Control of Hydrophobic Character of Super-water-repellent Surface by UV Irradiation

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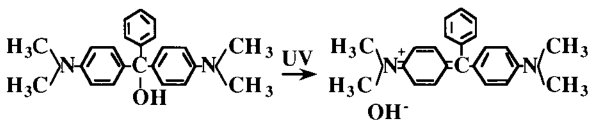
The hydrophobic character of a super-water-repellent surface (the contact angle for water is more than 150 degrees) can be changed by UV irradiation due to photoisomerization of malachite green carbinol base coated on the surface.

In recent years, several groups have investigated water-repellent and super-water-repellent surfaces.[1-6] Water-repellent surfaces have been applied to many articles, such as outersurfaces of coats and sportswear,[1] and automobile window glass.[5] Super-water-repellent surfaces have been proposed to prevent telecommunication antennas from frosting[6] and to increase the efficiency of electrochemical reactions.[4] If the hydrophobic character can be controlled by external stimulation, new printing system can be developed. We report here a UV irradiation method to control the hydrophobic character of super-water-repellent surfaces.

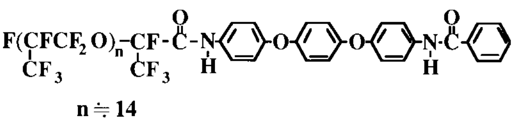
The principle to control the hydrophobic character of the super-water-repellent surface by UV irradiation in the present work is as follows. Malachite green carbinol base (compound **1**) changes into a less hydrophobic structure (compound **1'**) when hydroxide anion is detached by UV irradiation.[7]



Compound 1 **Compound 1'**

This way result in the reduction of the water repellency of a super-water-repellent surface coated with compound **1** by UV irradiation.

The super-water-repellent surface was prepared as follows. Tetraepoxy monomer (XD 9053, by Dow Chemical Co., USA) (10.0 g), poly(p-vinylphenol) (Maruka Lincur-M, by Maruzen Petrochemical Co. Ltd., Japan) (5.4 g), triethylammonium tetraphenylborate (0.1 g), ethylene glycol 2-butoxyethyl acetate (7.0 g), and compound **2**[8] (0.3 g) were dissolved in 2-butanone (132 g).



Compound 2

The two kinds of SiO_2 particles[9] (Aerosil 130, by Nihon Aerosil Co. Ltd., Japan, the average particle size is 16 nm (0.3 g) and Nipsil E-220A, by Nippon Silica Co. Ltd., Japan, the average particle size is 1500 nm (0.3 g)) were added to the 2-butanone solution. The mixture was shaken and placed in an ultrasonic water bath for a few hours to facilitate dispersion of SiO_2 particles. A glass plate (40 mm, 30 mm, 1 mm) was dipped in the mixture for 10 seconds, and then raised at a rate of 3 mm / s. The glass plate was heated at 393 K for 30 min and then at 473 K for 45 min. During these procedures, the monomer in the mixture which was coated on the glass plate was polymerized. Then, the glass plate was dipped in a dichloromethane solution (conc.; 0.01, 0.03, 0.1, 0.5, 2.0, 3.0, and 5.0 wt%) of compound **1** for 10 s, and then raised at a rate of 3 mm / s. The glass plate was dried at room temperature. The thickness of the composite layer on the glass plate was found to be about 8 μm. The contact angle for water on the surface of the layer was more than 150 degrees. Therefore, we assumed that the surface has super-water-repellency.[10] Photoirradiation was performed with a 500 W xenon lamp (Ushio Electric Inc., Japan) using a cut off filter (Toshiba UV-D-36B) for isolating UV (300 nm < λ < 400 nm). The intensity of the photoirradiation was 6.6 mW / cm^2. The water repellency of the surface before and after UV irradiation was evaluated using the contact angle for water.

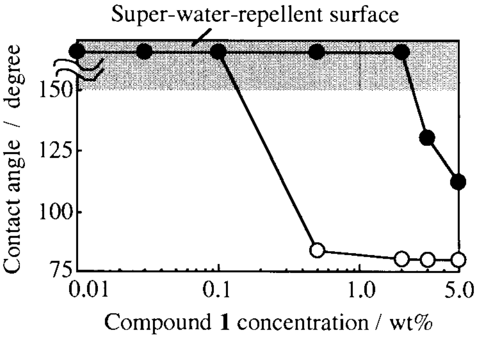


Figure 1. Dependence of the contact angle on compound **1** concentration of dichloromethane solution.
● : Before UV irradiation, ○ : After UV irradiation

