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Unidirectional Control of Anisotropic Wetting through Surface Modification of PDMS Microstructures

Daisuke Tanaka,[†,‡] Daniel Buenger,[†] Haika Hildebrandt,[†] Martin Moeller,[†] and Juergen Groll*[,†,§]

[†]Interactive Materials Research − DWI e.V. and Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Forckenbeckstr. 50, 52056 Aachen, Germany

[‡]Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

[§]Department and Chair of Functional Materials in Medicine and Dentistry, University of Wurzburg, Pleicherwall 2, 97070 Würzburg, Germany

⑤ Supporting Information

ABSTRACT: It has been shown before that anisotropically micro-structured surfaces exhibit anisotropic wetting phenomena. This study presents a possibility to control the anisotropy of wetting by tailoring the surface chemistry. PDMS microchannels were permanently hydrophilized and subsequently functionalized further. Thereby, systematic studies on the effect of the surface modification on the wetting properties of microstructures have been possible. Importantly, we found that the wetting parallel to the groove strongly depended on the chemical modification of the structure although the wetting perpendicular to the groove is almost unaffected. Through immobilization of a monolayer of Si nanoparticles (SiNPs) exclusively on the elevations of the hydrogel-coated microstructured PDMS substrate, the anisotropic wetting could be selectively altered unidirectionally along the pattern direction.
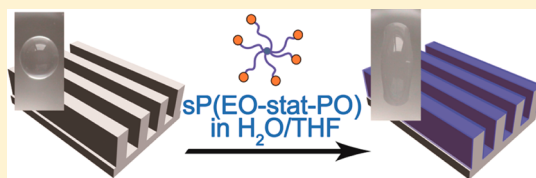
■ INTRODUCTION

Anisotropic wetting phenomena are of general fundamental interest but also bear application potential in microfluidic devices, evaporation-driven formation of patterns, and easy-to-clean coatings.[1,2] Micrometer-scale directional patterns on surfaces have been considered to be a key factor for anisotropy, and so far, most reports in the literature have addressed anisotropic wetting on 1D groove structures.[3−15] Line-patterned substrates were prepared by various fabrication techniques such as lithography and imprinting, and the effect of the topographical variation on their anisotropic wettability was studied.

Several reports have demonstrated that the chemical modification of 1D groove structures can drastically alter their anisotropic wetting properties.[10,13,16,17] The combination of fabricating a micrometer-sized structure and chemical modification would open up opportunities for well-designed anisotropic surfaces. However, precise control over anisotropic wetting by further modification of unidirectional structures remains challenging. For example, poly(dimethyl siloxane) (PDMS) is an elastomer commonly used in medical applications, microfluidic devices, and lab-on-a-chip applications because it is cheap and easy to mold into application-designed microstructures.[18,19] However, precisely controlling anisotropic wetting on chemically engineered PDMS with microstructure is rare mainly because of its chemical inertness. Its hydrophobicity, in fact, has limited the use of PDMS in many applications. If the chemical properties of a PDMS surface could be altered precisely and permanently without

changing its original structure, then the desired anisotropic wetting surfaces could be achieved.

