Super-Water-Repellent Fractal Surfaces

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Letters

Super-Water-Repellent Fractal Surfaces

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Wettability of fractal surfaces has been studied both theoretically and experimentally. The contact angle of a liquid droplet placed on a fractal surface is expressed as a function of the fractal dimension, the range of fractal behavior, and the contacting ratio of the surface. The result shows that fractal surfaces can be super water repellent (superwettable) when the surfaces are composed of hydrophobic (hydrophilic) materials. We also demonstrate a super-water-repellent fractal surface made of alkylketene dimer; a water droplet on this surface has a contact angle as large as 174°.

Ultrahydrophobic solid surfaces, which perfectly repel water, would bring great convenience on our daily life. Conventionally, the wettability of solid surfaces has been controlled by chemical modifications of the surfaces, such as fluorination.[1] The present Letter highlights the other factor determining the wettability, i.e., the geometrical structure of solid surfaces.[2−4] There exists, as Mandelbrot has emphasized in his textbook,[5] a fascinating geometrical structure called fractal, which is characterized by self-similarity and a noninteger dimension. Then a question arsies: What is the wettability of the solid surface with a fractal structure? This Letter shows both theoretically and experimentally that fractal surfaces can be either superrepellent or superwettable to a liquid. Furthermore, we demonstrate a super-water-repellent fractal surface made of alkylketene dimer; a water droplet on this surface has a contact angle as large as 174°.

The contact angle θ of a liquid placed on a flat solid surface is given by Young's equation[2]

$$\cos\theta = \frac{\alpha_{13} - \alpha_{12}}{\alpha_{23}} \tag{1}$$

where α_{12}, α_{13}, and α_{23} denote the interfacial tensions of the solid−liquid, the solid−gas, and the liquid−gas interface, respectively. When a solid surface is rough, Young's equation is modified into[2]

$$\cos\theta_{\mathrm{r}} = r\,\frac{\alpha_{13} - \alpha_{12}}{\alpha_{23}} \quad (= r\cos\theta) \tag{2}$$

where r is a coefficient giving the ratio of the actual area of a rough surface to the projected area.

A fractal surface is a kind of rough surface, so that the wettability of the fractal surface is basically described by eq 2.[3] The coefficient r of the fractal surface, however, is very large and can even be infinite for a mathematically ideal fractal surface. Therefore, the modification of the wettability due to surface roughness can be greatly enhanced in the fractal surface;[3] that is, the fractal surface will be superrepellent (superwettable) to a liquid when θ is greater (less) than 90°.

Strictly speaking, applicability of eq 2 is limited. In fact, eq 2 cannot give any contact angle when the absolute value of its right-hand side exceeds unity. A correct expression for the contact angle can be derived conveniently by introducing the effective interfacial tension of

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(1) Watanabe, N.; Tei, Y. *Kagaku* **1991**, *46*, 477 [in Japanese].
(2) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley & Sons: New York, 1990; Chapter X, Section 4.
(3) Hazlett, R. D. *J. Colloid Interface Sci.* **1990**, *137*, 527.
(4) Good, R. J.; Mikhail, R. S. *Powder Technol.* **1981**, *29*, 53.
(5) Mandelbrot, B. B. *The Fractal Geometry of Nature*; Freeman: San Francisco, CA, 1982.

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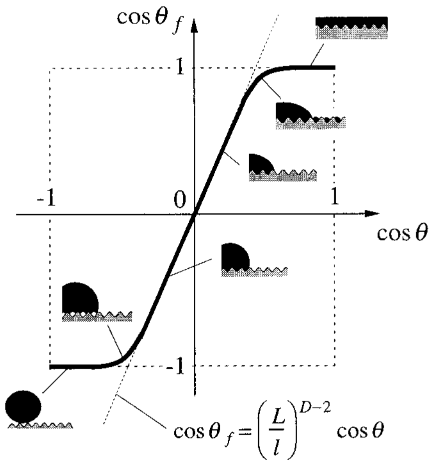

Figure 1. Schematic illustration for $\cos\theta_f$ vs $\cos\theta$ theoretically predicted.

