Surface Chemistry

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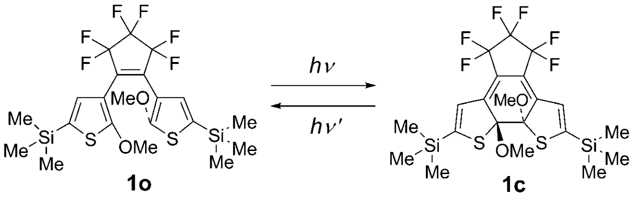
Phototunable Diarylethene Microcrystalline Surfaces: Lotus and Petal Effects upon Wetting**

Kingo Uchida, Naoki Nishikawa, Norikazu Izumi, Seiji Yamazoe, Hiroyuki Mayama, Yuko Kojima, Satoshi Yokojima, Shinichiro Nakamura,* Kaoru Tsujii, and Masahiro Irie*

In nature, many plants and insects have superhydrophobic surfaces with water contact angles (CAs) larger than 150°. For example, the leaves of the plume poppy (*Macleaya cordata*) and a lotus are covered with micrometer-sized rods or protrusions that cause water droplets to roll over the surface.[1] In particular, lotus leaves are well-known for their superhydrophobic surface, where the contact angle and sliding angle (SA) of a water droplet are $(161.0\pm2.7)°$ and 2.0°,[1] respectively (the "lotus effect"). Rose petals also show super water repellency with a CA of about 152.4°; however, these droplets become pinned to the surface and cannot roll off, even when the petal is turned upside down. This phenomenon is the "pinned effect" or "petal effect."[2] Such surfaces have attracted great interest for both basic research and practical applications in recent years.[3] To explain the effects of surface topography on the enhancement of hydrophobicity, Wenzel[4], and Cassie and Baxter[5] have proposed models showing the roles of both the surface area and air trapped in concavities on the surface. Jiang and co-workers noted how the lotus effect represents the Cassie state[6] (Figure S9 in the Supporting Information), while the petal effect represents the Cassie impregnating wetting state.[6] These two states are differentiated by the microstructures of both surfaces. A Cassie state could be achieved in theory by reducing the microstructure scale.

Studies on the fabrication of super water-repellant surfaces with artificial materials have also been reported.[7] Recently, we investigated reversible wettability changes by using a photochromic diarylethene derivative.[8] Photochromic compounds are molecules that can be switched by light activation between two distinct states that have different properties.[9] Some photochromic compounds show light-induced reversible polarity changes, therefore wettability changes can be controlled by using these compounds.[10] Among the photochromic compounds, diarylethenes have excellent thermal stability of both isomers and a high fatigue resistance; however, no remarkable polarity changes are observed during the photochromic switching.[9c] We previously reported how the reversible wettability changes on the microcrystalline surface of such diarylethene derivatives were accompanied by photoinduced topographical changes on the surface.[8,11] Upon alternate irradiation with UV and visible light, reversible crystal growth and melting was observed. After UV irradiation, needle-shaped crystals of **1c** (Scheme 1) grew on the surface and enhanced the superhydrophobicity; these crystals were melted by irradiation with visible light and the CA reverted to the initial value.



Scheme 1. Photochromic reaction between open-ring isomer **1o** and closed-ring isomer **1c**.

Herein, we report the selective formation of surfaces that show the lotus effect (Figure 1a) and the petal effect (Figure 1b) on a microcrystalline film of the diarylethene derivative **1o** by controlling the UV irradiation and storage temperature. On the surface in Figure 1a, the CA of a water droplet was $(162.9\pm0.8)°$ and the droplet rolled off when the surface was tilted by only 2°. Figure 1b shows the case of a water droplet that stayed pinned onto the surface with superhydrophobic character, even if the surface was turned upside down ($\mathrm{CA}=(154.1\pm0.9)°$).

The two surfaces were prepared as follows: upon UV irradiation (for 10 minutes), the diarylethene **1o** (mp 100 °C)

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[*] Prof. Dr. K. Uchida, N. Nishikawa, N. Izumi, Dr. S. Yamazoe
Department of Materials Chemistry
Faculty of Science and Technology
Ryukoku University, Seta, Otsu 520-2194 (Japan)
Fax: (+81) 77-543-7483
E-mail: uchida@rins.ryukoku.ac.jp
Homepage: http://www.chem.ryukoku.ac.jp/uchida/
Dr. H. Mayama, Dr. K. Tsujii
Nanotechnology Research Center
Research Institute for Electronic Science
Hokkaido University, N21, W10 Kita-ku, Sapporo 001-0021 (Japan)
Dr. Y. Kojima, Dr. S. Yokojima, Prof. Dr. S. Nakamura
Mitsubishi Chemical Group Science and Technology Research Center, Inc., and
CREST, Japan Science and Technology Corporation
1000 Kamoshida, Yokohama 227-8502 (Japan)
E-mail: nakamura.shinichirou@md.kaiteki-institute.com
Prof. Dr. M. Irie
Department of Chemistry and Research Center for Smart Molecules
Rikkyo University, Tokyo 171-8501 (Japan)

