Adaptive Wettability of a Programmable Metasurface

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Metasurfaces with specific wettabilities have recently gained relevance in numerous areas of science and industry. This has led to technical requirements of these functional metasurfaces increasing in cost and complexity. Examples can be found in adjustable filters and membranes, as well as in lab-on-chip systems. For a large number of these applications, surfaces with adaptive properties offer unique advantages compared to traditionally engineered systems. Such surfaces with adaptable surface energies and, thus, wetting properties, can be realized by either a change in the surface chemistry or structure. Due to novel additive manufacturing methods such as two-photon lithography, high-resolution 3D microstructures can be prototypically fabricated and highly specific adjustments of the surface structure can be realized. These advances have enabled a field with particularly broad development possibilities in the area of metamaterials. Herein, a novel mechanoadaptive surface with strain-dependent wettability states is detailed. The surface was designed, fabricated, and experimentally characterized with a custom test setup that combines the capabilities of contact angle measurements and mechanical straining in one. The results demonstrate a mechanically induced, topologically driven modification of the surface’s wetting properties from the hydrophilic to the super-hydrophobic regime.

Inspired by bionics and natural phenomena, the adaptable wettability of solid surfaces is receiving more and more interest. For example, self-cleaning of super-hydrophobic leaves, like the lotus leaf, is adapted to functional surfaces for new technologies and applications.[3–4] In general, there are two main approaches to adjust the wettability of solid surfaces: either by changing chemical composition, or by adapting the morphology of the surface.[5,6] In nature, lotus leaves achieve their unique wetting behavior using a combination of a microstructured surface as well as a functional layer of epicuticular wax.[7–9] As a result, the contact area between droplet and surface, and thus the resultant adhesive forces are reduced to achieve super-hydrophobicity and self-cleaning effects. With this, the lotus leaf is protected against fouling or contamination by microorganisms and particles, resulting in an effective increase in incident photosynthetically active radiation.[10,11]

Several research groups have been working on different technical solutions to manufacture super-hydrophobic surfaces which can be used for applications like microdosing or filter systems.[1,12–14] Usually the focus is on static surface structures with certain chemical treatments or coatings. The topologies are stochastically ordered and hierarchically structured, whereas the maximum structure sizes are typically smaller than 100 μm to achieve super-hydrophobicity.[7,11] Fabrication methods like two-photon polymerization allow the realization of nearly arbitrarily complex 3D geometries in this size regime. Within the metamaterial community, novel designs for artificial surfaces are getting more popular and many results of super-hydrophobic surfaces are published.[15–18] They show great utility of hierarchical structures for micro-patternning but are limited to a static surface morphology.

Other groups work on functional surfaces with switchable wettability. They make use of molecular reactions at the surface, controlled by different stimuli like temperature,[19] pH-value,[20,21] UV-light exposure,[22,23] or electric potential change. They obtain great contact angle changes of water, from hydrophilic to super-hydrophobic, but only consider chemical effects with a static surface morphology. In addition, these chemical reactions have a certain time dependency and are rather slow (180 min,[23] 200 s[15]).

Mechanical metamaterials, and especially programmable materials, represent a new possibility to change not only material properties, but also functionalities. In contrast to the common understanding in the literature, we transfer these principles to wetting phenomena and show the design and implementation of programmable adaptive metasurfaces.

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The implemented surface structures aim to have an adaptive contact angle. Therefore, a novel unit cell design was created, which can change its structural morphology with applied strain. If the base material of the structure is slightly hydrophobic, an adaptive surface structure will lead to a change of the hydrophobicity and therefore change the contact angle of water.

