Reversible switching between superhydrophobic states on a hierarchically structured surface

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Nature offers exciting examples for functional wetting properties based on superhydrophobicity, such as the self-cleaning surfaces on plant leaves and trapped air on immersed insect surfaces allowing underwater breathing. They inspire biomimetic approaches in science and technology. Superhydrophobicity relies on the Cassie wetting state where air is trapped within the surface topography. Pressure can trigger an irreversible transition from the Cassie state to the Wenzel state with no trapped air—this transition is usually detrimental for nonwetting functionality and is to be avoided. Here we present a new type of reversible, localized and instantaneous transition between two Cassie wetting states, enabled by two-level (dual-scale) topography of a superhydrophobic surface, that allows writing, erasing, rewriting and storing of optically displayed information in plastrons related to different length scales.

micropillars | silicone nanofilaments | optical data storage | bistable | two-tier

The lotus plant has become famous by its ability to always keep its leaves clean and dry (1), making superhydrophobic wettability a vibrant topic of research in recent years (2). However, nature also offers other concepts for exploiting nonwettability, in particular layers of trapped air (*plastrons*) that some underwater insects maintain within the hair growing on their exterior to keep them dry or to serve as a physical gill (3, 4). Plastrons on immersed artificial superhydrophobic surfaces have been under active study as well (5–9). Because the formation of an air layer between water and the surface is the essential feature of superhydrophobic surfaces in general, a transition from a state with an air layer (Cassie state) to a state where it is lost (Wenzel state) means loss of nonwetting properties (10, 11). Therefore, superhydrophobic surfaces are typically designed to provide the most stable Cassie state possible using hydrophobic surface chemistry and rough microtopography (12).

Reversing the Cassie-Wenzel transition is very challenging (13–16)—in particular for immersed surfaces (involving a plastron, see Fig. 1) where it has so far only been accomplished by electrochemical generation of gas on the surface to create a new plastron (17) or by exploiting the expansion of gas at low pressure (18). Hierarchical topographies are known to improve the stability of the Cassie state (19) (as well as to promote mechanical resilience, ref. 20, and nonwettability, ref. 21), but it is less widely realized that complex topographies also provide new approaches to wetting state switching by giving rise to a larger number of wetting states, making the term "Cassie state" less well defined: there exist several possible states that involve trapped air, but vary in terms of wetted solid fraction and the volume of the air layer (4, 22, 23). Wetting hysteresis depends on the amount of wetted solid, so states with little wetting are of particular interest for designing bistable systems.

Here we present, for the first time, reversible and localized pressure-induced transitions between two distinct Cassie-type wetting states on a hierarchical superhydrophobic surface immersed in water. The states arise from the two topographical levels on the surface: a pattern of silicon microposts and a superhydrophobic nanofilament coating grown on the microtopography (Fig. 1*B*). In one wetting state the plastron occupies the space between the microposts—we call this state the *micro-Cassie* state as the plastron has micron-scale dimensions. In the other state the space between the posts is mostly filled with water but air still remains in the nanofilament layer, which is only hundreds of nanometers thick. Because of this thin plastron, the state is also of the Cassie type because the water-solid contact area fraction is small. This state is called the *nano-Cassie* state, accordingly. We will show that the wetting states can be locally and reversibly switched by using a nozzle to cause pressure-driven transitions (Fig. 1*B*).

Results

Superhydrophobic surfaces with two-level topography were constructed from silicon wafers patterned with a square array (pitch 20 μm) of cylindrical microposts (diameter 10 μm, height 5 or 10 μm) that are further coated with silicone nanofilaments (24–26). The nanofilaments are themselves superhydrophobic (advancing and receding contact angles of planar coating $170°/145° \pm 5°$), which is necessary for a stable nano-Cassie state.

Submerging the hierarchical surface in water leads to the formation of a plastron in the micro-Cassie state. A local switching to the nano-Cassie state can be induced by "writing" with a jet of water (see Fig. 1*B*). The dynamic pressure of the jet gives rise to Laplace pressure (pressure difference between water and plastron) that pushes the water between the microposts, causing a localized and immediate transition. Calculations predict a transition Laplace pressure of 6.9 kPa (see *SI Text*). Yet, even a large pressure will not cause a transition to the Wenzel state due to the high stability of the plastron within the nanofilaments. An optical micrograph of a nano-Cassie/micro-Cassie boundary is shown in Fig. 2*A*.

