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Preparation and characterization of super-hydrophobic and oleophobic surface

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Abstract A novel method for preparing and characterizing super-hydrophobic and oleophobic surface is presented. Aluminum (Al) substrate was roughened by sandblasting and electrolytic etching to obtain micro- and nano-sized complex morphologies. Then, its substrate was covered by a chemically adsorbed monolayer (CAM) containing a fluorocarbon group. The surface of Al substrate roughened and covered with CAM was observed by scanning electron microscope and atomic force microscope. The roughnesses of the surface were ca. 100 µm and ca. 30–60 nm, respectively. The surface of the wettability was characterized by contact angle measurements and its surface indicated super-hydrophobicity and oleophobicity: the water contact angle (WCA) and oil contact angle (OCA) of hexadecane was 158.9° and 139.6°, respectively. The wettability was also characterized by solid surface energy. The solid surface energy of each solvent was obtained from the equation by Neumann et al. These values were extremely low, ranging from 0.31 to 1.29 mN/m. The total solid surface energy was obtained from the equation by Kaelble et al. The value was 0.3 mN/m. Their values indicated that the hydrophobicity and oleophobicity of our sample reached the highest level possible. In addition, our research demonstrates that it is easy to compare many different surfaces with super-hydrophobicity and oleophobicity using the solid surface energy.

Introduction

The interface properties of objects, in particular, the wettability is of great importance in industrial fields. Hence, research on the control of wettability has been conducted in the past [1–7]. The interfaces are classified as hydrophilic and hydrophobic. It is common knowledge that low surface energy of interface lead to the hydrophobic surface. For example, the surface of highly ordered CF_3 functional group obtains the lowest surface energy in case of a flat substrate. However, WCA of its surface is approximately 120° [5]. To realize a WCA of greater than 120°, it is required not only to decrease the surface energy of the material but also to decrease the contact area by roughening the substrate surface. Generally, a super-hydrophobic surface is prepared by roughening the surface of the substrate and by covering with hydrophobic matter [8–10]. In recent years, the preparation method of the super-hydrophobic surface that has a WCA of 178° was reported [11]. Evaluation of wettability on the super-hydrophobic and oleophobic surface was difficult. Thus, it is important to have another method to evaluate this surface.

In this article, the super-hydrophobic and oleophobic surface was prepared by the combination of sandblasting, electrolytic etching, and chemical adsorption technique, and then the wettability of the super-hydrophobic and oleophobic surface was evaluated by not only contact angles but also solid surface energy.

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Experimental section

Materials

As shown in Fig. 1, Heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane (HDFS, Toshiba Silicon Co., Ltd.) was used as the chemical adsorbent molecule to prepare a chemically adsorbed monolayer (CAM) [12–15] containing fluorocarbon group (HDFS-CAM) on the surface of the aluminum (Al) substrate. Dehydrated chloroform (Wako Pure Chemical Industries, Ltd.) was used as the dilute solvent for HDFS. The chloroform was dehydrated by adding molecular sieve 4A (Nacalai Tesque, Inc.) for over 1 week. Fluorochemical solvent (365LIVE, Yamato chemicals Co., Ltd.) was used as the organic solvent for the HDFS chemical adsorption (HDFS-CA) solution. Phosphoric acid (H_3PO_4, Wako Pure Chemical Industries, Ltd.) was used as the chemical etching solution for the Al substrate. All chemicals were used without further purification. Grained Al_2O_3 (type of grain #30, diameter range 707–595 μm) was used for sandblasting. Al substrate (50 × 25 × 3 mm) was used for the sample substrate.

Process

Forming micro-level roughness on the surface of the Al substrate

A large roughness of micro-level on the surface of the Al substrate was formed by sandblasting using grained Al_2O_3. The sandblast processing equipment (SGK-3, Japan Blast Process Researches Co., Ltd.) was used for the surface of the Al substrate. The pressure was 4 kg/cm^2 and the treatment time was 2.4 s/cm^2.