It has been known that exposing PDMS to various energy sources, such as UV/ozone treatment and O$_2$ plasma, renders PDMS surfaces hydrophilic. However, because of the high flexibility of the polymer backbone, the generation of high-energy hydrophilic functional groups on PDMS directly induces a surface-energy-driven reorganization process that results in the recovery of the hydrophobicity.[20] To achieve permanent hydrophilication, the substrates have to be chemically derivatized directly after the generation of the functional groups. Very recently, anisotropic wetting on strained micro-wrinkled PDMS substrates that were exposed to UV/ozone followed by subsequent treatment with semifluorinated silane to stabilize the surface has been reported. This process, however, induces wrinkling of the surface so that the original microstructures of the substrate cannot be maintained.[16] We have reported a facile and versatile coating method for PDMS through activation with NH$_3$ plasma followed by modification with six-armed star-shaped poly(ethylene glycol)-based prepolymers terminated with isocyanate functional groups (sP(EO-stat-PO)).[21,22] This method has several advantages. (1) Because the sP(EO-stat-PO) layers are ultrathin (<30 nm), the original PDMS microstructures are maintained after the coating. (2) The covalent attachment of sP(EO-stat-PO) to the PDMS substrates and cross-linking in the layers stabilize the
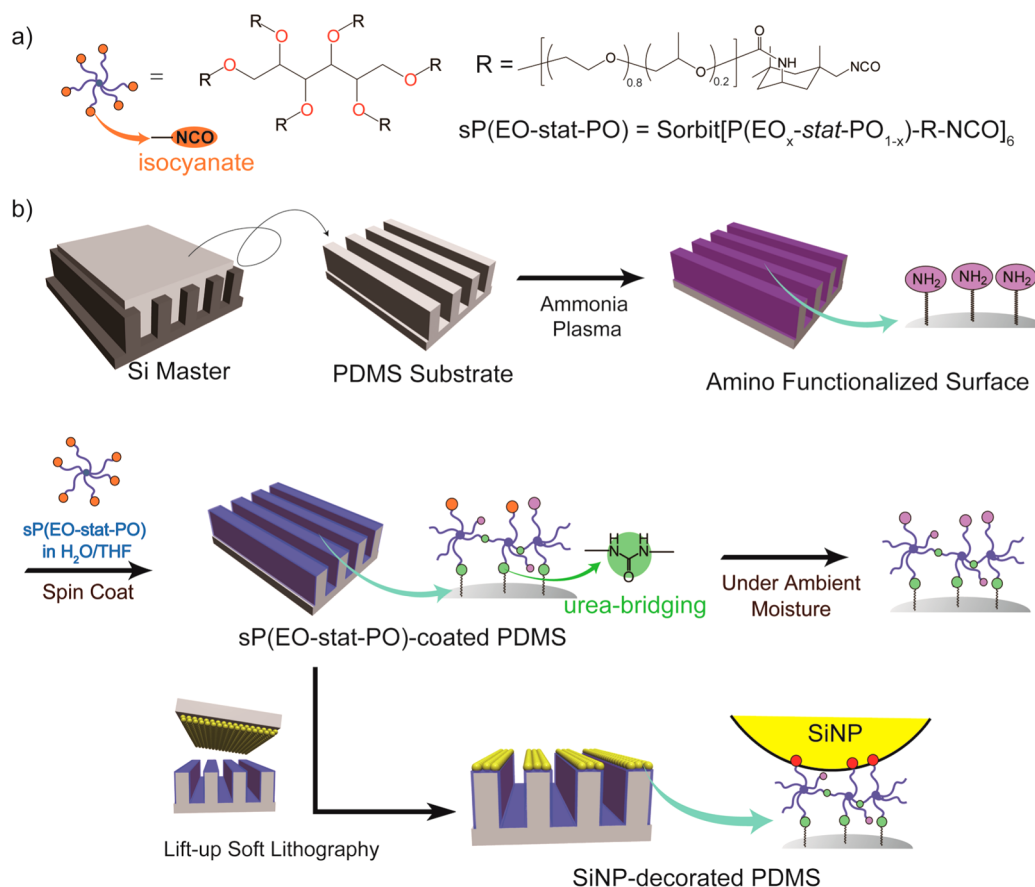
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Figure 1. (a) Chemical composition of sP(EO-stat-PO). (b) Schematic illustration of the preparation of the surface-functionalized 1D groove structure.

system. (3) The high functionality of the sP(EO-stat-PO) layers allows straightforward further functionalization (e.g., by reaction with the isocyanate groups in freshly prepared layers).

This study presents the easy and versatile chemical modification of topographically microstructured PDMS architectures by sP(EO-stat-PO) coatings and their functionalization (Figure 1). Thereby, systematic studies on the effect of the surface modification on the wetting properties of microstructures have been carried out and have provided deep insight into anisotropic wetting phenomena. Importantly, we found that the wetting parallel to the groove strongly depended on the chemical modification of the structure although the wetting perpendicular to the groove is almost unaffected. Through the immobilization of a monolayer of Si nanoparticles (SiNPs) exclusively on the elevations of the sP(EO-stat-PO)-coated microstructured PDMS substrate, the anisotropic wetting could be selectively altered unidirectionally along the pattern direction.