Figure 1 shows the contact angles for water on the surfaces. Before UV irradiation, these surfaces dipped in five different concentration from 0.01 to 2.0 wt% solution of compound **1**, showed super-water-repellency. The contact angle of these surfaces dipped in 3.0 and 5.0 wt% solution of compound **1**, are 130 degrees and 113 degrees, respectively. However after 120 seconds of UV irradiation (total light energy, 0.79 J/cm^2), the contact angles of these surfaces dipped in from 0.5 to 5.0 wt% solution of compound **1**, dropped to about 80 degrees. On the other hand, the contact angle of any polished Si wafer, which dipped in from 0.5 to 5.0 wt% solution of compound **1**, were about 80 degrees. Each layer formed by various concentrations of compound **1** solution is almost flat. Therefore compound **1** may adhere partially on the super-water-repellent surface.

Figure 2 shows the change in the contact angle of the surface induced by UV irradiation. More than 90 seconds of UV irradiation, the surface did not show super-water-repellency. More than 120 seconds of UV irradiation, the contact angle of the surface was about 80 degrees.

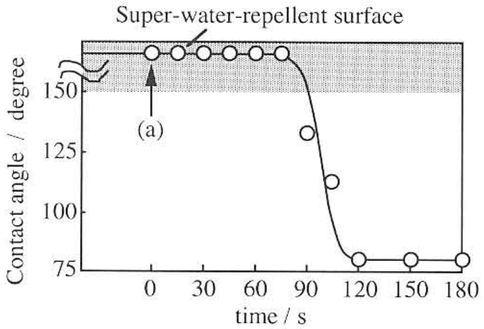


Figure 2. The change of contact angle of the surface induced by UV irradiation.
The surface was dipped in 2.0 wt% of compound **1**.
(a) : The start of UV irradiation.

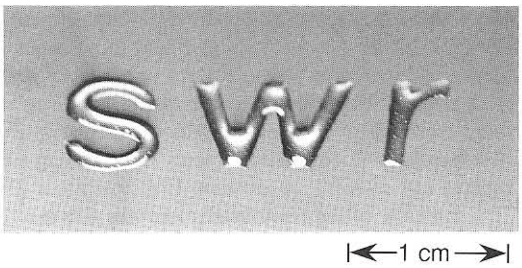


Figure 3. Water adhesion condition of UV irradiated (area showing letters; s,w,r) and non-irradiated area.
The letters (UV irradiated area) are water. No water adheres to the non-irradiated area. Compound **1** concentration was 2.0 wt%.

Figure 3 shows a picture of the surface, which had UV irradiated (the letters s,w,r) and non-irradiated (masked) area, was dipped in water for 5 seconds. The color of the exposed surface changed from pale yellow to greenish yellow by UV irradiation. We did not observe any difference in the SEM images on the surface before and after UV irradiation. The magnitude of the fractal dimension of each surface was found to be nearly equal.[11] It is known that the triphenylmethanol derivatives, which have the same photofunctional group as compound **1**, turn green due to photo-isomerization.[12,13] Accordingly, we conjecture that the color change in the surfaces is caused by the isomerization of compound **1** to compound **1'**. The surface looses its super-water-repellency by isomerization from compound **1** to compound **1'**.

We conclude that it is possible to use UV irradiation to control super-water-repellency. The technique may be useful for a new printing system.

References and Notes

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8 Compound **2** was obtained by two steps of amidation reactions. In the first step, one of the amino groups of 1,4-bis(4-aminophenoxy)benzene reacts with benzoyl chloride, while in the second step, the other amino group reacts with poly (perfluoroisopropyleneoxy)carbonylchloride. Poly (perfluoroisopropyleneoxy) carbonylchloride was obtained by chlorination of poly(perfluoroisopropyleneoxy) carboxylic acid (Krytox 157 FS-L, E. I. du Pont de Nemours & Co. Inc. USA) using thionyl chloride. Satisfactory spectral data were obtained for **2**.

9 These SiO_2 particles were used to construct the surface roughness with large and small projections. The roughness is necessary for bringing about super-water-repellency of the surface.[2,3]

10 All measurements were repeated at least three times and the repeatability of the results was better than 10 degrees. As test plates were not perfectly horizontal, a water drop moved on the surfaces when the contact angle was more than 150 degrees. Therefore we assumed that the surface showed a contact angle of more than 150 degrees is a super-water-repellent surface.

11 Fractal dimension was calculated by the surface roughness analysis using AFM technique.[14] Before UV irradiation, fractal dimension of the surface was 2.29. However after UV irradiation, the fractal dimension was 2.37. Before coating compound **1**, the fractal dimension of the surface that shows super-water-repellency was 2.34.

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