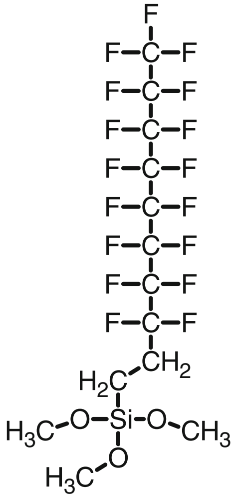

Fig. 1 Chemical formula of the chemical adsorbent molecule (HDFS). The molecule has a fluorocarbon group at the molecular end, a trimethoxysilyl group at the other molecular end and a hydrocarbon chain at the middle portion. The trimethoxysilyl group reacts to a hydroxyl group on the Al substrate surface. The fluorocarbon group decreases the surface energy on the surface of the Al substrate

Forming nano-level roughness on the micro-level roughness

A small roughness of nano-level on the micro-level roughness was formed by electrolytic etching, where electrolytic direct current was supplied between the Al substrate roughened by sandblasting (anode) and the other Cu electrode (cathode) in the electrolytic cell containing H_3PO_4 of 1 N. Roughness was controlled by supplying voltage while monitoring current. The optimal current density and etching time were 1.44 A/cm^2 and 60 s, respectively.

Pre-cleaning of the roughened Al substrate

Before forming HDFS-CAM, the Al substrate roughened by sandblasting and electrolytic etching was fully washed to remove dust, oil, etc. Because when these are placed on the surface of the substrate, HDFS-CAM is never formed perfectly. Thus, the Al substrates roughened by sandblasting and electrolytic etching were cleaned using the ultrasonic cleaner (US cleaner, AS ONE Co., Ltd.) with water for 5 min, and washed with ethanol for 5 min, and chloroform for 5 min, in sequence.

Preparation of HDFS-CAM on the roughened Al substrate

At first, the HDFS diluted solution of 0.1 mol/L was prepared with the dehydrated chloroform. The HDFS-CA solution of 5×10^{-3} mol/L was also prepared by adding the HDFS diluted solution of 0.1 mol/L with the fluorochemical solvent (365LIVE).

All the cleaned Al substrates roughened by sandblasting and electrolytic etching were immersed in the above HDFS-CA solution of 5×10^{-3} mol/L for 2 h at room temperature to react methoxy groups ($-OCH_3$) of HDFS with hydroxyl groups on the surface of the Al substrate [16, 17].

After pulling out the Al substrates roughened and immersed in the HDFS-CA solution, all the specimens were dried at room temperature for 24 h in air to completely react HDFS and the substrate surface. Then, these samples were washed thoroughly with an ultrasonic cleaner using ethanol and chloroform in sequence to remove physically adsorbed HDFS. Thus, HDFS-CAM was formed on the surface of the roughened Al substrate. All process is shown in Fig. 2.

Evaluation

Scanning electron microscopy

The surface topography of the Al substrate roughened by sandblasting was observed by scanning electron

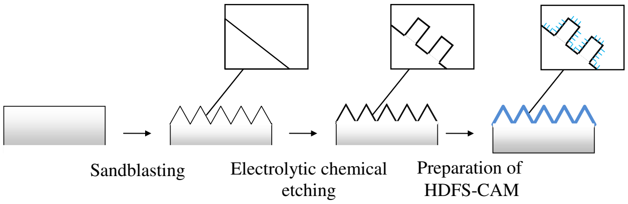

Fig. 2 Schematic diagram of the experimental procedure

microscope (SEM, JSM-5500, JEOL Ltd.). In order to prevent the static charge, gold thin layer was deposited on the surface of the Al substrate roughened by sandblasting prior to an observation.

The surface topography of the Al substrate roughened by sandblasting and electrolytic etching was observed by field emission scanning electron microscope (FE-SEM, Hitachi S-900, Hitachi Ltd.). In order to prevent the static charge, palladium thin layer was deposited on the surface of the Al substrate roughened by sandblasting and electrolytic etching prior to an observation.

