact area between solid and water allows inhibition or reduction of several surface phenomena, such as snow-sticking or water resistance. A superhydrophobic surface is producible by combining surface roughness with low surface energy. So far, various preparation methods have been developed for processing of superhydrophobic surfaces.[1,2]

A superlipophobic surface whose contact angle of oil is greater than 150° can also be prepared under the same concept as that for preparation of a superhydrophobic one. However, it is presumable that superlipophobic surface is much more difficult to attain because of oil's small surface energy (commonly ca. 30 mJ/m^2). So far, few reports have examined such. Shibuichi et al. have attained superlipophobicity using a special fluorinated monoalkyl phosphate for the dense packing of CF_3 group on the surface;[3] Li et al. have employed aligned carbon-nanotube films with thickness of 2 µm order to provide sufficient air at the oil and solid surface interface.[4] Fundamental requirements of surface roughness and surface energy for superlipophobicity remain unclear because of the small number of preparations of superlipophobic surfaces.

Recently, we imparted surface roughness to boehmite (AlOOH) and silica film through sublimation of aluminum acetylacetonate (AACA: $Al(C_5H_7O_2)_3$) during calcination. We also prepared transparent superhydrophobic films from these materials by subsequent coating with heptadecafluorodecyltrimethoxysilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, hereafter referred to as FAS-17).[5–7] The present study, which addresses this coating process, investigates effects of coating thickness and surface roughness on surface lipophobicity.

A commercial boehmite powder (DISPAL 18N4; Condea Chemie GmbH, Hamburg, Germany) and reagent-grade AACA (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), were mixed with ethanol (Wako Jyunyaku Kogyo Co., Tokyo, Japan). The respective weight ratios of boehmite and AACA to ethanol were 0.002 and 0.0366. The suspensions were sonicated for 20 min: AACA was dissolved into ethanol during sonication. The sonicated suspensions were spread over Pyrex glass plates (5 × 7 cm^2, 1 mm thickness) by spin coating at 1000 rpm for 10 s. The coated glass plates were dried at room temperature for a few minutes until they became opaque. The glass plates' calcination was carried out on a hot plate heated at 400 °C for 20 s. During this heat treatment, white smoke was generated from the opaque films, and the glass plates reverted to their former transparency. This coating and calcination procedure was repeated 1–12 times, and the coating layer thickness was changed. FAS-17 (TSL8233; Toshiba Silicone Co., Japan) was evaporated at 200 °C and spread over the plates, creating an extremely hydrophobic film surface.

Contact angles were measured using a contact angle meter (CA-X; Kyowa Interface Science Co., Ltd., Saitama, Japan). Surface lipophobicity was evaluated using the contact angle of oleic acid ($CH_3(CH_2)_7(CH)_2(CH_2)_7COOH$ surface energy value: 32.0 mJ/m^2;[8] Wako Pure Chemicals Industries, Ltd.). The droplet size for contact angle measurement was ca. 1.0 µL. Average surface roughness (R_a) and coating thickness were evaluated using a laser profile micrometer (VF-7500; Keyence Co., Tokyo, Japan). Contact angles and surface roughness were measured at three different points. The microstructure was observed using SEM (S-4200; Hitachi Ltd., Tokyo, Japan). Surface chemical composition was evaluated using XPS (JPS-9010MX; JEOL, Tokyo Japan).

Figure 1 shows the layer-number dependence of surface roughness and coating on contact angles of water and oleic acid. Both hydrophobicity and lipophobicity are greater for coatings with more numerous layers. Superhydrophobicity is attainable through the use of five layers (average film thickness: 1.6 µm).

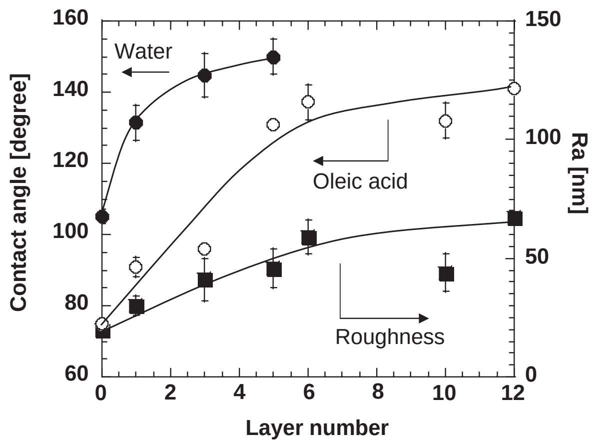

Figure 1. Layer-number dependence of coating on surface roughness and contact angles of water and oleic acid.