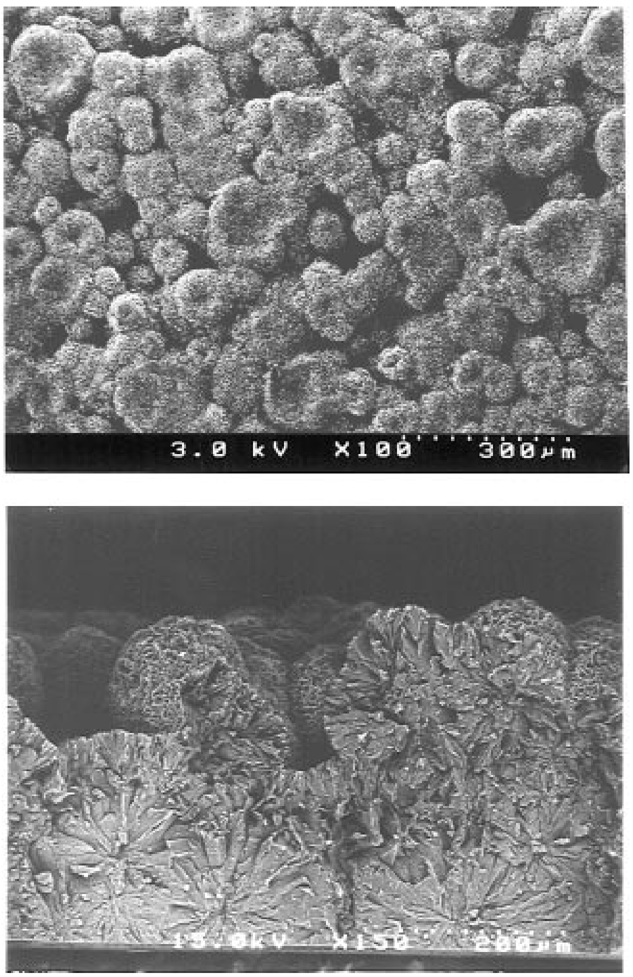

Figure 2. SEM images of the fractal AKD surface: (a, top) top view, (b, bottom) cross section.

the solid−liquid fractal interface, α_{f12}, and that of the solid−gas fractal interface, α_{f13}. Then the contact angle θ_f is given by

$$\cos\theta_f = \frac{\alpha_{f13} - \alpha_{f12}}{\alpha_{23}} \tag{3}$$

Since α_{f1j} ($j = 2, 3$) may be considered the total interfacial energy of the fractal surface per unit projected area, α_{f1j} can be estimated, as a first approximation, by $\alpha_{f1j} = (L/l)^{D-2}\,\alpha_{1j}$. Here, D ($2 \le D < 3$) is the fractal dimension of the surface; L and l are respectively the upper and the lower limit lengths of fractal behavior. Substitution of this α_{f1j} into eq 3 yields eq 2 in which $(L/l)^{D-2}$ is substituted for r.