■ EXPERIMENTAL SECTION

Preparation of PDMS Substrates with a One-Dimensional Groove. The two components of Sylgard 184 were mixed extensively in the ratio given by the manufacturer, and the pressure was slowly reduced until no more gas bubbles were developing in the PDMS. The fluorinated silicon masters were covered with a layer of this mixture with the desired substrate thickness. The elastomer was then cured at 120 °C for 2 h, released from the masters, and cut to the desired size.

Ammonia Plasma. Ammonia plasma treatment was carried out using low-pressure ammonia plasma from a Microwave Discharge AK 330 Plasma Apparatus (Roth & Rau Oberflächentechnik AG,

Germany). Plasma-treatment conditions were optimized to the following: pressure = 0.4 mbar, power = 360 W, treatment time = 300 s, and ammonia gas inlet flow rate = 30 sccm.

sP(EO-stat-PO) Coating. After ammonia plasma activation, PDMS samples were treated with sP(EO-stat-PO) solution by spin coating. Preparation of the sP(EO-stat-PO) solutions was achieved by dissolving 50 mg of sP(EO-stat-PO) prepolymer (M_n = 12 000 g mol^{-1}) under an inert gas atmosphere in 0.5 mL of dry THF. This solution was mixed with 4.5 mL of ultrapure water. After 5 min, the solutions were filtered through 0.2 μm syringe filters (Whatman) and used for coating. For spin coating, the substrates were placed on the spin coater, covered with the sP(EO-stat-PO) solution, and then accelerated within 5 s to 2500 rpm for 40 s. The resulting films were stored overnight under ambient conditions for cross-linking.

Preparation of Silica Nanoparticles (SiNPs). Monodisperse silica nanoparticles with a diameter of 130 nm were synthesized by Stöber's method.[23] Therefore, 220 mL of ethanol was mixed with 12 mL of ammonium hydroxide (25%). Under vigorous stirring, 7.7 mL of tetraethyl orthosilicate (TEOS), which was used as a precursor, was added. After 2 h, the solution became turbid, indicating the condensation process. After 24 h, the solution was heated to 60 °C to remove the ammonium hydroxide.