Atomic force microscopy

Before and after the preparations of HDFS-CAM on the Al substrate roughened by sandblasting and electrolytic etching, the surface topography of the Al substrate was also observed by atomic force microscope (AFM, Nano scope 2I Dimension 5000, Digital Instruments Inc.) in order to confirm whether HDFS-CAM was formed on the roughened surface without decreasing roughness. NanoProbe silicon tips were used. One 2 × 2 μm area was imaged for each sample.

Contact angle measurement

The automatic contact angle meter CA-VP150 equipped with CCD camera (Kyowa Interface Science Co, Ltd.) was used for measuring the static contact angles. Purified water, tetrabromoethane (Wako Pure Chemical Industries, Ltd.), methyl benzoate (Wako Pure Chemical Industries, Ltd.), *n*-hexadecane (Wako Pure Chemical Industries, Ltd.), and dimethyl silicone (KF-96L-5cs, Shin-Etsu Chemical Co., Ltd.) were used as mensurative solvents of contact angle. The water was purified using a cabinet-type water purifier PRO-0100-002 (Organo Corporation). Purified water was also used for the evaluation of hydrophobicity. Hexadecane (hydrocarbon oil) and dimethyl silicone (silicone oil) were also used for the evaluation of oleophobicity. The droplet volume was 3 μL, and the $\theta/2$ method was applied. The contact angles were measured at different five points and these data were averaged except the lowest and highest data. Before measurement of the contact angle, the surface of all samples was washed fully to remove dust and oil, and then dried to remove water in every measurement.

Calculation of solid surface energy

Several methods are available for calculating solid surface energy. In this study, the solid surface energy γ_S for each solvent and the total solid surface energy γ_S^{total} were calculated.

Solid surface energy for each solvent [18, 19]

Equation 1, derived by Neumann et al., was used to obtain the solid surface energy for each solvent, where γ_L is the liquid surface energy, γ_S is the solid surface energy, θ is the experimental contact angle, and β is a constant (=1.247 × 10^{-4} m^2/mJ). Equation 2 was developed by expanding Eq. 1. Each side in Eq. 2 has an unknown value. Therefore, the liquid surface energy of each solvent and the contact angles were assigned values in Eq. 2. Two curves were drawn, and their intersection point was defined as the solid surface energy:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}}\exp\{-\beta(\gamma_L - \gamma_S)^2\}, \tag{1}$$

$$\ln\gamma_S - \ln\left\{\gamma_L \cos^4\left(\frac{\theta}{2}\right)\right\} = 2.494 \times 10^{-4}(\gamma_L - \gamma_S)^2. \tag{2}$$

Total solid surface energy [19–21]

The total solid surface energy γ_S^{total} was obtained using Eqs. 3 and 4, derived by Kaelble et al., where θ is the experimental contact angle, and γ_L^{total} is the total liquid surface energy. Subscripts L and S denote liquid and solid surfaces, respectively; superscripts d and p represent energy of the dispersion force component and energy of the polarization force component, respectively. In Eq. 3, the corresponding values of the abovementioned parameters for water and *n*-hexadecane were used; two equations that included two unknowns, γ_S^d and γ_S^p, were derived. These unknowns were obtained by solving the simultaneous equations. The resulting values were used in Eq. 4 to obtain γ_S^{total}:

$$\gamma_L^{total}(1 + \cos\theta) = +2\sqrt{\gamma_S^d\gamma_L^d} + 2\sqrt{\gamma_S^p\gamma_L^p}, \tag{3}$$

$$\gamma_S^{total} = \gamma_S^d + \gamma_S^p. \tag{4}$$

Results and discussion

SEM

Figure 3 shows the SEM image of the surface of the Al substrate roughened by sandblasting; from an inspection of the image, the roughness was estimated to be ca. 20–100 μm. Micro-sized morphology was formed by sandblasting.

