Lotus Effect Amplifies Light-Induced Contact Angle Switching

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Received: June 18, 2004

A rough surface morphology is shown to significantly amplify the light-induced change in water contact angle of a photoresponsive surface. Smooth Si surfaces and fractally rough Si nanowire surfaces grown on a Si substrate were studied, both coated with a hydrophobic monolayer containing photochromic spiropyran molecules. Under visible irradiation the spiropyran is in a closed, hydrophobic form, whereas UV irradiation converts the spiropyran to a polar, hydrophilic form, reducing the contact angle. The superhydrophobic nanowire surface both amplifies the light-induced contact angle change by a factor of 2 relative to a smooth surface and reduces the contact angle hysteresis. As a result the UV-induced advancing contact angle is lower than the receding contact angle under visible irradiation, allowing water drops to be moved solely under the influence of a UV−visible light gradient. The amplification of the reversible light-induced wetting angle change was predicted using the Wenzel model for fractally rough surfaces. The model and amplification effects are expected to apply to other types of stimuli-induced contact angle changes such as that by heat or electrical potentials.

The physics of scale require that microfluidic devices exploit new approaches to fluid movement because of an inherently large ratio of liquid surface area to volume. One promising method is the manipulation of surface energy by light to influence the water wettability of chemically modified surfaces.[1,2] Light fluxes can be easily imposed, accurately controlled, and mild enough to pose no danger to biological materials. Such wettability changes are predicted to result in water drop motion if the light induces a contact angle at the advancing edge of the aqueous phase that is below that of the receding edge. However, moving water with light has not been possible previously because the contact angle hysteresis (the difference between advancing and receding contact angles) has been larger than the light-induced contact angle change.[1]

We now report a solution to this limitation based on materials that mimic biological surfaces such as lotus leaves, which use high microscopic roughness and hydrophobic molecular coatings to produce nonwettable superhydrophobic surfaces. Using rough, hydrophobic, photoresponsive surfaces, we demonstrate amplification of stimulus-induced contact angle switching and a substantial decrease in contact angle hysteresis. The combination allows drops of water to be moved about solely under the influence of light for the first time, opening the door to enhancement of liquid motion in surface-tension driven microfluidic systems.

There have been several recent reports of superhydrophobic surfaces that combine hydrophobic molecular coatings with surface roughness characterized by either well-ordered microstructures[3,4] or random fractal geometry.[5,6] Rough fractal surfaces are particularly interesting due to the extremely high degree of roughness that they possess. Our studies exploit molecular monolayer coatings containing a photochromic spiropyran on fractally rough Si nanowire surfaces.

The Cassie[7] and Wenzel[8] models describe the dependence of the apparent solid−liquid contact angle on surface roughness in terms of the flat-surface contact angle. Cassie's model is based on the assumption that the liquid does not fill the crevices of the rough surface but rests on a composite surface composed of the solid material and air. In contrast, Wenzel's model hypothesizes that the liquid completely fills the depressions in the rough surface over the projected area of solid−liquid contact. In the Wenzel model, the apparent contact angle on the fractal surface, θ_f, may be expressed as[6]

$$\cos \theta_f = \left(\frac{L}{l}\right)^{D-2} \cos \theta \qquad (1)$$

where θ is the contact angle on a flat surface with identical chemistry and D is the fractal dimension of the surface between the upper and lower scale limits, L and l. This implies that if the flat surface contact angle is changed from a value θ_1 to θ_2 by the action of an external stimulus such as light, the apparent contact angle change on the fractal surface ($\theta_{f1} - \theta_{f2}$) may be expressed by

$$(\cos \theta_{f1} - \cos \theta_{f2}) = \left(\frac{L}{l}\right)^{D-2} (\cos \theta_1 - \cos \theta_2) \qquad (2)$$

Because the term $(L/l)^{D-2}$ is always >1 for a rough surface, this implies that the use of a superhydrophobic rough surface will always amplify the magnitude of the stimulus-induced contact angle change relative to the smooth surface (until the theoretical limit of a 180° contact angle is reached). Thus, by combining photoswitchable surface chemistry with control of surface morphology, it should be possible to amplify the photoinduced changes in the water contact angle.

A second reason for using superhydrophobic rough surfaces in surface-tension driven microfluidic applications is that the

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10.1021/jp0473568 CCC: $27.50
Published on Web 00/00/0000 PAGE EST: 2.8

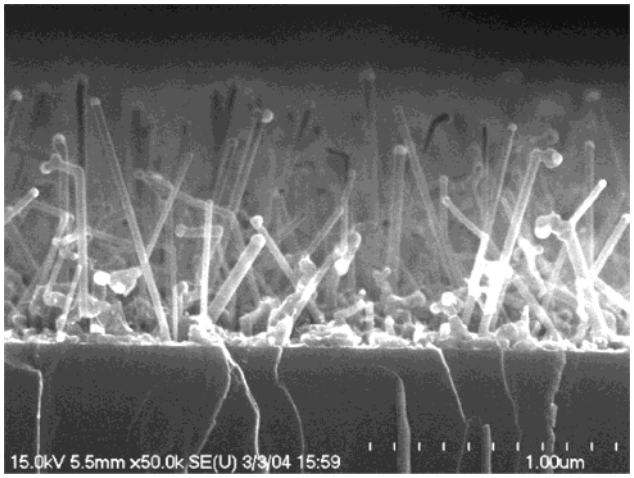

Figure 1. Cross sectional SEM micrograph of air-oxidized Si nanowire surface grown on a Si (111) substrate.