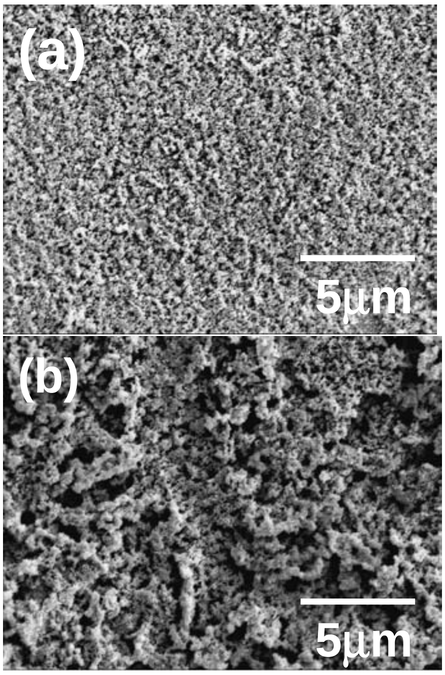

Figure 2. SEM micrographs of the surface coated by 12 layers. (a): center part, (b): edge part.

However, the contact angle of oleic acid increases to 141.1 ± 1.4° even with 12 layers (average film thickness: 3.6 μm). The surface roughness value became nearly constant around 60 nm for layer numbers greater than five, indicating that superlipophobicity is difficult to obtain with roughness of 60 nm, even by increasing the layer thickness. This difference is attributable to the different surface energies of liquids, and their consequent penetration depth differences for rough surfaces.

Figure 2a shows SEM micrographs of the center part of the surface coated by 12 layers. The fractal microstructure comprising boehmite nanoparticles and voids produced by the sublimation of AACA was observed in the film. A surface coated with five layers exhibited a similar microstructure at the center part.

Through the repeated coating procedure to increase layer thickness, the heterogeneity of roughness in the coating gradually becomes remarkable. Furthermore, the surface color changes to white from the edge of the plate because of the increased roughness and resultant light scattering. This will be due to the surface tension unbalance of coating liquid at the substrate edge, and resultant difference in the rate between solvent evaporation and the precipitation of nonvolatile components. Figure 2b shows SEM micrographs of the edge part of the surface coated by 12 layers. The structure was much rougher than the center; the R_a value of the edge was 565 nm. Although the average contact angle of oleic acid at the center of the 12-layer coating was around 141°, the maximum contact angle was 150° at the edge. Figure 3 shows the oleic acid droplet shapes along with SEM micrographs of Figure 2. These results suggest that surface roughness higher than 565 nm is a fundamental requirements for the design of a superlipophobic surface using this process. The effect of surface roughness on lipophobicity is the same as that on hydrophobicity when the surface energy is low enough, namely, Wenzel's mode or Cassie's mode or both.[10] Since an oleic acid droplet was pinned on the surface whose oleic acid contact angle is 150°, we think that the contribution of Wenzel's mode exists to some extent. This roughness value is a requirement and not a sufficient condition. Detailed analysis of the surface shape or fractal dimensions is required to establish sufficient conditions.

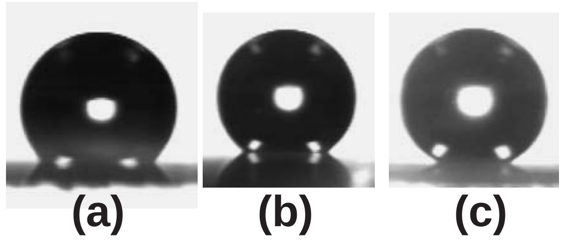

Figure 3. Shapes of the droplet shapes of oleic acid (a) 5-layers: center part (131°), (b) 12 layers: center part (141°), (c) 12 layers: edge part (150°).

It is difficult to obtain a flat boehmite surface. For that reason, we employed a Pyrex glass plate as a model flat oxide substrate and FAS-17 was spread on the surface using the same procedure. The R_a value of this coating was less than 10 nm: the same level of the Pyrex glass plate. Therefore, this coating can be regarded as a smooth surface. Contact angles of water (surface energy value: 72.8 mJ/m^2), methylene iodide (CH_2I_2, 50.8 mJ/m^2; Wako Pure Chemicals Industries, Ltd.), and *n*-hexadecane ($CH_3(CH_2)_{14}CH_3$, 27.6 mJ/m^2; Wako Pure Chemicals Industries, Ltd.) on the surface were evaluated to calculate the surface energy using extended Fowkes method.[9] The corresponding contact angles are 113.8 ± 0.8°, 87.5 ± 0.6°, and 66.8 ± 3.8°, respectively; the obtained surface energy value was 14 mJ/m^2. We infer that the surface energy of oxide decreased to around this value by coating with FAS-17. On the surface of boehmite, because of high density of surface OH groups as the anchors for FAS-17, surface energy might be less than this value.

The present study demonstrated that a superlipophobic surface is attainable using a combination of boehmite nanoparticles and fluoroalkylsilane, and requires larger surface roughness than a superhydrophobic one. Requirements for superlipophobicity by this process are surface roughness greater than 565 nm and surface energy of approximately 14 mJ/m^2. The required roughness value for a superlipophobic surface is around ten times of that for a superhydrophobic one in this process.

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