Unlike the Wenzel to Cassie transition, the nano-Cassie to micro-Cassie transition involves only a low kinetic barrier due to the small amount of wetted solid in the nano-Cassie state. In fact, the micro-Cassie state is energetically more stable than the nano-Cassie state (see *SI Text*). We were able to restore the

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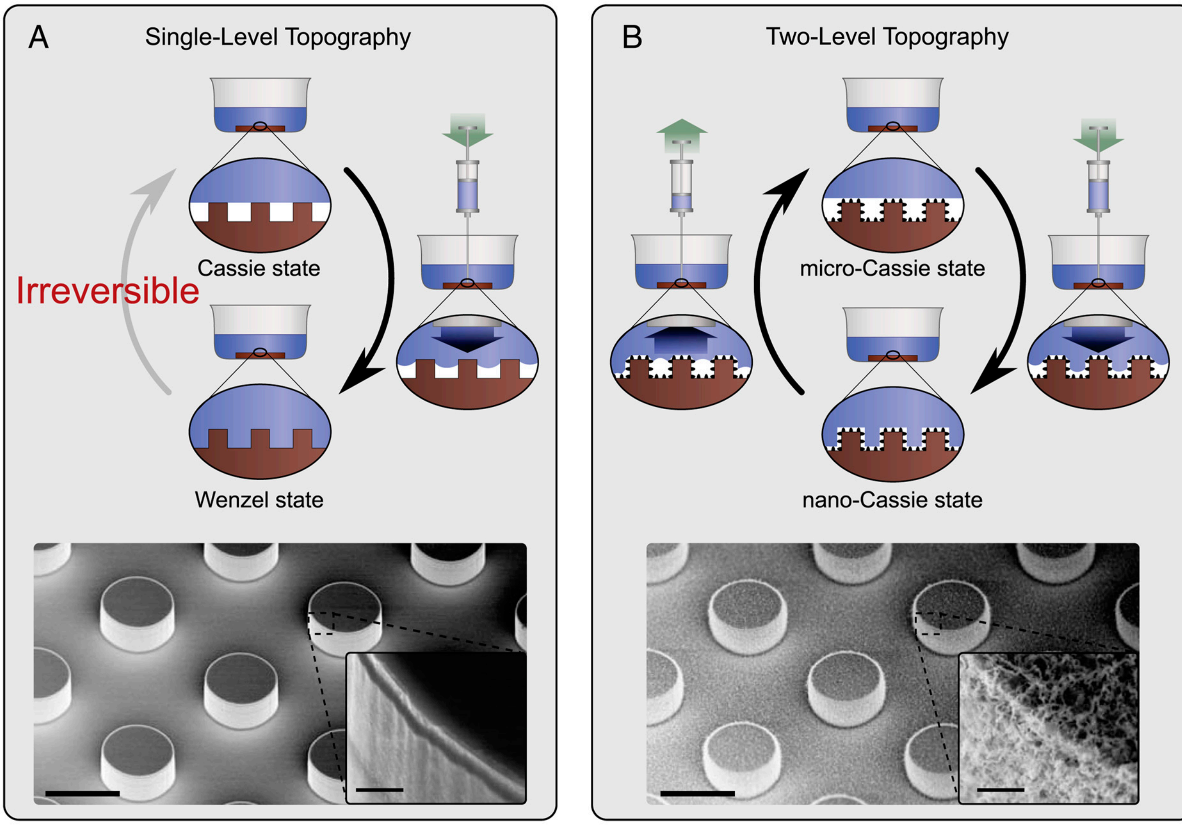

Fig. 1. Wetting states and transitions between them on surfaces with different topographies. (*A*) With single-level topography, positive Laplace pressure causes a transition from the Cassie to the Wenzel state. The transition involves wetting of the whole solid surface and is irreversible in most cases. (*B*) Hierarchical topography. Nanofilaments suppress the transition to the Wenzel state and positive Laplace pressure will cause a transition to the nano-Cassie state instead, where wetted solid area remains small due to the plastron in the nanofilament layer. This transition can be reversed by negative Laplace pressure. Constant pressure in the plastron is maintained by a gas reservoir such as a macroscopic bubble on the edge of the surface. Scale bar in the scanning electron micrographs is 10 μm (in the inset, 500 nm). The post height in the micrographs is 5 μm.

micro-Cassie state by a reverse writing process: local negative Laplace pressure was built between water and the plastron by sucking water with the needle close to the surface, causing the plastron to fill the space between the posts once again (see Fig. 1*B*). According to our calculations (*SI Text*) the nano-Cassie state becomes unstable at a Laplace pressure between −5.0 kPa and −1.3 kPa. The local transitions do not alter the pressure of the plastron because a gas reservoir (like an air bubble on the surface shown in Fig. 3*A*) will store and release air as needed.

