JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Dip-Coating Crystallization on a Superhydrophobic Surface: A Million Mounted Crystals in a 1 cm^2 Array

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ABSTRACT: Silicon wafers (silicon dioxide surfaces) were patterned by photolithograpy to contain 3 μm (width) × 6 μm (length) × 40 μm (height) staggered rhombus posts in a square array (20 μm center-to-center spacing). These surfaces were hydrophobized using a vapor phase reaction with tridecafluorooctyldimethylchlorosilane and exhibit "superhydrophobicity" (water contact angles of θ_A/θ_R = 169°/156°). When a section of a wafer is submerged in and withdrawn from water, the superhydrophobic surface emerges, apparently completely dry. If the same procedure is performed using aqueous sodium chloride as the liquid bath, individual crystals of the salt can be observed on the top of each of the posts. "Dip-coating crystallization" using an aqueous sodium chloride solution of 4.3 M produces crystals with ~1 μm dimensions. A less concentrated solution, 1 M NaCl, renders crystals with ~500 nm dimensions. These experiments suggest that superhydrophobic surfaces that emerge from water and are "apparently completely dry" are, in fact, decorated with micrometer-size (several femtoliters) sessile water drops that rapidly evaporate. This simple technique is useful for preparation of very small liquid drops or puddles (of controlled composition) and for preparation of arrays of controlled size, crystalline substances (dip-coating crystallization).

During studies of three-phase contact line dynamics at certain water—solid interfaces, we made the conjecture[1] that microcapillary bridge rupture during receding events should produce microdroplets at pinning sites. These drops have not been directly observed, presumably because of the rapid evaporation of micrometer-scale water drops. Similar conjectures involving water "left behind" receding contact lines have been made by others.[2−6] These include Bikerman,[2] who in 1950 described "ribbons" that were stretched and finally ruptured; Fort,[3] who predicted in 2002 that experiments designed to observe water "left behind" a drop would fail; and Li, Ma, and Lan,[6] who in 2010 ascribed a "dark stripe" observed in a high speed video recording to a "liquid layer being left behind on the microposts" due to the "pinch-off of liquid threads." We recently reported[7] that replacing water with a high-surface-tension, nonvolatile ionic liquid probe fluid reinforces and permits refinement of these conjectures and should be applicable to contact line pinning studies on a variety of surfaces. Scanning electron microscopy was a convenient technique to observe the dewet surfaces as well as the micrometer scale and smaller ionic liquid droplets that were directly detected at pinning sites. These observations led us to examine aqueous sodium chloride solutions, and we report these results here to demonstrate a simple technique for the preparation of arrays of millions of pedestal-supported crystals.

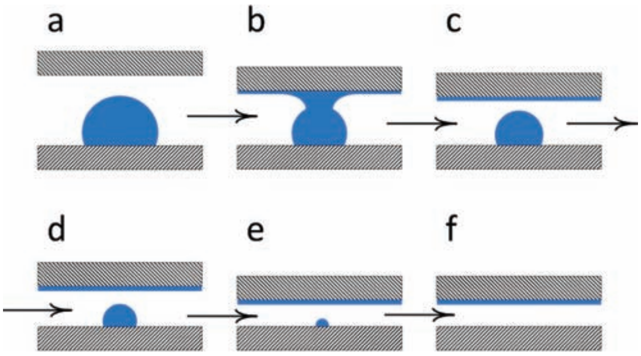

Figure 1. A hydrophilic surface (θ_A/θ_R = 0°/0°) being lowered onto a sessile water drop on a hydrophobic (θ_A/θ_R = >100°/>100°) surface. The sessile drop is transferred in sequential events through capillary bridges to a thin water film on the hydrophilic surface. The drop decreases in volume during each of these events until a very small droplet spontaneously evaporates.

When a drop of water is mechanically removed in tension (perpendicularly) from a flat surface, even from a surface generally regarded as hydrophobic (θ_R > 100°), a smaller droplet remains on the surface. An example of this (Figure 1) occurs when a surface that exhibits θ_A = 0° is brought toward a sessile drop from above. The drop forms a capillary bridge between the two surfaces that ruptures, leaving a thin film of water on the θ_A = 0° surface and a smaller sessile drop on the θ_R > 100° surface. This process repeats itself as the two surfaces are brought closer to one another and progressively smaller sessile drops form as liquid is transferred to the thin water film through smaller and smaller capillary bridges that form and rupture. With smooth surfaces, these drops of decreasing volume can be observed until a very small sessile drop evaporates (apparently instantaneously when videotaped at 10 frames/s) as it is formed. Selected frames of a videotape of this experiment have been published.[8]

The experiment described in Figure 1 led us to the conjecture that we made[1] and review in the first sentence of this manuscript. It follows that if submerged superhydrophobic surfaces containing microscopic posts with smooth flat tops are removed from water, microcapillary bridges will form between the post tops and the bulk liquid and that the bridges will subsequently rupture to