The design of the representative unit cell is shown in Figure 1. The base of the unit cell has a conical shape with a large surface area to enhance adhesion and stability at the substrate. A narrow neck improves flexibility to enable the mechanical interaction between unit cells. These measures ensure that the elongation of the substrate is fully translated into a displacement between the unit cells. The curved framework consists of several sections with a tapered shape. These act as local joints and are designed to optimize the unfolding, whereas the thicker parts in between form the base for the inner conical structures. The plate on the top has two functions. On one hand, in the closed configuration, it covers the inner structures from the fluid and therefore acts as a flat surface to the liquid, leading to a more hydrophilic behavior. On the other hand, it is used as a structural connection element between neighboring unit cells to apply and transmit the displacement from one cell to the other (see Figure 1e,f).

Figure 1. Top: Schematic illustration of unit cell design in initial and final states. The force is applied at the connectors between neighboring cells (black arrows). The unfolding transformation is implied with the red arrow. Bottom: schematic illustration of micropatterned section in initial/closed (left) and final/unfolded (right) states. a,b) Front view, c,d) top view, and e,f) close-up view of the connection between neighboring cells.
To minimize local deformations and prevent failure, an additional mechanical element was implemented at the top edges. It is important to note that this hinge element is fabricated on the micrometer scale and is able to transmit real forces under the performed loading conditions. For fabrication, both components of the hinge were connected with a thin predetermined breaking bar. When mechanical deformation is applied, the connection breaks and releases the movement of the bar.

This specific unit cell design allows to change the morphology of the metasurface by elongation of the substrate. Depending on the choice of the inner structures, the surface texture can be adjusted gradually. To maximize the change in surface morphology, hierarchical conical spikes have been implemented.

As previously mentioned, individual unit cells are repeated in an algorithmic printing loop with alternating arrangement, minimum spacing, as well as overlapping connector elements to link the neighboring cells for interaction (see Figure 1c–f). The exact positioning is controlled via piezoactuators and step motors.

The initial state of the metasurface is shown in Figure 1a–c. Due to the design of the unit cell’s upper part, the array is an almost flat surface. An elongation of the substrate then leads to an unfolding and release of the inner structures. In this specific case, the inner structures consist of conical spikes with sharp tips at the top. In the final state, the unit cells are unfolded and the conical spikes are exposed completely (see Figure 1b,d). This drastic surface morphology change can be used for adaptive wetting phenomena, which is shown in the following.

Experimental results of the fabricated unit cells is shown in Figure 2, as close-up in situ SEM images (Figure 2a–c), as well as a top-view 3D laser images (Figure 2d–f) for three different strain states ($\varepsilon = 0\%$, 10\%, and 30\%). It can also be seen that the unit cells are able to be fabricated and transform due to substrate strain, as it is intended in the design. The corresponding contact angle measurements for each strain state are shown in Figure 2g–i. Here, the resulting contact angle is the mean value of three measurements with a single drop of pure water at different spots on the pattern. Deviations from the mean value are displayed with “±” sign and additional error bars in Figure 3.

In Figure 2a,d, the initial state of the fabricated structures is shown before the mechanical deformation of the substrate. Due to the prior hexamethyldisiloxane (HMDSO) coating step, the surface is already hydrophobic with a mean contact angle of 131° ± 4°. In Figure 2g–i, the influence of mechanical deformation of the unit cells on the metasurface’s wetting behavior. a–c) In situ SEM side-view images of representative unit cells at different strain states. d–f) In situ 3D laser microscope top-view images of a micropatterned section at different strain states. g–i) Result images of associated contact angle measurements at different strain states.

Figure 3. Measured water contact angle versus strain for three samples with similar design and fabrication process (red and gray lines). The contact angle increases with progressing mechanical elongation. The implied linear trend shows a change of the water contact angle of 30° from initial to final strain state (strain = 30\%).
The mechanical elongation of the substrate leads to gradual unfolding and release of the inner conical structures. With this, the interface area between surface and water drop is reduced and the solid-to-liquid ratio is decreased. This decrease can be confirmed by the increasing contact angle from the initial state (131°) to the final state (160°). This is not only a considerable increase by ≈30°, but also a shift from the hydrophobic to the super-hydrophobic regime (>150°).