For comparison with the hierarchical topography, we also fabricated a superhydrophobic surface with single-level topography (see Fig. 1*A*) by coating a micropatterned silicon surface with a hydrophobic fluoroalkylsilane monolayer (advancing and receding contact angles of coating on flat surface $118°/102° \pm 3°$) instead of nanofilaments. The plastron on an immersed single-level surface is in the Cassie state, and the water jet writing technique shown in Fig. 1*A* can be used to cause a local Cassie-Wenzel transition, which is irreversible.

To study in detail the shape of the water-air interface in the micro-Cassie and nano-Cassie states we introduced a new laser scanning confocal imaging technique that makes use of fluorescent polymer nanoparticles dispersed in the water. Two confocal scanning modes are combined: reflection of 633-nm-wavelength laser light and fluorescence from the nanoparticles that are excited with a 543-nm-wavelength laser light. The reflection signal provides information on topography while the fluorescent nanoparticles help to differentiate water from air. Fig. 2*B* shows a series of micrographs of the boundary between nano-Cassie and micro-Cassie regions, focused 15, 10, 5 and 0 μm above the substrate. The fluorescence image shows that, while the space between the posts in the micro-Cassie region is filled with air, in the nano-Cassie region water occupies most of the space except the filament layer, as depicted in the schematic picture in Fig. 2*B*.

The interference fringes in the reflectance images—caused by interference between reflections from the water-air interface and the air-silicon interface at the bottom—reveal the shape of the water-air interface. The vertical distance between two intensity maxima corresponds to a half of the wavelength of the laser light, 317 nm. The interface starts to curve downwards about 30 μm from the boundary between the micro-Cassie and nano-Cassie states with the slope increasing close to the boundary.

Although water fills most of the space between the posts in the nano-Cassie state, the "coronae" surrounding the posts in the microscope images in Fig. 2 suggest that micrometer-sized pockets of air still remain around the bases of the posts (see also Figs. S1 and S2). Indeed, theoretical considerations (see *SI Text*) show that small air pockets are expected to remain in the corners between the posts and the bottom if the advancing contact angle of the nanopattern is greater than 135°. Negative Laplace pressure is shown (*SI Text*) to destabilize the air pockets, ultimately inducing transition to micro-Cassie state.

Fig. 3*A* shows a sample with two-level topography and another with single-level topography in water. The sample with two-level topography is mostly in the micro-Cassie state but has regions, made in the shape of letters ("2 TIER"), which are in the nano-Cassie state. These regions appear remarkably bright due to intense light scattering. In fact, nano-Cassie regions exhibit an order of magnitude stronger scattering intensity than micro-

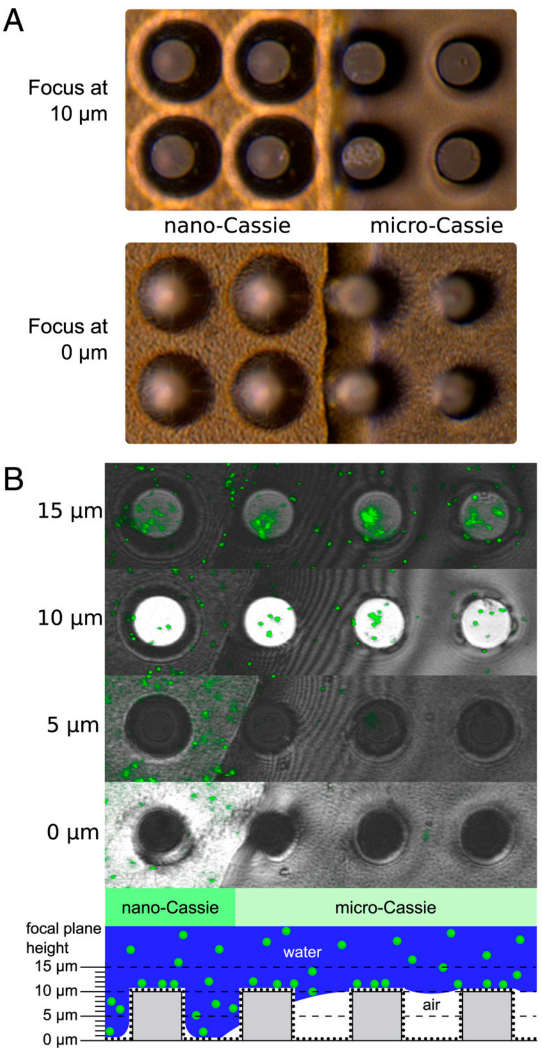

Fig. 2. The boundary between nano-Cassie and micro-Cassie states. (*A*) Optical microscope images of a nano-Cassie/micro-Cassie boundary, one focused at the post tops and the other at the bottom. In the nano-Cassie region the posts are surrounded by "coronae" that are pockets of remaining air. (*B*) Combined confocal images where the reflectance scan is shown in greyscale while fluorescence signal coming from dispersed nanoparticles is shown in green (false color). When the confocal plane is below 10 μm, nanoparticles are seen only in the nano-Cassie region where water fills most of the space between posts. A schematic interpretation is below the images. The diameter and height of silicon posts is 10 μm.