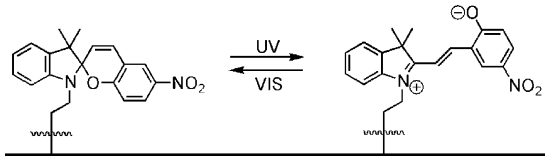

Figure 2. Switching of surface-bound spiropyran between nonpolar (left) and polar (right) forms under visible and UV irradiation, respectively.

level of contact angle hysteresis reported on these surfaces is often low.[3,4,9] One probable reason for the small degree of hysteresis is the very low solid-surface free energy resulting from the hydrophobic molecular coating.[10] Fractally rough surfaces are particularly interesting for microfluidic applications, as there are indications that they possess a smaller level of contact angle hysteresis than well-ordered ones.[9,11] This is thought to be due to the instability of the three-dimensional, tortuous solid−liquid−gas contact line in randomly rough surfaces as compared to that in well-ordered two-dimensional rough surfaces.

On the basis of these considerations we have hypothesized that photoresponsive monolayer coatings on fractally rough, superhydrophobic surfaces will exhibit contact angle magnification and lowered contact angle hysteresis. Using this approach we show here contact angle amplification and hysteresis reduction by as much as a factor of 2. The system investigated was a polished silicon wafer bearing random silicon nanowires with diameters of 20−50 nm grown by the vapor−liquid−solid technique[12] (Figure 1). The air-oxidized silicon surface was treated with *tert*-butyldiphenylchlorosilane and perfluorooctyltrichlorosilane, followed by (3-aminopropyl)diethoxymethylsilane, to which a photochromic spiropyran molecule was later covalently bound by a technique described previously.[2] Spiropyrans are a class of organic photochromes that undergo a reversible transition from a closed, nonpolar form to a highly polar, open form when irradiated with UV (366 nm) light (Figure 2). Irradiation with visible light (450−550 nm) converts the molecule back to its closed form. Visible light irradiation of the spiropyran coating yields a relatively hydrophobic surface (higher contact angle) that can be reversibly converted into a more hydrophilic surface (lower contact angle) with UV light irradiation.[2] We have previously demonstrated that the reversible switching of contact angles using UV and visible light for these molecular monolayers on smooth silica surfaces is due to the photon-modulated conversion of the spiropyran molecules between open and closed forms.[2,13]

Figure 3. Examples of water drops on surfaces having identical spiropyran coatings and irradiated with visible light: smooth (left) and rough nanowire (right) surfaces.

After derivatization with the spiropyran-containing monolayers, Si nanowire and smooth Si surfaces were studied by multiple measurements of advancing and receding water contact angles under UV and visible irradiation using the sessile drop method. Direct comparisons of adjacent polished and nanowire areas are shown in Figure 3. The combination of the surface roughness and the hydrophobic coating resulted in significantly higher contact angles on the nanowire surface compared to the smooth surface.

Patankar has shown that both Cassie and Wenzel types of wetting represent local energy minima for drops on rough surfaces.[14] They found that drops that were gently deposited onto superhydrophobic rough surfaces resulted in extremely high contact angles that were well represented by the Cassie model, whereas drops that were allowed to fall onto the surface from a height gave lower contact angles that were better represented by the Wenzel model.[15] Bico has also reported that contact angles on rough surfaces can transition from Cassie to Wenzel behavior when pressure is applied to the drop.[4] We found that when smaller drops ($<5\ \mu$L) were used, visible irradiation of the coated nanowire surface resulted in advancing contact angles $>170°$. Larger drops ($\sim 15\ \mu$L) produced advancing contact angles of 157°. We suggest that the weight of the larger drops forced the liquid into the depressions in the surface, making the Wenzel model applicable under these conditions. Larger drops were used for all further contact angle measurements.

The average advancing contact angle on the smooth surface was 12° lower under UV irradiation than under visible irradiation (Figure 4). On the nanowire surface, this light-induced contact angle change increased to 23° (Figure 4). The increase in the light-induced contact angle changes on the nanowire surface confirmed that roughness has the effect of amplifying stimulus-induced contact angle changes relative to smooth surfaces by a factor of nearly 2.