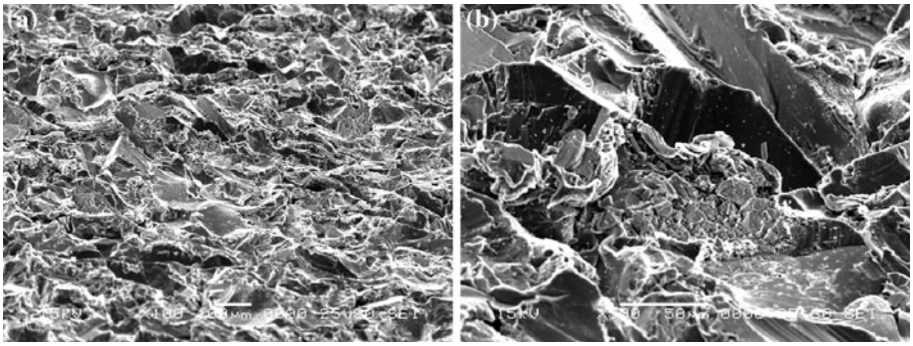

Fig. 3 SEM images of the surface of the Al substrate roughened by sandblasting: **a** ×100; **b** ×500

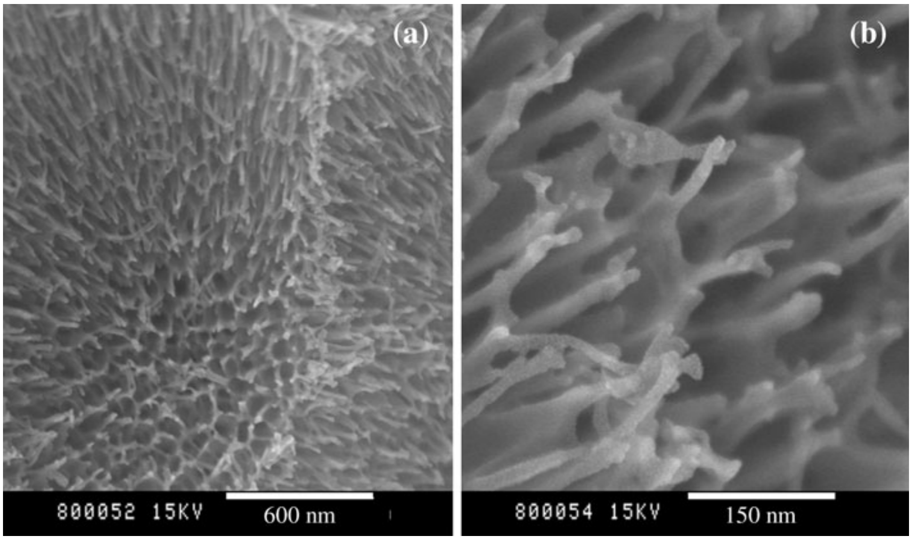

Fig. 4 FE-SEM images of the surface of the Al substrate roughened by sandblasting and electrolytic etching: **a** ×50,000; **b** ×200,000

Figure 4 shows the FE-SEM image of the surface of the Al substrate roughened by sandblasting and electrolytic etching; the roughness was ca. 30–60 nm. Nano-sized morphology was formed by electrolytic etching. Thus, micro-sized and nano-sized complex morphologies were obtained by the combination process of sandblasting and electrolytic etching.

AFM

Figure 5a shows the AFM image of the surface of the roughened Al substrate before the preparations of HDFS-CAM. In Fig. 5a, the root mean square roughness R_r(a) was ca. 30.2 nm, and the average roughness R_a(a) was ca. 23.8 nm on the surface of the roughened Al substrate before the preparation of HDFS-CAM. Figure 5b shows the AFM image of the surface of the roughened Al substrate after the preparations of HDFS-CAM. In Fig. 5b, the root mean square roughness R_r(b) was ca. 34.5 nm, and the average roughness R_a(b) was ca. 27.8 nm on the surface of the roughened Al substrate after the preparation of HDFS-CAM. The differences could indicate that HDFS is deposited on just the tip of convex part.