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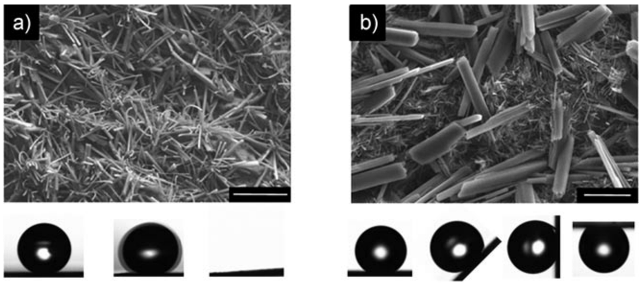

Figure 1. a) Contact and sliding angles of a water droplet on the surface after storage at 30 °C for 24 h after UV irradiation were (162.9 ± 0.8)° and 2°, respectively. (SEM image corresponds to Figure 2c). b) The contact angle of the water droplet on the surface prepared by the procedure explained in Figure 2 was (154.1 ± 0.9)° and the droplet stayed pinned onto the surface, even when it was turned over (SEM image corresponding to Figure 2h). Scale bars: 20 μm for all images, which are magnified 1000×.

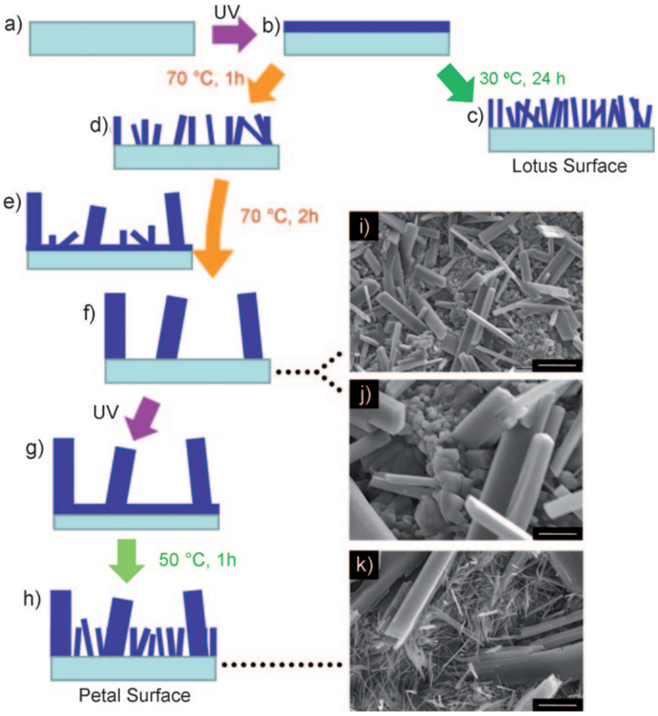

Figure 2. Schematic explanation of the formation of the surfaces that show lotus and petal effects. Upon UV irradiation of the surface of a coated film of diarylethene **1o** (a), closed-ring isomer **1c** (dark blue layer) was formed only on the irradiated side of the surface (b). After storage in the dark, the surface was covered with closely packed small fibrils (c). After storage of the film shown in (b) for 1 h at 70 °C, small fibrils grow sparsely within 1 h (d) After additional heating in the dark, larger rod-shaped crystals grew while fine fibrils melted (e) and finally the surface was covered only with rod crystals (f). The surface was photoisomerized by a second UV light irradiation (g). After storing the film at 50 °C for 1 h in the dark, the surface was covered with rod crystals and also newly formed fibrils (h). SEM images of the microcrystalline surfaces of diarylethene **1** (i–k). i) SEM image of surface corresponding to (f) (1000×); j) Magnified image of (i) (2000×); k) Magnified image of Figure 1b (3000×). (Scale bar: 20 μm for 1000× images, 6.7 μm for 3000× images).