Preparation of SiNP-Decorated Microstructures. The self-assembly of SiNPs to form colloidal crystal was followed as described in the literature.[24,25] A drop of 20 μL of the SiNP suspension was applied to the slightly tilted silicon substrate and then slowly evaporated, resulting in a 2D colloidal crystal. The bare PDMS microstructure was covered with sP(EO-stat-PO) prepolymer as described above. The PDMS substrates after ammonia activation were treated with sP(EO-stat-PO) solution by spin coating. The preparation of the sP(EO-stat-PO) solutions was the same as described above. After 5 min, the solutions were filtered through 0.2 μm syringe filters (Whatman) and used for coating. For spin coating, the substrates were
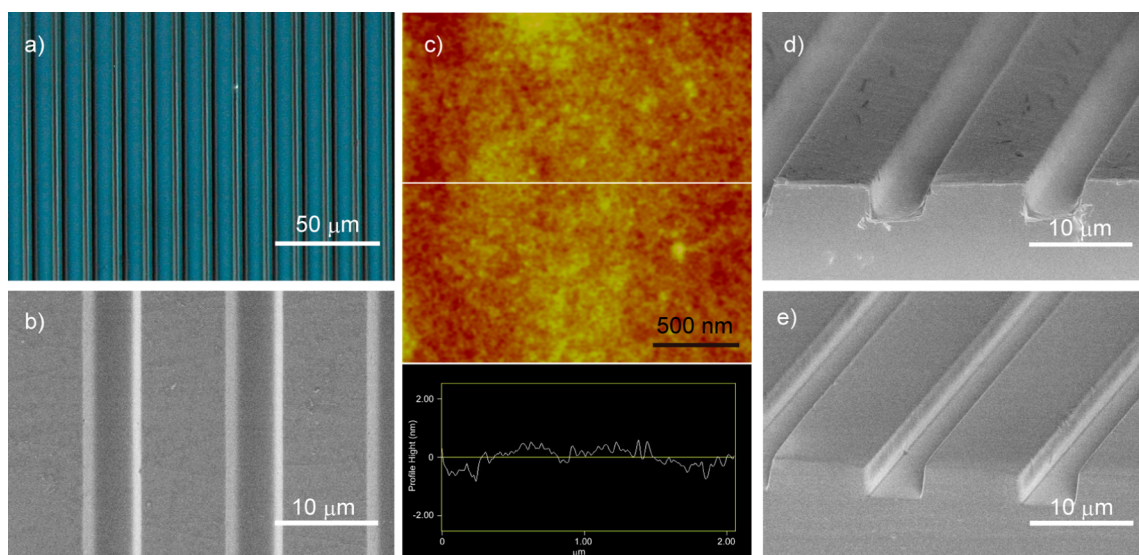
Figure 2. Images of sP(EO-stat-PO)-coated microstructured PDMS ($p = 10$ μm, $g = 5$ μm). (a) Optical microscopy and (b) FE-SEM images. (c) AFM image highlighting the smoothness of the polymer films. Side view of FE-SEM images of (d) the sP(EO-stat-PO)-coated microstructured PDMS and (e) the bare PDMS.
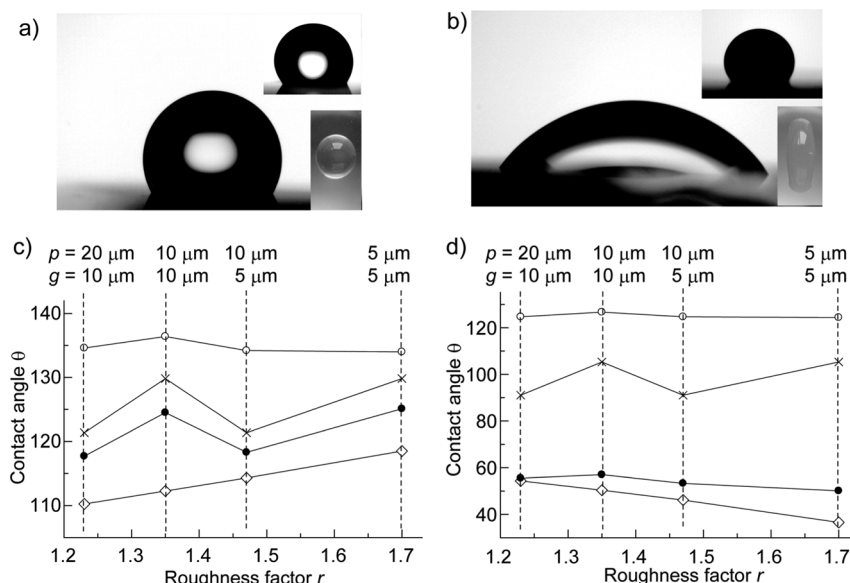

Figure 3. Profile view of a sessile drop (1.5 μL) from the direction perpendicular to the grooves ($p = 10$ μm and $g = 5$ μm). (a) The bare microstructured PDMS and (b) the sP(EO-stat-PO)-coated microstructured PDMS. The upper inset is profile view of the drops parallel to the grooves, and the lower inset is the top view of a 1.5 μL water drop on the microstructures. Relationship between the roughness factor r and water contact angle on (c) the bare PDMS and (d) the polymer-coated PDMS. The open circle and the dot represent the experimental results of θ_x and θ_y, and the diamond and the cross represent the calculated values from Wenzel's equation and Cassie's equation, respectively. The upper values are the corresponding structure parameters. All pillar heights are 3.5 μm.

placed on the spin coater, covered with the sP(EO-stat-PO) solution, and then accelerated within 5 s to 2500 rpm for 40 s, and the resulting film was stored for 2 h under ambient conditions. Then, the SiNP colloid crystal on the silicon substrate was placed on the sP(EO-stat-PO)-coated PDMS microstructure overnight at ambient atmosphere for cross-linking, and the PDMS substrate was carefully peeled off of the colloid crystal on the silicon substrate. The obtained SiNP monolayer on PDMS was observed by FE-SEM.