Contact angle measurement

Table 1 shows the list of contact angles of different solvents on the surface of the Al substrate roughened and covered with HDFS-CAM. The WCA was too high to measure when the droplet volume of water was 3 μL. The surface of the Al substrate roughened and covered with HDFS-CAM was clearly super-hydrophobicity. It was very difficult for us to measure the WCA on the super-hydrophobic Al substrate, and therefore the droplet volume of water was increased to 9 μL. The WCA was 158.9° when the droplet volume of water was 9 μL. The OCA of hexadecane was about 140°. In addition, the contact angle of dimethyl silicone was greater than 120°, although dimethyl silicone (silicone oil) had low surface energy (less than 20 mN/m). Figure 6 show the photography of the dimethyl silicone taken using CCD camera. Two of the other OCAs were also much greater than 90°. Thus,

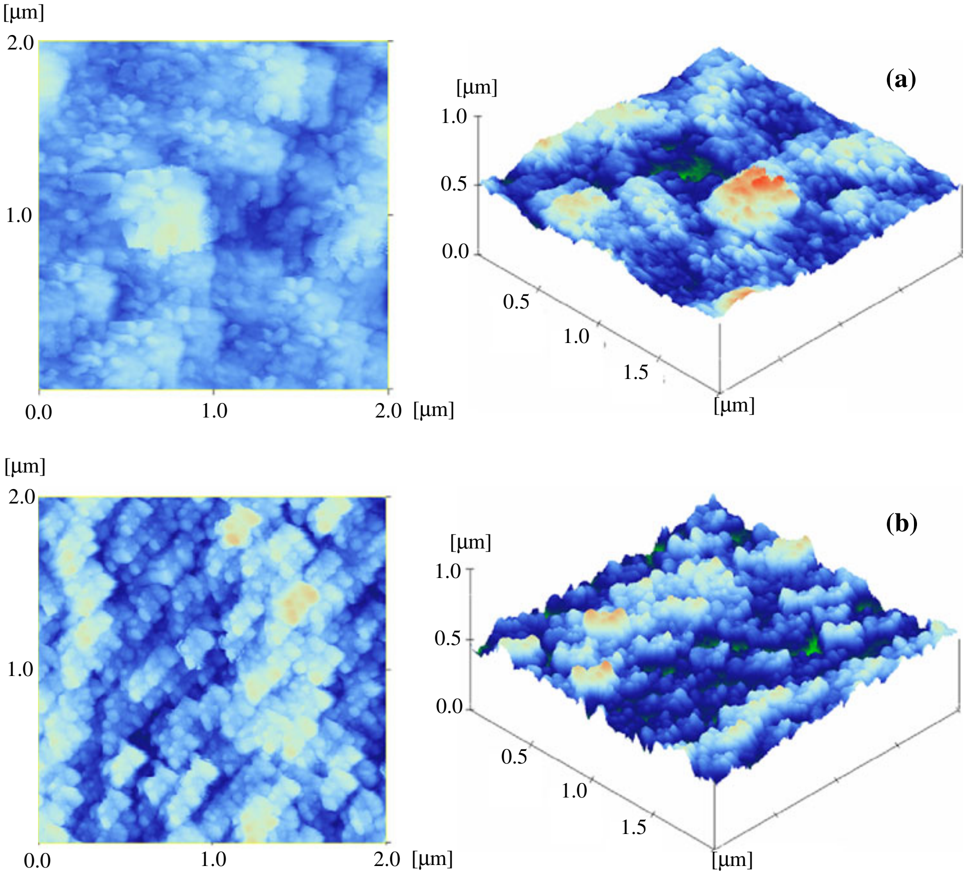

Fig. 5 AFM images of the surface of the Al substrate roughened by sandblasting and electrolytic etching: **a** before the preparations of HDFS-CAM; **b** after the preparations of HDFS-CAM. The topography differences of these images are presented in colors where the black is low and the white is high