underwent a cyclization reaction to the closed-ring isomer **1c** on the surface of the film. Then, the surface melted when the films were kept above 30 °C, which is the eutectic temperature of **1o** and **1c**, and the formation of needle-shaped crystals of **1c** (around 1–2 μm in diameter and 10 μm in length) occurred within 15–24 hours (Figure 1a). The surface covered with the needle-shaped crystals of **1c** had a superhydrophobic character (24 hours after UV irradiation, the CA was (163 ± 2)°).[8] We examined the SA of a water droplet on the surface and found that it was less than 2°. Thus, the CA and SA of the surface in Figure 1a strongly resemble those of a water droplet on lotus leaves (that is, the lotus effect). For the preparation of the surfaces, the microcrystalline surface of the coated film of **1o** was irradiated with UV light for 10 minutes to convert compound **1o** into **1c** on the surface (Figure 2b), followed by storage at 30 °C in the dark for 24 hours to cover the surface with fibrils (Figure 2c). For the preparation of the surface that displayed the “petal effect”, larger crystal sizes are desired in order to pin the water droplet. By storage of the film shown in Figure 2b at an elevated temperature, small fibrils sparsely appeared (Figure 2d), then larger rod-shaped crystals of **1c** were generated by Ostwald ripening. After the film was stored at 70 °C for 3 hours in the dark, the surface was covered with rod-shaped crystals instead of fibrils (Figure 2f,i,j). Then, the surface was irradiated with UV light for a second time, and **1o** that appeared at the surface (Figure 2f) was converted into **1c** (Figure 2g). By keeping the film at 50 °C for 1 hour in the dark, the surface below the larger rod-shaped crystals were covered with newly formed fibrils (Figure 1b, and Figure 2h,k).

In order to explain the principle of petal surface preparation, we investigated the storage-temperature dependence of the topographical changes of the surface after UV irradiation. The SEM images of surfaces stored at 30, 50, 70, and 90 °C in the dark for 1, 3, and 15 hours are summarized in Figure 3. At 30 °C, small fibrils started to grow after 1 hour (Figure 3a), the number of fibrils increased after 3 hours (Figure 3b), and finally most of the surface was covered with fibrils (Figure 3c). The SEM images at 50 °C are shown in Figure 3d–f. After 1 hour, the surface (Figure 3d) was already covered with larger populations of small fibrils compared to the image in Figure 3a. This phenomenon is attributed to the fast growth rate and the larger amount of nucleating fibrillar crystals at higher temperatures. After 15 hours, larger rod-shaped crystals were observed on the surface (Figure 3f). The diameters and lengths were approximately 5–10 μm and 20–30 μm, respectively, which were much larger than those of the initially formed fibrils. At 70 °C, the large rodlike crystals were already observed after 1 hour (Figure 3g), and the surface was completely covered by these rods after 3 hours (Figure 3h,i). Storage of the surface at 90 °C led to its coverage with block-shaped crystals after 1 hour (Figure 3j). When monitoring the surface at 60 °C, we observed the growth of large rod-shaped crystals, accompanied by the melting of the initially formed small fibrils. From this observation, the phenomenon can be attributed to Ostwald ripening (see the Supporting Information).

According to the magnified SEM images of the film stored at 70 °C for 3 hours (Figure 2i,j), the sizes of the newly

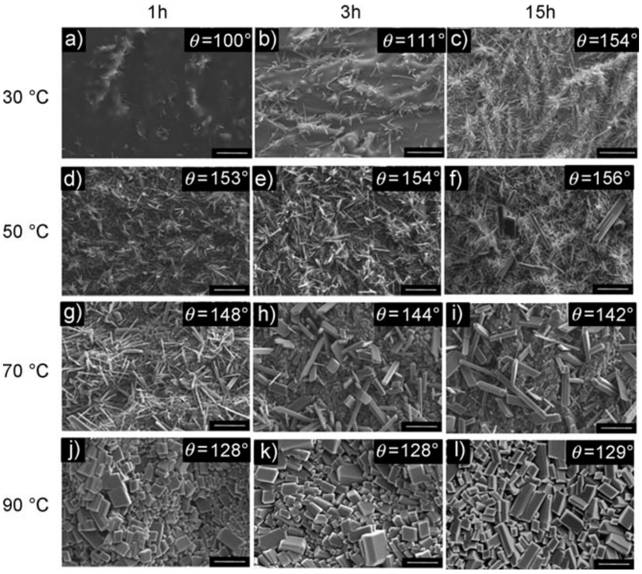

Figure 3. SEM images (1000×) of microcrystalline diarylethene surfaces stored at a–c) 30 °C, d–f) 50 °C, g–i) 70 °C, and j–l) 90 °C in the dark after UV irradiation. CAs are shown at the top right corner of each panel. Scale bars: 20 μm.

formed rodlike crystals were 5–10 μm in width and 20–30 μm in length. The diffraction peaks in the XRD pattern of the rodlike crystals obtained by scratching the surface are found at 5.1, 7.7, and 15.0°, which are identical to those of single crystal of **1c** (Figure S4 in the Supporting Information). These peaks are attributed to the (001), (010), and (111) lattice planes of the closed-ring isomer crystal. As shown previously,[8,11a] these peaks were also observed for the fibrillar crystals formed during storage at 30 °C after UV irradiation. Therefore, the rodlike crystals formed at 70 °C have the same crystal structure as the fibrillar crystals formed at 30 °C and the crystals of **1c** obtained by recrystallization from the solution.