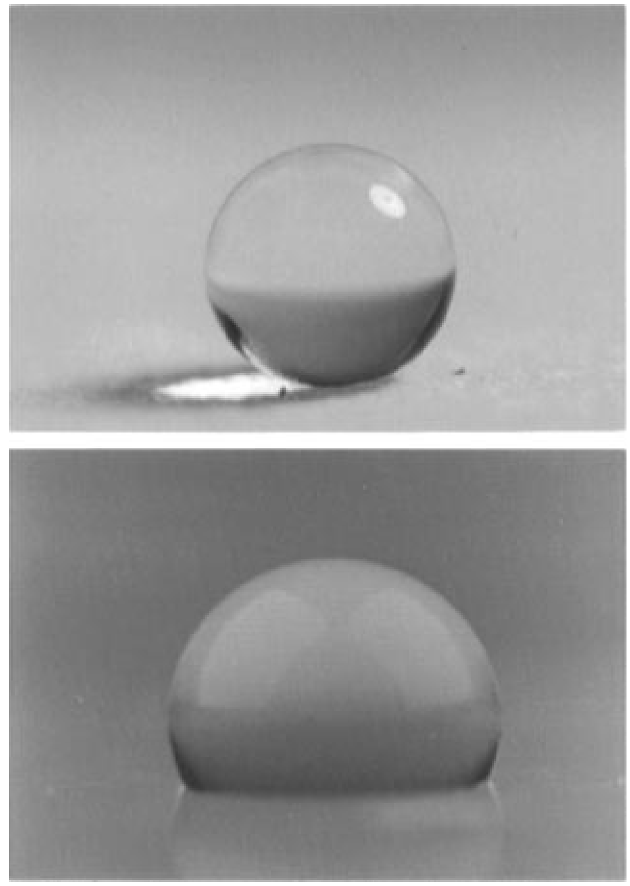

Figure 3. Water droplet on AKD surfaces: (a, top) fractal AKD surface ($\theta_f = 174°$); (b, bottom) flat AKD surface ($\theta = 109°$). The diameter of the droplets is about 2 mm.

To be more precise in estimating α_{f1j}, we must take account of the adsorption of a gas on the solid−liquid fractal interface and that of a liquid on the solid−gas fractal interface. Then α_{f1j} can be expressed by

$$\alpha_{f12} = \min_x\left\{\alpha_{13}\left(\frac{L}{l}\right)^{D-2} x + \alpha_{12}\left(\frac{L}{l}\right)^{D-2}(1-x) + \alpha_{23}S_{23}(x)\right\} \tag{4}$$

$$\alpha_{f13} = \min_y\left\{\alpha_{13}\left(\frac{L}{l}\right)^{D-2}(1-y) + \alpha_{12}\left(\frac{L}{l}\right)^{D-2} y + \alpha_{23}S_{23}(y)\right\} \tag{5}$$

where x ($0 \le x \le 1$) is the fraction of the area of the fractal surface covered with the adsorbed gas, y ($0 \le y \le 1$) is that covered with the adsorbed liquid, and S_{23} is the area of the gas−liquid interface per unit projected area. The symbol "min" expresses the operation of minimizing the succeeding quantities with respect to x or y; this operation corresponds to the fact that adsorption so occurs as to minimize the total interfacial energy. Typically, $S_{23}(z)$ ($z = x, y$) can be approximated by a cubic function of z, given by

$$S_{23}(z) = z + \left\{\left(\frac{L}{l}\right)^{D-2} - 1\right\} z(1-z)\left\{\frac{(1-\xi)(1-3\xi)}{1-2\xi} - z\right\} \tag{6}$$

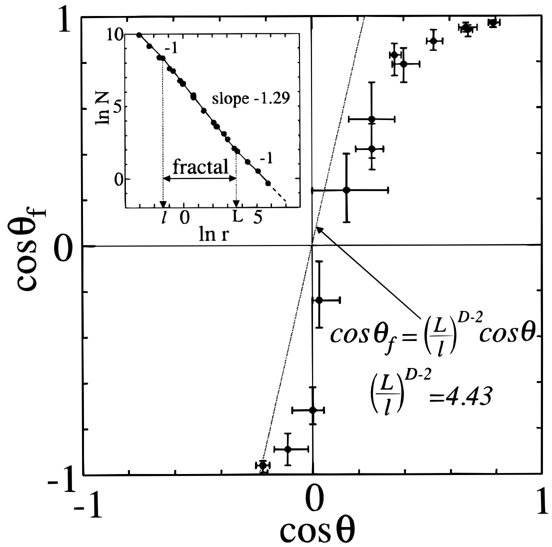

Figure 4. cos θ_f vs cos θ determined experimentally for the AKD surface. The line of cos $\theta_f = (L/l)^{D-2}$ cos θ deduced from the box counting measurement of the fractal AKD surface is also drawn. In the inset, the result of the box counting measurement applied to the cross section of the AKD surface is shown.