Table 1 List of liquid surface energy, contact angles, and solid surface energies of different solvent on the surface of the Al substrate roughened and covered with HDFS-CAM

Solvent	γ_L (mN/m)	CA (°)	γ_S (mN/m)
Water	72.8	158.9	0.31
Tetrabromoethane	47.5	142.9	0.84
Methyl benzoate	37.6	141.6	0.62
Hexadecane	27.6	139.6	0.47
Dimethyl silicone	19.7	120.6	1.29

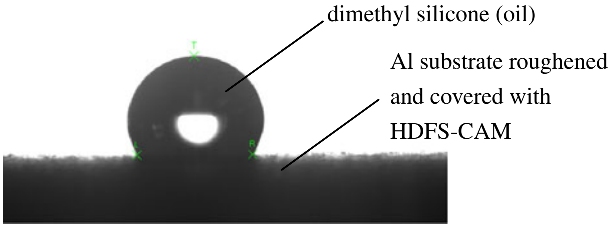

Fig. 6 Photography of the dimethyl silicone on the super-hydrophobic and oleophobic surface taken using CCD camera. The contact angle of the dimethyl silicone is greater than 120°

the surface of the Al substrate roughened and covered with HDFS-CAM was not only super-hydrophobic but also highly oleophobic.

Surface energy

Solid surface energy for each solvent

The values of θ and γ_L for each solvent given in Table 1 were used in Eq. 2. Figure 7 shows the intersection point of two curves for each solvent. The γ_S value for each solvent of our sample (Al substrate roughened and covered with HDFS-CAM) was easily obtained, as shown in Table 1. These values were extremely low, ranging from 0.31 to 1.29 mN/m.

Total solid surface energy

Table 2 shows the values of γ_S^d and γ_S^p obtained by calculating from the simultaneous equations. These values were used in Eq. 4 to obtain γ_S^{total}. The γ_S^{total} for our sample (Al substrate roughened and covered with HDFS-CAM) was 0.3 mN/m.

We then compared the hydrophobicity and oleophobicity of our sample to those of other super-hydrophobic and oleophobic surfaces by using values of γ_S^{total}. Two references were used as comparative data [22, 23]. In the first reference, a study by Shibuichi et al. [22], three kinds of Al samples indicated super-hydrophobicity and oleophobicity.