It is important to note that the measurement results tend to imply a linear behavior between contact angle and substrate strain (see Figure 3). In addition, during deformation, it was observed that the unit cells transform steady and uniform. The reason for this are the mechanical hinges, which are implemented at the connection elements between neighboring cells (see Figure 1e,f). These hinges ensure a smooth unfolding of the top components. In addition to that, they drastically reduce the mechanical stresses during the unfolding process and prevent local destructions and failure. Due to this linear behavior, the wettability can be adjusted very precisely, which could be used for controlling the fluid flow in applications like microdosing devices and lab-on-chip systems.

Different examples of smart surfaces, which switch their wettability between hydrophilic and hydrophobic are described in literature.[16,19-23] However, all of these smart surfaces change their properties in response to a chemical reaction of specific functional molecules. As a result, either polar or nonpolar molecules face toward the water drop. Concerning the results of Wang et al. and Zhang et al., a pH-change leads to the modification of the molecule structure between stretched and folded state.[20,21] Xia et al. used the combination of a pH and temperature change to manipulate the intramolecular hydrogen bonding,[19] whereas Myint et al. apply UV-light exposure to migrate electron–holes into ZnO microrod surfaces.[23] Their measurement results show large contact angle differences (Δθ ≈ 40° at Wang et al., Δθ ≈ 110° at Zhang et al., and Δθ ≈ 90° at Myint et al.)[20,21,23] but the effect is restricted to a specific material composition and/or chemical environment. In addition, the transformation has a time-dependency and may take several minutes or hours.[20,23]

In contrast, our approach does not depend on the used materials or chemicals. It is purely based on mechanics and the structural transformation of novel-designed unit cells. Essentially any material can be used as long as it can be fabricated with the given technology. Furthermore, additional functionalities can be implemented by a post-coating step, to satisfy further chemical requirements or expand the wetting state parameter space. On top of that, as the wettability change is accomplished by the morphology change of the microstructure, the process is not time dependent. The effect occurs with limitations only from strain rate and any previous surface-pinned wetting.

These arguments represent the key advantages of this innovative approach. The results of the contact angle experiments show a difference of ≈30°, which is slightly lower than expected with regards to the distinctive mechanical transformation of the structure. This could have several reasons: On one hand, as the closed metasurface is not completely flat, the contact angle of the initial state is too high. In comparison with a completely flat surface, the contact angle of the metasurface’s initial state is ≈28° higher (compare with Figure A1). The reasons for this are sharp edges  

θ = 103° ± 4°  

Figure A1. Reference water contact angle measurement of a complete flat and HMDSO coated surface with a mean contact angle of 103°.
and small gaps between the unit cells, which lead to nonwetting at some parts. Here, additional design optimization and geometry adjustments of the unit cell can minimize the initial values, comparable with those of a flat surface.

On the other hand, the final contact angle of the unfolded metasurface is relatively low. This is because the micropatterned surface does not fully consist of exposed conical spikes. When the cells are unfolded completely, flat connection bars, and broader edges are still remaining. These surface areas act as an additional interface to the water drop, which has a negative influence on the hydrophobicity. This can be optimized by arranging the joints at different positions which minimizes the surface of the connection bars, improves the opening angle (ideally 90°), and maximizes the final contact angle.

Furthermore, we suspect that not all inner conical spikes were covered in the prior coating step with the hydrophobic HMDSO coating. This is likely related to the metasurface’s complex structures. Overhanging parts might cover some areas and prevent a dense and complete coating. In the final unfolded state, these uncoated parts face toward the water drop, which lowers the hydrophobicity noticeably. To guarantee a complete coating, the process parameters have to be optimized, regarding the size and shape of the given microstructures. Moreover, the wettability difference could be maximized if the inner structures are coated hydrophobic, but the outer ones hydrophilic.

But the presented results clearly demonstrate the feasibility of a mechanically induced wettability change. The design and the resulting effect can be customized as desired.