where ξ denotes the contacting ratio of the fractal surface (the ratio of the area touching a flat plate placed on the fractal surface). Behavior of θ_f determined by eqs 3−6 is shown schematically in Figure 1, in which cos θ_f is plotted as a function of cos θ ($=(\alpha_{13} - \alpha_{12})/\alpha_{23}$). The obtained curve coincides with the line of cos $\theta_f = (L/l)^{D-2}$ cos θ in the vicinity of $\theta = 90°$, but deviates from it owing to the adsorption when θ approaches 0° or 180°.

To verify the theoretical prediction, we have experimentally examined the wettability of various kinds of fractal surfaces. In this Letter, we report the results of the fractal surface made of alkylketene dimer (AKD), which is a kind of wax and one of the sizing agents for papers.

Alkylketene dimer mostly used in our experiments was synthesized from stearoyl chloride with the use of triethylamine as a catalyst and purified up to 98% with a silica gel column. The purity was checked by gel permeation chromatography and capillary gas chromatography; the major impurity was dialkyl ketone, which was produced by the hydrolysis of AKD. AKD solid films with a thickness of about 100 μm were grown on glass plates; a glass plate was dipped into melted AKD heated at 90 °C and was then cooled at room temperature in the ambience of dry N_2 gas. AKD undergoes fractal growth when it solidifies, although the mechanism has not been clarified yet. SEM images of the AKD solid surface are shown in Figure 2.

To find the fractal dimension of the AKD surface, we applied the box counting method to the cross section of one of the AKD films. The AKD film peeled off from the glass plate was cleaved with the aid of a razor blade, and SEM images of its cross section (Figure 2b) were taken at several magnifications. Then the fractal dimension of the cross section, D_{cross}, has been measured by the box counting method and found to be 1.29 in the range between $l = 0.2\,\mu$m and $L = 34\,\mu$m (see the inset of Figure 4); below and above the range, D_{cross} is found to be unity. Thus, the fractal dimension of the AKD surface has been evaluated as $D \cong D_{cross} + 1 = 2.29$.

Figure 3a shows a water droplet placed on the fractal AKD surface. This surface, as expected, repels water completely and a contact angle as large as 174° has been obtained. For comparison, we have also examined the wettability of a mechanically flattened AKD surface, which was prepared by cutting a fractal AKD surface with a razor blade. The flat AKD surface, however, does not repel water very much, showing a contact angle not larger than 109° (Figure 3b). Comparison of parts a and b of Figure 3 highlights the importance of the fractal effect on the wettability.

The relationship between the contact angle for the fractal AKD surface, θ_f, and that for the flat AKD surface, θ, has also been studied with the use of liquids of various surface tensions. As the liquids, we used aqueous solutions of 1,4-dioxane at various concentrations; θ becomes smaller as the concentration of 1,4-dioxane increases. The result is shown in Figure 4, in which cos θ_f is plotted as a function of cos θ. The measurement of the contact angle has been performed several times at each concentration and the dispersion of the data is expressed by error bars. The fractal AKD surface showed advancing and receding contact angles, whose difference was not negligible particularly when θ_f was close to 90°, so that we have measured an average contact angle after bringing the water droplet into an equilibrium state by vibrating it. In Figure 4, we draw also the line of cos $\theta_f = (L/l)^{D-2}$ cos θ with the value of $(L/l)^{D-2}$ determined by the box counting measurement: $(L/l)^{D-2} = (34/0.2)^{2.29-2} \cong 4.43$. The result obtained agrees well with the behavior predicted in Figure 1.

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