RESULTS AND DISCUSSION

We fabricated microstructured PDMS substrates with parallel groove geometry by replication from the silica master according to the procedures for PDMS stamp preparation reported in the literature.[26] Four kinds of combinations of groove and pillar widths were prepared (Figure S1 in the Supporting Information). The height of all grooves was 3.5 μm. PDMS substrates were amine functionalized through treatment with ammonia plasma as reported earlier.[22] Surface coating was carried out by spin coating a solution of NCO-sP(EO-stat-PO) onto ammonia plasma-treated PDMS as shown in Figure 1b. Figure 2a−d shows an example of an sP(EO-stat-PO)-coated substrate (the pillar width (p) is 10 μm, and the groove width (g) is 5 μm.). The optical microscope image, the FE-SEM images, and the AFM image demonstrated that the sP(EO-stat-PO) film on the amino-functionalized PDMS is smooth and

homogeneous. A comparison of the FE-SEM image of the corresponding noncoated PDMS structure in Figure 2e demonstrates that the microstructure of the sP(EO-stat-PO)-coated PDMS agree well with the original PDMS structure.

The contact angles (CAs) of bare and coated PDMS structures with p = 10 μm and g = 5 μm were then measured in front and side views. CAs were measured with a G-40 contact angle measuring device (Krüss GmbH, Germany). The measurements were carried out with 1.5 μL of ultrapure water. θ_x and θ_y were the CAs measured parallel and perpendicular to the grooves, respectively, and the degree of wetting anisotropy was defined as $\Delta\theta$ (= $\theta_x - \theta_y$).[2] The measured angles are shown in Figure 3a,b. In the case of the bare PDMS structure, there is a difference in the contact angles for an isotropic surface of bare PDMS. (The intrinsic CA on the isotropic flat surface, θ_0, was determined to be 106° by measuring the CA of a flat PDMS surface.) However, the difference for both of θ_x (134°) and θ_y (118°) was not very pronounced, and $\Delta\theta$ was only 16°. In contrast, strong anisotropic wetting behavior was observed on the sP(EO-stat-PO)-coated PDMS structures. Here, although θ_0 of a sP(EO-stat-PO) layer on PDMS was determined to be 62° by measuring the CA of the sP(EO-stat-PO) layer on a flat PDMS substrate, θ_x equals 125° and is thus almost as high as for the uncoated structured PDMS. However, θ_y decreased even further to 53°, resulting in strong anisotropical wetting of $\Delta\theta$ = 72°. It is also worth noting that the anisotropic hydrophilicity of the sP(EO-stat-PO)-coated PDMS structure remained stable and unaffected even after storage under ambient conditions for 3 months, whereas the hydrophilicity of ammonia plasma-treated PDMS was lost in less than 1 week.

To explore the detail of the surface-modification effect, conventional models for CA were applied to the system. When the droplet wets the whole surface (homogeneous wetting), its CA is given by Wenzel's equation

$$\cos\theta = r\cos\theta_0$$

where θ is the measured CA and θ_0 is the intrinsic CA of the flat material.[9] r is the roughness ratio or the ratio of the real contact area to the projected area

$$r = \frac{p + g + 2h}{p + g}$$

where h is the pillar height. In this model, the surface roughness will amplify the hydrophilicity or hydrophobicity, depending on the chemical properties of the substrate. However, this model cannot predict the contact angles of superhydrophobic surfaces, where the chemical hydrophobicity is strongly enhanced by pronounced roughness. On such surfaces, a water droplet is in contact only with the top elevations, and air pockets are included along its contact with the substrate. Such a composite contact is governed by Cassie's equation

$$\cos\theta = f\cos\theta_0 + f - 1$$

where f is the fraction of the liquid droplet surface in contact with the solid.[9] According to this equation, the CA increases with the decreasing share of direct contact between water and the underlying substrate.