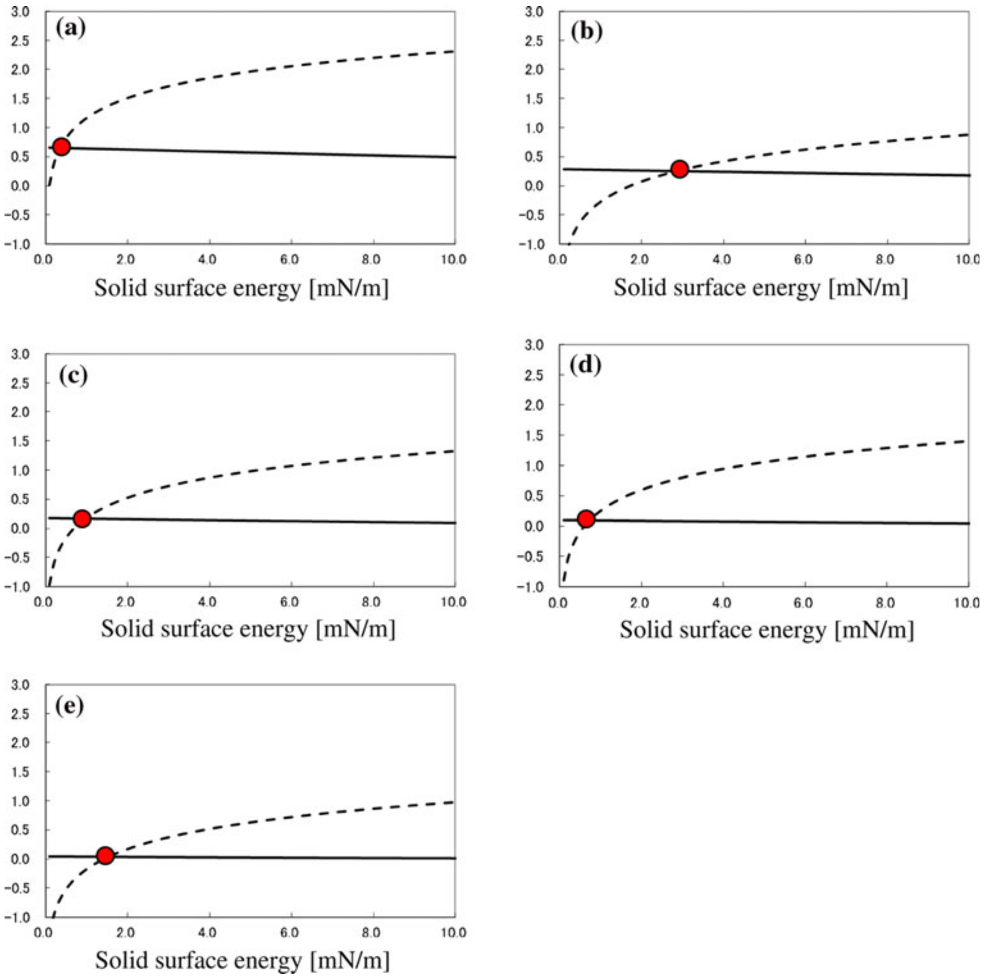

Fig. 7 Intersection points of two curve lines in Eq. 2 for the determination of the solid surface energy of each solvent: **a** purified water; **b** tetrabromoethane; **c** methyl benzoate; **d** hexadecane; **e** dimethyl silicone

Table 2 List of total solid surface energies on different super-hydrophobic and oleophobic surfaces

Sample	Solvent	CA (°)	γ_S^d (mN/m)	γ_S^p (mN/m)	γ_S^{total} (mN/m)
Our sample	Water	158.9	0.3	0.0	0.3
	Hexadecane	139.6			
Sample 1	Water	163.0	1.0	0.0	1.0
	Hexadecane	115.0			
Sample 2	Water	166.0	0.3	0.0	0.3
	Hexadecane	135.5			
Sample 3	Water	161.0	1.6	0.0	1.6
	Hexadecane	105.6			
Sample 4	Water	158.0	0.4	0.0	0.4
	Hexadecane	136.0			

Al sample 1, which was covered with F_8-MAP, had a WCA of 163.0° and an OCA of 115.0°; its γ_S^{total} was 1.0 mN/m. Al sample 2, which was covered with F_{10}-MAP, had a WCA of 166.0° and an OCA of 135.5°; its γ_S^{total} was 0.3 mN/m. Al sample 3, which was covered with Si-coupling, had a WCA of 161.0° and an OCA of 105.6°; its γ_S^{total} was 1.6 mN/m. In the second reference, a study by Han and Steckl [23], the fiber (sample 4) used in their study indicated super-hydrophobicity and oleophobicity, with a WCA of 158.0° and an OCA of 136.0°. The γ_S^{total} sample 4 was 0.4 mN/m. These results indicate that γ_S^{total} of our sample was similar to those of samples in other studies. We were able to compare our data to those from conventional reports on hydrophobicity and oleophobicity using values of γ_S^{total}.