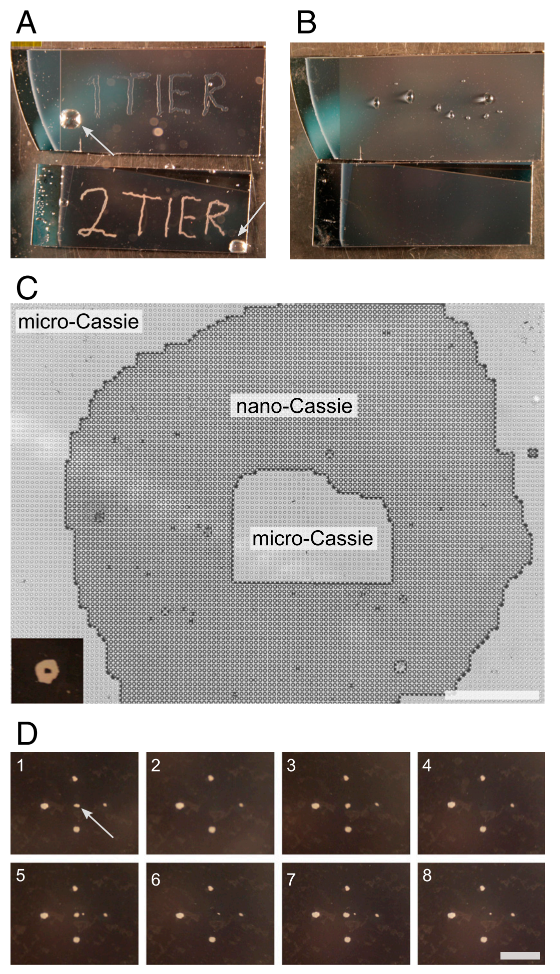

Fig. 3. Writing and erasing patterns. (*A*) A jet of water has been used to create letter-shaped regions of Wenzel and nano-Cassie state in the plastrons of single-level (1-tier) and two-level (2-tier) topography surfaces, respectively. The escaping air pushed aside by the jet has formed into macroscopic bubbles that act as gas reservoirs (indicated by arrows in the figure). (*B*) Water has been drained from the container. The sample with single-level topography has small droplets where the letters have been, whereas the sample with hierarchical topography has emerged from the water completely dry. (*C*) Demonstrating the reverse transition: a small region of micro-Cassie state is created by suction inside a larger region of nano-Cassie state (created by a jet of water). The inset is a photograph taken with a camera. Scale bar is 40 μm. (*D*) The middle one of the 5 nano-Cassie dots is repeatedly erased (returned to micro-Cassie state) and rewritten. Scale bar is 4 mm.

Cassie regions, leading to substantial optical contrast (see Fig. S3). The scattering is caused by the curved interface between water and the air pockets around the bases of the posts that cause reflections to a wide range of angles (see Fig. S2). Unlike nano-Cassie regions, Wenzel regions on single-level topography (letters "1 TIER" in Fig. 3*A*) do not scatter much due to the absence of a water-air interface.

The difference in terms of wettability between the nano-Cassie and the Wenzel state is demonstrated in Fig. 3*B*, which shows the samples from Fig. 3*A* after water has been drained out. A thin film of water stays on the Wenzel regions on the single-level surfaces and assembles into droplets, while the two-level surface emerges completely dry: this is because the nano-Cassie state is nonwetting whereas Wenzel is wetting.

Fig. 3*C* confirms that although the nanofilament layer is just hundreds of nanometers thick and thus the nano-Cassie plastron is very thin, air can still flow through it to form a micro-Cassie region inside a larger nano-Cassie region.

Discussion

We wish to emphasize that the two wetting states can be thought of as bistable logic states to store binary data. For example, the surface could be divided into an array of dots that represent bits. Also, the optical contrast between the states suggests that such an array of bits could be used for a bistable reflective display. To demonstrate repeated write/erase cycles, we present in Fig. 3*D* a series of photographs of a group of five nano-Cassie dots. The dot in the center is repeatedly erased and rewritten. Furthermore, to verify stability and reversibility even after prolonged storage, a pattern was written on a surface and inspected after 30 days. The pattern was found to be unchanged and still erasable.