Under visible irradiation of the spiropyran-coated surfaces, the water contact angle hysteresis was measured to be 37° on the smooth surface, whereas on the nanowire surface a significantly lower value of only 17° was observed. On the smooth spiropyran-coated surface, the advancing water contact angle under UV irradiation (110°) was higher than the receding water contact angle under visible irradiation (85°). This does not fulfill the criterion for liquid motion, and it was found that water drops on the smooth surface could not be moved using light. However, on the spiropyran-coated nanowire surface the advancing water contact angle under UV irradiation (133°) was lower than the receding water contact angle under visible irradiation (140°). Accordingly, when we applied a UV−visible light gradient across water drops sitting on the nanowire surface, the drops moved toward the UV end of the gradient. Control experiments performed on drops sitting on nanowire surfaces coated with a hydrophobic layer without the spiropyran did not result in any drop motion. Therefore, it can be concluded that the motion of the water droplets on the photoresponsive nanowire surface was due to the roughness-magnified light-

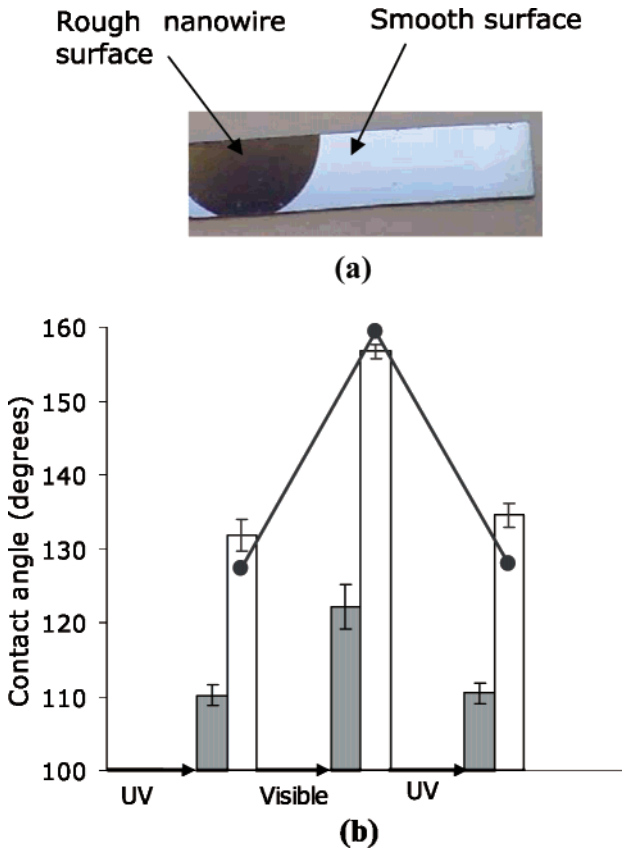

Figure 4. (a) Silicon sample having smooth and rough (nanowire) areas, treated with a photoresponsive coating. (b) Advancing contact angle changes on the smooth (gray bars) and rough (white bars) photoresponsive surfaces after UV and visible light irradiation. Results are the average of 10 contact angle measurements for each condition (error bars represent 1 standard deviation). Circles represent the predicted rough contact angle using a Wenzel model for fractally rough surfaces (eq 1).

induced switching of surface energy by the spiropyrans coupled with the lower contact angle hysteresis of the superhydrophobic surface.

Cross sectional micrographs of our fractally rough air-oxidized Si nanowire surfaces were obtained using scanning electron microscopy (SEM) (Figure 1). A box-counting fractal analysis was performed on trace curves of the cross sectional SEM images, and the cross sectional fractal dimension, D_{cross}, was determined to be 1.54 between the lower and upper limits of fractal behavior of 71 and 202 nm, respectively. The fractal dimension of the surface was estimated[16] to be $D \sim D_{cross} + 1 = 2.54$. The use of these fractal roughness parameters in the Wenzel model for contact angles on fractal surfaces (eq 1) gave an excellent fit with the experimental contact angles on the rough surface, as shown by the solid line in Figure 4. This further supports our hypothesis that in this case the large water drops filled the crevices in the nanowire structure, as described by the Wenzel model.

These findings demonstrate that surface roughness can be an effective tool for the amplification of stimulus-induced contact angle switching. The degree of amplification due to roughness was predicted using a Wenzel model. The combination of roughness-amplification of contact angle change with the reduced contact angle hysteresis of the nanowire photoresponsive surfaces resulted in advancing contact angles under UV irradiation that were lower than receding angles under visible irradiation. This permitted water drops on the nanowire surface to be moved solely using gradients of UV and visible light. This result should lead to the development of photonic control of water movement in microfluidic devices. Additionally, because the fluid driving force in electrowetting[17,18] and thermowetting[19,20] microfluidic systems is also the stimulus-induced difference between advancing and receding contact angles, our findings also point the way to enhanced fluidic motion and control in these systems.

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