Figure 3 shows the changes in experimental and calculated CAs for four kinds of prepared groove structures against the roughness factor r. The plots clearly demonstrate that the periodicity of the 1D pattern for both bare and sP(EO-stat-

PO)-coated PDMS has only a modest effect on θ_x. Neither Wenzel's equation nor Cassie's equation can describe the weak dependency on the pattern periodicity. Moreover, the observed θ_x is much higher than the calculated value. It is known that a potential free-energy barrier is formed at a groove and induces the pinning of the fluid at the edge of the pillars, which is the origin of the large θ_x.[6,15,27,28] This would be the reason that θ_x is inert to the pattern variation. This assumption also suggests that the formation of a free-energy barrier is not very sensitive to homogeneous chemical modification because the sP(EO-stat-PO) coating does not change θ_x significantly. In contrast, the observed θ_y is similar to the corresponding CA calculated by the classical models. In the case of bare PDMS, θ_y does not depend on r but on the fraction factor, f, and Cassie's equation well describes the geometry dependency, which indicates the existence of a composite contact. However, θ_y for sP(EO-stat-PO)-coated PDMS is close to the CA calculated by Wenzel's equation. In fact, direct observation by optical microscopy indicated that the water droplet wets the whole surface, and the grooves were filled with water (Figure S2 in the Supporting Information). These results suggest that the chemical modification of a 1D structure directly influences the wettability parallel to the groove although the wettability perpendicular to the groove is governed by the formation of a free-energy barrier. Because the free-energy barrier formation weakly depends on the surface chemical modification, the sP(EO-stat-PO) coating influences θ_y more directly than it influences θ_x.

These results imply that if the surface modification can be achieved without disturbing its free-energy barrier then the wettability in only one direction (parallel to the groove) can be changed selectively. To prove the assumption, the top of the sP(EO-stat-PO)-coated structure was decorated with a monolayer of silica nanoparticles with an average diameter of 130 nm (SiNPs) by making use of the lift-up soft lithography technique.[24,29] As shown in Figure 1b, the hydroxyl groups on SiNPs react with unreacted isocyanate groups in freshly coated substrates to form covalent bonds between the nanoparticles and the sP(EO-stat-PO) layer. Figure 4 shows an FE-SEM images of the SiNP-covered structure (p = 10 μm, g = 5 μm). The images clearly indicate that there are no SiNPs in the
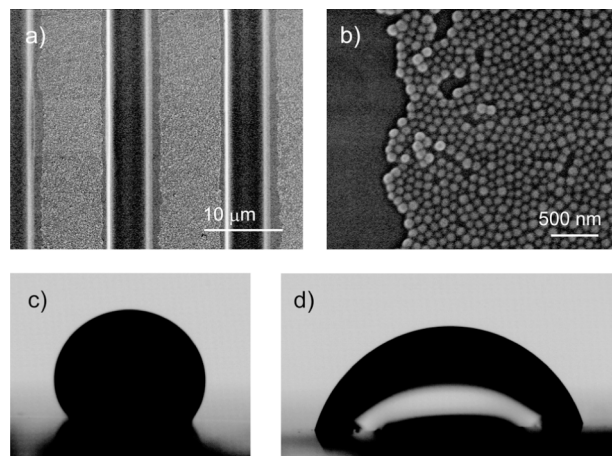

Figure 4. (a) FE-SEM images of the SiNP-coated microstructure. (b) Higher-magnification image at the edge of a pillar. Profile view of a sessile drop (1.5 μL) on an SiNP-coated surface (c) parallel and (d) perpendicular to the grooves.

groove or at the edge of the pillar. Because the fluid is pinned on the edge of the horizontal pillars, it is expected that this modification does not change the CA perpendicular to the groove. The SiNP layer was not afected by extensive rinsing of the substrate with water. The CA measurement demonstrated that the θ_x of 126° is identical to that for the corresponding non-SiNP-modified structure although θ_y (72°) is significantly larger than that for the non-SiNP-coated structure ($\theta_y = 53°$). The increase in θ_y is probably due to the surface roughness on the pillar induced by the SiNP modification. To the best of our knowledge, this is the first report of the unidirectional alternation of anisotropic wetting behavior.