Received: February 6, 2011
Published: March 29, 2011

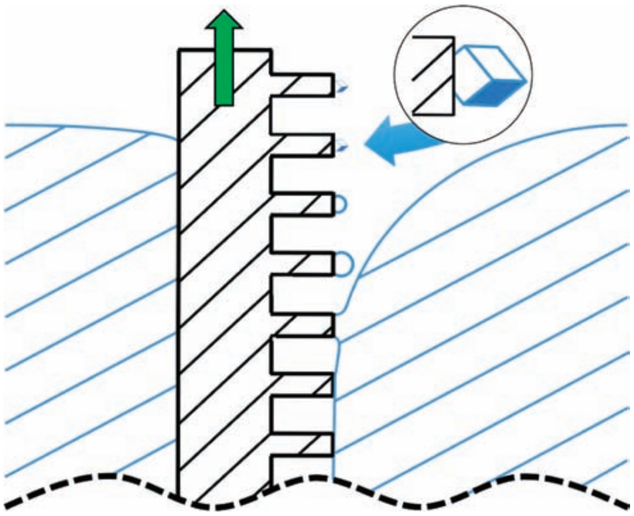

Figure 2. Depiction of a superhydrophobic, post-containing surface being withdrawn from an aqueous solution of NaCl. The receding contact angle is >150°. Capillary bridges form between the post tops and bulk liquid and rupture forming sessile drops. The drops evaporate and the NaCl crystallizes.

form sessile microdroplets (or femtodroplets, if the volume is considered) on the post tops. These microdroplets will evaporate, apparently instantaneously. It also follows that if the water contains a solute, the solute will become concentrated during evaporation and when the concentration exceeds the solubility, phase separation will be favored thermodynamically. Figure 2 shows a depiction of these events for a crystalline solute.

Silicon/silicon dioxide surfaces containing 3 μm (width) × 6 μm (length) × 40 μm (height) staggered rhombus posts were prepared using photolithography[9] and hydrophobized using a perfluoroalkyl-containing monofunctional silane.[10] This surface exhibits macroscopic water contact angles of $\theta_A/\theta_R = 169°/156°$, but the tops of posts (that are smooth) exhibit microscopic water contact angles of $\theta_A/\theta_R \approx >100°/>100°$.[11] This particular condition (a higher macroscopic than microscopic receding contact angle) inhibits recession on post tops and causes capillary bridge formation. Withdrawal of sections of this surface from 1 and 4.3 M aqueous NaCl by hand using tweezers at a rate of ~1 cm/s yielded samples that were analyzed by scanning electron microscopy[12] (Figure 3). One crystal of NaCl is observed on every post, and the size of the crystals is a function of the initial NaCl concentration. In both cases, the surface was removed in the direction oriented upward in the micrographs. The staggered rhombus geometry was designed originally to contort receding contact lines and raise receding contact angles. In principal the different orientations should give rise to different structured capillary bridges, different volume sessile droplets, and different mass NaCl crystals. The horizontally pointing rhombi in Figure 3b have, on average, larger crystals than the vertically pointed ones, but we hesitate to overanalyze these data that were obtained using hand-held tweezers and a benchtop SEM. The crystals form in locations that are generally away from the edges of the posts and not in particular locations on the post tops. This suggests that the sessile drops recede as they evaporate (do not form "coffee rings") and become pinned on defects at random locations in the interiors of the post tops. Simple estimates[13] of the mass of crystals from the micrographs are ~2.3 and ~0.3 picograms from 4.3 and 1 M NaCl, respectively. The initial volumes of the sessile drops are estimated to be ~10 and ~7 femtoliters (10^{-15} L), respectively, from these data and the original concentrations. These volumes correspond to sessile drops (calculated using $\theta_R = 100°$) with initial (immediately after capillary bridge failure) contact diameters of ~3.2 μm (4.3 M NaCl) and ~2.8 μm (1 M NaCl). These values are consistent with the 3 μm × 6 μm dimensions of the rhombus-shaped post tops.