Conclusion

We presented a novel process for preparing a super-hydrophobic and oleophobic surface. First, an Al substrate was roughened by sandblasting and electrolytic etching. The formation of micro- and nano-sized morphologies was confirmed by SEM and FE-SEM observations. Then, HDFS-CAM was prepared on the roughened Al substrate. The wettability of the resulting surface was evaluated by contact angle measurement. The surface of Al substrate roughened and covered with HDFS-CAM indicated super-hydrophobic and oleophobic properties.

The super-hydrophobic and oleophobic surface was also characterized by solid surface energy. We demonstrated that γ_S for each solvent on the super-hydrophobic and oleophobic surface could be easily obtained using Eq. 2. In addition, we also demonstrated that γ_S^{total} could be easily obtained using Eqs. 3 and 4. The results indicate that the hydrophobicity and oleophobicity of our data reached the highest level possible.

In this study, we attempted to quantify the wettability of a hydrophobic and oleophobic surface. Finally, the wettability was quantified using solid surface energy. It was easy to compare the hydrophobicity and oleophobicity though the surface was super-hydrophobic and oleophobic. Our research would be important and useful in the future to characterize super-hydrophobic and oleophobic surfaces and to compare many different surfaces using the mathematically derived solid surface energy.

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References

1. Wenzel RN (1936) Ind Eng Chem 28:988
2. Ulman A (1996) Thin Solid Film 273:48
3. Guan K, Lu B, Yin Y (2003) Surf Coat Technol 173:219. doi:10.1016/S0257-8972(03)00521-8
4. Kiuru M, Alakoski E (2004) Mater Lett 58:2213. doi:10.1016/j.matlet.2004.01.024
5. Zhu L, Feng Y, Ye X, Zhou Z (2006) Sens Actuators A 130–131:595. doi:10.1016/j.sna.2005.12.005
6. Zhang J, Huang W, Han Y (2006) Langmuir 22:2946. doi:10.1021/la053428q
7. Gao L, McCarthy TJ (2007) Langmuir 23:3762. doi:10.1021/la062634a
8. Qian B, Shen Z (2005) Langmuir 21:9007. doi:10.1021/la051308c
9. Zhang X, Jin M, Liu Z, Nishimoto S, Saito H, Murakami T, Fujishima A (2006) Langmuir 22:9477. doi:10.1021/la0618869
10. He B, Patankar NA, Lee J (2003) Langmuir 19:4999. doi:10.1021/la0268348
11. Hosono E, Fujihara S, Honma I, Zhou H (2005) J Am Chem Soc 127:13459. doi:10.1002/adma.200500275
12. Sagiv J (1979) Isr J Chem 18:339
13. Sagiv J (1980) J Am Chem Soc 102:92
14. Ulman A (1996) Chem Rev 96:1533
15. Schreiber F (2000) Prog Surf Sci 65:151. doi:10.1016/S0079-6816(00)00024-1
16. Tada T, Noriyasu H, Kawamura Y, Ohkubo Y, Ogawa K (2009) J Textile Eng 55:13. doi:10.4188/jte.55.13
17. Yamamoto H, Ohkubo Y, Ogawa K, Utsumi K (2009) Precis Eng 33:229. doi:10.1016/j.precisioneng.2008.07.006
18. Li D, Neumann AW (1992) J Colloid Interface Sci 148:190. doi:10.1016/0021-9797(92)90127-8
19. Kaelble DH, Uy KC (1970) J Adhesion 2:50. doi:10.1080/0021846708544579
20. Kaelble DH (1970) J Adhesion 2:66. doi:10.1080/0021846708544582
21. Jańczuk B, Kerkeb ML, Biatrowicz T, González-Caballero F (1992) J Colloid Interface Sci 151:333. doi:10.1016/0021-9797(92)90482-2
22. Shibuichi S, Yamamoto T, Onda T, Tsuji K (1998) J Colloid Interface Sci 208:287
23. Han D, Steckl AJ (2009) Langmuir 25:9454. doi:10.1021/la900660v