■ CONCLUSIONS

This study presents a facile and powerful technique for PDMS microstructure modification. The PDMS substrates were functionalized with NH_3 plasma and modified with sP(EO-stat-PO), resulting in permanent hydrophilic surfaces. These sP(EO-stat-PO)-coated 1D groove structures show much stronger anisotropic wetting than the corresponding bare PDMS structures. The results of our comparison study suggested that the free-energy barrier formation weakly depends on the surface chemical modification and thus the CA perpendicular to the groove is not sensitive to the coating although the coating directly influences the wettability parallel to the groove. Moreover, SiNP decoration on top of the pillar results in the unidirectional alternation of the CA because the modification does not disturb its free-energy barrier. These results provide new insights into the phenomenon of anisotropic wetting and present the possibility to design the anisotropic wetting of surfaces freely and precisely through controlled surface modification of topographically micro-structured substrates. It also opens a way to switch the anisotropic wetting of surfaces through the use of, for example, photoswitchable coatings, which holds great potential for application in microfluidics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Summary of the prepared PDMS microstructures and their CA measurements. Optical microscope images for all of the structures coated with the sP(EO-stat-PO) hydrogel film. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: juergen.groll@fmz.uni-wuerzburg.de. Tel: +49-931-201-73610. Fax: +49-931-201-73-500.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Hancock, M. J.; Demirel, M. C. Anisotropic Wetting on Structured Surfaces. *MRS Bull.* **2013**, *38*, 391−396.

(2) Xia, D. Y.; Johnson, L. M.; Lopez, G. P. Anisotropic Wetting on One-Dimensional and Directional Patterned Surfaces. *Adv. Mater.* **2012**, *24*, 1287−1302.

(3) Yoshimitsu, Z.; Nakajima, A.; Watanabe, T.; Hashimoto, K. Effects of Surface Structure on the Hydrophobicity and Sliding Behavior of Water Droplets. *Langmuir* **2002**, *18*, 5818−5822.

(4) Morita, M.; Koga, T.; Otsuka, H.; Takahara, A. Macroscopic-Wetting Anisotropy on the Line-Patterned Surface of Fluoroalkylsilane Monolayers. *Langmuir* **2005**, *21*, 911−918.

(5) Zhang, F. X.; Low, H. Y. Anisotropic Wettability on Imprinted Hierarchical Structures. *Langmuir* **2007**, *23*, 7793−7798.

(6) Zhao, Y.; Lu, Q. H.; Li, M.; Li, X. Anisotropic Wetting Characteristics on Submicrometer-Scale Periodic Grooved Surface. *Langmuir* **2007**, *23*, 6212−6217.

(7) Wu, H.; Zhang, R.; Sun, Y.; Lin, D. D.; Sun, Z. Q.; Pan, W.; Downs, P. Biomimetic Nanofiber Patterns with Controlled Wettability. *Soft Matter* **2008**, *4*, 2429−2433.

(8) Li, W.; Fang, G. P.; Li, Y.; Qiao, G. Anisotropic Wetting Behavior Arising from Superhydrophobic Surfaces: Parallel Grooved Structure. *J. Phys. Chem. B* **2008**, *112*, 7234−7243.

(9) Yang, J.; Rose, F. R. A. J.; Gadegaard, N.; Alexander, M. R. Effect of Sessile Drop Volume on the Wetting Anisotropy Observed on Grooved Surfaces. *Langmuir* **2009**, *25*, 2567−2571.

(10) Khare, K.; Zhou, J. H.; Yang, S. Tunable Open-Channel Microfluidics on Soft Poly(dimethylsiloxane) (PDMS) Substrates with Sinusoidal Grooves. *Langmuir* **2009**, *25*, 12794−12799.

(11) Yong, X.; Zhang, L. T. Nanoscale Wetting on Groove-Patterned Surfaces. *Langmuir* **2009**, *25*, 5045−5053.

(12) Xia, D. Y.; He, X.; Jiang, Y. B.; Lopez, G. P.; Brueck, S. R. J. Tailoring Anisotropic Wetting Properties on Submicrometer-Scale Periodic Grooved Surfaces. *Langmuir* **2010**, *26*, 2700−2706.