Apart from data storage or display applications, we also envision uses in microfluidics. While the micro-Cassie state is expected to have a large slip length (5), the nano-Cassie state most likely involves little slip regardless of the plastron, as water between the microposts is unlikely to flow well. The micro-Cassie/nano-Cassie transition could enable dynamical creation of configurable flow barriers or fast-flowing channels.

To summarize, we demonstrated reversible bistable switching between two Cassie-type wetting states on a hierarchical superhydrophobic surface and used a novel confocal microscopy technique based on dye-labeled nanoparticles for imaging the plastron. A localized writing/erasing procedure was used for instant switching of wetting state, enabling storage of binary data, and a substantial scattering intensity contrast between the states allows optical reading of information. We believe the result opens a new perspective to wetting-functionalized surfaces as reversibly configurable information-carrying media.

Materials and Methods

Silicon Micropatterning. Microposts were fabricated on (100) silicon wafers. A UV-lithography step defined the patterns of the microposts to a 500 nm thick layer of AZ1505 photoresist (Clariant). Subsequently, cryogenic deep reactive ion etching (Oxford Instruments, Plasmalab 100) was used to etch the microposts in silicon. (temperature −120 °C, inductively coupled plasma power 1,000 W, capacitively coupled plasma power 3 W, pressure 10 mTorr, SF_6 flow 40 sccm, O_2 flow 6 sccm). The etch rate was measured to be 2.0–2.5 μm/ min. After etching, the remaining photoresist was removed in acetone.

Deposition of Nanofilament and Fluoroalkylsilane Coatings. For nanofilament deposition, patterned silicon samples were kept in oxygen plasma (Gatan Solarus Model 950) for 5 minutes to increase the density of surface OH groups (plasma power 65 W, pressure 70 mTorr, O_2 flow 40 sccm). Samples were then placed to a glass reaction vessel (volume ca. 1 L) which was flushed with humidified argon (relative humidity 30%). After flushing, the gas inlet and outlet were closed and ca. 100 μl of methyltrichlorosilane (Sigma-Aldrich, 99%) was injected with a syringe through a silicone septum into a Teflon cup inside the vessel. After at least 14 hours the samples were taken out and rinsed with deionized water. Fluoroalkylsilane coatings were made in a similar manner except the vessel was flushed with dry argon and $CF_3(CF_2)_5(CH_2)_2SiCl_3$ precursor (ABCR, 97%) was used (injected amount was ca. 30 μl).

Scanning Electron Microscopy. Scanning electron microscopy was performed on a JEOL JSM-7500FA field-emission microscope. Micrographs were taken at 5 kV voltage.

Optical Microscopy. A Leica DM4500 P optical microscope was used with an immersion objective. Photographs were taken with a Leica DFC 420 camera.

Confocal Imaging. Samples were immersed in water containing fluorescently labelled nanoparticles (Fluoro-Max red fluorescent polymer microspheres, 0.21 μm diameter, Thermo Scientific). Confocal laser scanning microscopy (LSM 510, Zeiss, Germany; 25 × water immersion objective, NA = 0.8) was used to record z-stacks of the samples. Interfaces between media with different refractive indices (e.g., water and air) were visualized by recording the reflection of a HeNe laser ($\lambda = 633$ nm), fluorescence of the beads was measured with a second HeNe laser ($\lambda = 543$ nm). For visualization, the fluorescence signal was superimposed on the reflectivity signal (Fig. 2*B*). Noise was removed from the fluorescence signal by Gaussian convolution and removal of low-intensity pixels. Unmodified data is shown in Fig. S4.

Wetting Transitions. Switching between micro-Cassie and nano-Cassie states was done using a syringe or a pressurized hose and a needle with a nonbeveled tip. The pressurized hose could be used to provide a steady pressure for careful drawing (Fig. 3*A*) whereas a syringe could be used for both blowing (micro-Cassie to nano-Cassie transition) and sucking (nano-Cassie to micro-Cassie transition) water. Surfaces with 5 μm tall posts were used for reversible writing and erasing.

Light Scattering Intensity Measurement. Sample (in a petri dish filled with water) was illuminated from above with light focused on either a nano-Cassie or micro-Cassie region. Scattered light was collected with an optical fiber directed at the illuminated spot at an angle of 55° relative to the surface normal. The intensity as a function of wavelength was measured with an Ocean Optics USB4000-VIS-NIR spectrometer.

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