Shown metasurfaces demonstrate, along with their design, fabrication, and characterization, the feasibility of programmable adaptive wetting behavior. They do not rely on electromagnetic radiation, temperature, electrical potential, pH, or an added solvent, which would potentially limit the application environment. Here, the main effect comes from the mechanically triggered transformation mechanism of the unit cell structure, which changes its surface morphology via elongation of the substrate. Utilizing mechanical triggering opens up a typically unused design space, and allows the chemical composition for a specific process environment to be chosen as desired through separate compositional changes; for example, additional coatings can be applied to readjust the chemical or physical properties and provide, e.g., electric conductivity, optical activity, or chemical resistance.

Combinations with functional or smart materials as substrates could open up new possibilities of multifunctionality as well. Furthermore, using strain-dependent elements within the unit cells, new combinations with other mechanisms can be realized. With this, the local behavior of a liquid on the surface can be adjusted even more specifically.

**Experimental Section**

**Design:** Structural design was carried out using a commercial Computer-Aided Manufacturing (CAD) program (Inventor Autodesk Inc., USA). The surface structures were developed as unit cells, with connector parts for patterning.

**Fabrication:** The designed 3D unit cell was exported as a stereolithographic file (.stl) and then sliced into a small layer-by-layer voxel format (described by Nanoscribe GmbH, Germany). In addition, copies of this unit cells were arranged in a $40 \times 40$ periodic pattern ($\approx 10 \text{ mm}^2$), using an algorithmic positioning command.

The micropatterned samples were fabricated with a commercially available two-photon lithography system (Nanoscribe Photonic Professional GT, by Nanoscribe GmbH, Germany) using liquid negative-tone photoresist (IP-Dip) and a $63 \times$ oil objective with Numerical Aperture = 1.4 by Carl Zeiss AG, Germany. The resist was solidified via two-photon polymerization (2PP) using a frequency-doubled 780 nm fiber laser with 100 fs pulses, 50 mW power, and 10,000 $\mu$m/s speed.

Substrates were commercially available 0.2 mm-thick Indium-Tin Oxide-coated Polyethylene terephthalate foils with 300 $\Omega$ sq$^{-1}$ surface resistivity by Sigma Aldrich Chemie GmbH, Germany.

Before the writing process, substrates were plasma etched with 2 kW power under 50 cm$^3$ min$^{-1}$ air pressure for 5 min to enhance adhesion of the acryl-based resist to the polymer substrates.

After the 2PP process, the samples were developed and cleaned in PGMEA for 30 min (solvent from Sigma-Aldrich) and subsequently washed in isopropyl alcohol with additional UV–light exposure for 5 min to enhance polymerization.

The base material is a hydrophilic acrylic photopolymer. To prevent capillary forces and wetting of the inner structures, an additional coating of HMDSO was deposited for 90 s at 100 W with a constant frequency of 13.56 MHz and pressure of 3 $\times 10^{-2}$ mbar.

**Mechanical Deformation Characterization:** The mechanical deformation of the unit cells was controlled by the strain of the flexible substrate. Here, a custom-built micro-tensile testing machine was used. For guidance, a top-view camera, as well as a piezoactuator and a stepper motor, was used. For topographic imaging with better resolution, a 3D laser microscope from Keyence was used.

**Wettability Characterization:** The wettability of the micropatterned samples was measured by the contact angle using the sessile drop method and 2–3 μL drops of pure water. (As dynamic wettability measurements require large surfaces, but 2PP is limited in fabrication volume and speed, a simple contact angle measurement method was used.) The used device was an OCA 20 setup with a SNS 021/011 flat-tipped needle by DataPhysics Instruments GmbH, Germany. The volume of the drop was controlled by a motor-driven syringe. The contact angles were captured by the setup’s camera with a white-illuminated background.

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**Conflict of Interest**

The authors declare no conflict of interest.

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