In order to examine the difference between the two surfaces, dynamic advancing (θ_A) and receding (θ_R) contact angles were measured. Values for θ_A and θ_R for the lotus surface were $(163.0 \pm 1.1)°$ and $(162.1 \pm 1.0)°$, while those for the petal surface were $(154.5 \pm 0.8)°$ and $(145.0 \pm 0.7)°$, respectively. The difference of θ_A and θ_R, which is considered a measure of wetting by McCarthy and co-workers,[12] is larger than 5° for the petal surface. The better wetting property is attributable to the ease of the penetration of water into the petal surface grooves, which have larger available space than those of the lotus surface (see the Supporting Information). The procedure of fabricating the lotus-effect surface followed by a petal-effect surface could be repeated three times.

In conclusion, we have successfully fabricated surfaces that show lotus and petal effects from one photochromic compound. These properties were achieved by controlling the UV irradiation and heating profiles of the compound. This technique will be applicable to the control of surface wettability in the future.

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[1] a) W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1–8; b) C. Neinhuis, W. Barthlott, *New Phytol.* **1998**, *138*, 91–98; c) S. Shibuichi, T. Onda, N. Satoh, K. Tsujii, *J. Jpn. Oil Chem. Soc.* **1997**, *46*, 649–659 (in Japanese).

[2] a) L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, L. Jiang, *Langmuir* **2008**, *24*, 4114–4119; b) Z. Cheng, L. Feng, L. Jiang, *Adv. Funct. Mater.* **2008**, *18*, 3219–3225; c) D. Wang, Y. Liu, X. Liu, F. Zhou, W. Liu, Q. Xue, *Chem. Commun.* **2009**, 7018–7020.

[3] a) R. Blossey, *Nat. Mater.* **2003**, *2*, 301–306; b) A. Lafuma, D. Quéré, *Nat. Mater.* **2003**, *2*, 457–460.

[4] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988–994.

[5] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546–551.

[6] F. Xia, L. Jiang, *Adv. Mater.* **2008**, *20*, 2842–2858.

[7] a) K. Tsujii in *Surface Activity—Principles, Phenomena, and Applications*, Academic Press, New York, **1998**, p. 52; b) T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125–2127; c) S. Shibuichi, T. Onda, N. Satoh, K. Tsujii, *J. Phys. Chem.* **1996**, *100*, 19512–19517; d) H. Yan, K. Kurogi, H. Mayama, K. Tsujii, *Angew. Chem.* **2005**, *117*, 3519–3522; *Angew. Chem. Int. Ed.* **2005**, *44*, 3453–3456; e) W. Fang, H. Mayama, K. Tsujii, *J. Phys. Chem. B* **2007**, *111*, 564–571; f) T. Minami, H. Mayama, S. Nakamura, S. Yokojima, J.-W. Shen, K. Tsujii, *Soft Matter* **2008**, *4*, 140–144; g) H. Y. Erbil, A. L. Demirel, Y. Avcı, O. Mert, *Science* **2003**, *299*, 1377–1380; h) A. R. Wheeler, *Science* **2008**, *322*, 539–540.

[8] K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura, M. Irie, *Angew. Chem.* **2006**, *118*, 6620–6623; *Angew. Chem. Int. Ed.* **2006**, *45*, 6470–6473.

[9] a) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, **1971**; b) H. Dürr, H. Bouas-Laurent, *Photochromism, Molecules and Systems*, Elsevier, Amsterdam, **1990**; c) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.

[10] a) K. Ichimura, S.-K. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624–1626; b) S. Wang, Y. Song, L. Jiang, *J. Photochem. Photobiol. C* **2007**, *8*, 18–29; c) S. Wang, X. Feng, J. Yao, L. Jiang, *Angew. Chem.* **2006**, *118*, 1286–1289; *Angew. Chem. Int. Ed.* **2006**, *45*, 1264–1267.

[11] a) N. Izumi, T. Minami, H. Mayama, A. Takata, S. Nakamura, S. Yokojima, K. Tsujii, K. Uchida, *Jpn. J. Appl. Phys.* **2008**, *47*, 7298–7302; b) N. Izumi, N. Nishikawa, S. Yokojima, Y. Kojima, S. Nakamura, S. Kobatake, M. Irie, K. Uchida, *New J. Chem.* **2009**, *33*, 1324–1326.

[12] a) D. Öner, T. J. McCarthy, *Langmuir* **2000**, *16*, 7777–7782; b) L. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 2966–2967.