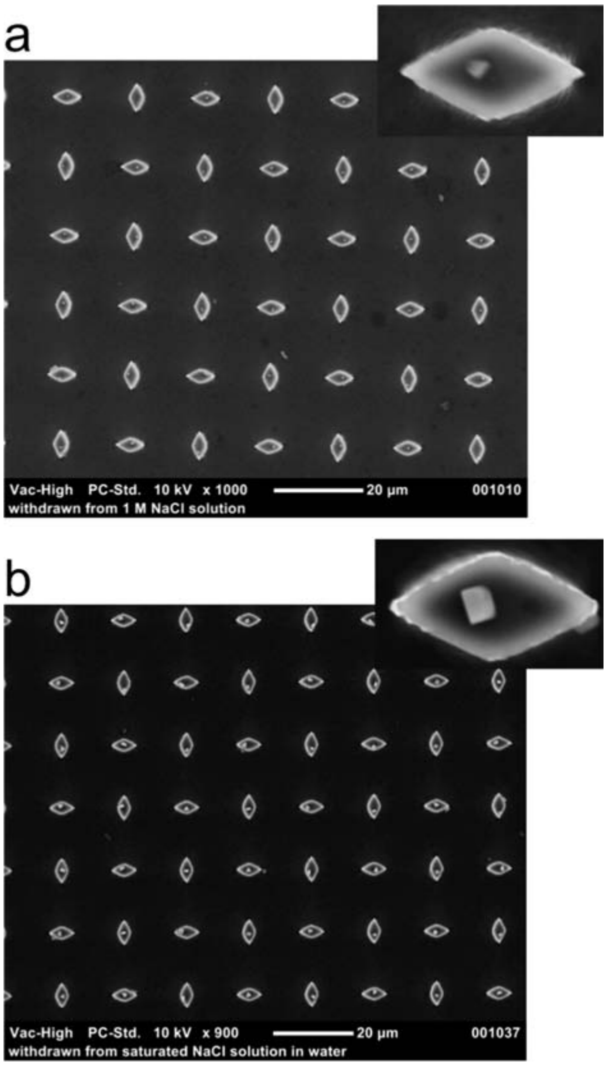

Figure 3. Scanning electron micrographs of superhydrophobic surfaces that were withdrawn from (a) 1 M NaCl and (b) 4.3 M NaCl.

We close with comments concerning and criticisms of these experiments: (1) The simple process of dipping a post-containing superhydrophobic surface in an aqueous solution is useful for the preparation of an array of many submicrometer individual crystals of the solute.[14−16] (2) Having post-mounted crystals should facilitate visualization in studies involving crystalline solids. (3) The experiments described were performed in the open laboratory with no humidity control. Withdrawal of surfaces into controlled/maintained humidity vapor phases would control evaporation/condensation and hence crystallization/dissolution kinetics and permit "annealing" and perfection of crystals. (4) The surface with staggered rhombus posts contains sharp edges and different orientations. If circular posts were used, more uniform capillary bridges, sessile drops, and NaCl crystals would have been prepared. This particular superhydrophobic surface was designed and prepared for another purpose[9] and was used for the experiments reported here simply because it was available in our laboratory. (5) The surface used contains features (posts) that are relatively large (cross sectional area) among reported superhydrophobic surfaces. Smaller features should render smaller capillary bridges, lower volume sessile droplets, and smaller crystals. (6) The rate of withdrawal of the surface from the solution should affect the size of the capillary bridges, sessile drops, and NaCl crystals. (7) Although useful as a demonstrative model material, sodium chloride is not a particularly interesting solute. (8) This may be a useful method for preparing controlled volume droplets. Recent studies on small droplets emphasize the difficulties in their preparation.[17,18]

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ACKNOWLEDGMENT

We thank the Materials Research Science and Engineering Center (DMR-0213695) and the Center for Hierarchical Manufacturing (CMMI-0531171) at the University of Massachusetts for support and 3M, Henkel, and Shocking Technologies for unrestricted funding.

REFERENCES

(1) Krumpfer, J. W.; McCarthy, T. J. *Faraday Discuss.* **2010**, *146*, 103.
(2) Bikerman, J. J. *J. Colloid Sci.* **1950**, *5*, 349.
(3) Roura, P.; Fort, J. *Langmuir* **2002**, *18*, 566.
(4) Patankar, N. A. *Langmuir* **2003**, *19*, 1249.
(5) Chibowski, E. *Adv. Colloid Interface Sci.* **2003**, *103*, 149.
(6) Li, X.; Ma, X.; Lan, Z. *Langmuir* **2010**, *26*, 4831.
(7) Krumpfer, J. W.; Bian, P.; Zheng, P.; Gao, L.; McCarthy, T. J. *Langmuir* **2011**, *27*, 2166.
(8) Gao, L.; McCarthy, T. J. *Langmuir* **2008**, *24*, 9183.
(9) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777.
(10) This reaction was carried out in the vapor phase at elevated temperature using a standard procedure: Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3759.
(11) The contact angles of a carefully prepared smooth surface with this composition are $\theta_A/\theta_R = 119°/110°$. The actual contact angles on post tops were not measured and are likely less than this due to defects that form during photolithography and development, hence, the estimated values. See: Gao, L.; McCarthy, T. J. *Langmuir* **2007**, *23*, 3762.
(12) Scanning electron micrographs were recorded using a JEOL Omniscope.
(13) These estimates are made using cubes with lengths of 1 and 0.5 μm.
(14) We note other research directed at preparing arrays of crystals and filling microwells by withdrawal from liquids (refs 15 and 16).
(15) You, E.-A.; Ahn, R. W.; Lee, M. H.; Raja, M. R.; O'Halloran, T. V.; Odom, T. W. *J. Am. Chem. Soc.* **1999**, *131*, 10863.
(16) Jackman, R. J.; Duffy, D. C.; Ostuni, E.; Willmore, N. D.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 2280.
(17) Golovko, D. S.; Butt, H.-J.; Bonaccurso, E. *Langmuir* **2009**, *25*, 75.
(18) Arcamone, J.; Dujardin, E.; Rius, G.; Pérez-Murano, F.; Ondarcuhu, T. *J. Phys. Chem. B* **2007**, *111*, 13020.