(13) Wu, D.; Chen, Q. D.; Yao, J.; Guan, Y. C.; Wang, J. N.; Niu, L. G.; Fang, H. H.; Sun, H. B. A Simple Strategy to Realize Biomimetic Surfaces with Controlled Anisotropic Wetting. *Appl. Phys. Lett.* **2010**, *96*, 053704.

(14) Honda, K.; Morita, M.; Masunaga, H.; Sasaki, S.; Takata, M.; Takahara, A. Room-Temperature Nanoimprint Lithography for Crystalline Poly(fluoroalkyl acrylate) Thin Films. *Soft Matter* **2010**, *6*, 870−875.

(15) Neuhaus, S.; Spencer, N. D.; Padeste, C. Anisotropic Wetting of Microstructured Surfaces as a Function of Surface Chemistry. *ACS Appl. Mater. Interfaces* **2012**, *4*, 123−130.

(16) Chung, J. Y.; Youngblood, J. P.; Stafford, C. M. Anisotropic Wetting on Tunable Micro-Wrinkled Surfaces. *Soft Matter* **2007**, *3*, 1163−1169.

(17) Xia, D. Y.; Brueck, S. R. J. Strongly Anisotropic Wetting on One-Dimensional Nanopatterned Surfaces. *Nano Lett.* **2008**, *8*, 2819−2824.

(18) Whitesides, G. M. Overview: The Origins and the Future of Microfluidics. *Nature* **2006**, *442*, 368−373.

(19) Kane, R. S.; Takayama, S.; Ostuni, E.; Ingber, D. E.; Whitesides, G. M. Patterning Proteins and Cells Using Soft Lithography. *Biomaterials* **1999**, *20*, 2363−2376.

(20) Hillborg, H.; Tomczak, N.; Olah, A.; Schonherr, H.; Vancso, G. J. Nanoscale Hydrophobic Recovery: A Chemical Force Microscopy Study of UV/Ozone-Treated Cross-Linked Poly(dimethylsiloxane). *Langmuir* **2004**, *20*, 785−794.

(21) Gasteier, P.; Reska, A.; Schulte, P.; Salber, J.; Offenhausser, A.; Moeller, M.; Groll, J. Surface Grafting of PEO-Based Star Shaped Molecules for Bioanalytical and Biomedical Applications. *Macromol. Biosci.* **2007**, *7*, 1010−1023.

(22) Salber, J.; Grater, S.; Harwardt, M.; Hofmann, M.; Klee, D.; Dujic, J.; Huang, J. H.; Ding, J. D.; Kippenberger, S.; Bernd, A.; Groll, J.; Spatz, J. P.; Moller, M. Influence of Different ECM Mimetic Peptide Sequences Embedded in a Nonfouling Environment on the Specific Adhesion of Human Skin Keratinocytes and Fibroblasts on Deformable Substrates. *Small* **2007**, *3*, 1023−1031.

(23) Stöber, W.; Fink, A.; Bohn, J. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968**, *26*, 62−69.

(24) Yao, J. M.; Yan, X.; Lu, G.; Zhang, K.; Chen, X.; Jiang, L.; Yang, B. Patterning Colloidal Crystals by Lift-Up Soft Lithography. *Adv. Mater.* **2004**, *16*, 81−84.

(25) Micheletto, H.; Fukuda, R.; Ohtsu, M. A Simple Method for the Production of a Two-Dimensional, Ordered Array of Small Latex Particles. *Langmuir* **1995**, *11*, 3333−3336.

(26) Groll, J.; Haubensak, W.; Ameringer, T.; Moeller, M. Ultrathin Coatings from Isocyanate Terminated Star PEG Prepolymers: Patterning of Proteins on the Layers. *Langmuir* **2005**, *21*, 3076−3083.

(27) Chen, Y.; He, B.; Lee, J. H.; Patankar, N. A. Anisotropy in the Wetting of Rough Surfaces. *J. Colloid Interface Sci.* **2005**, *281*, 458−464.

(28) Youngblood, J. P.; McCarthy, T. J. Ultrahydrophobic Polymer Surfaces Prepared by Simultaneous Ablation of Polypropylene and Sputtering of Poly(tetrafluoroethylene) Using Radio Frequency Plasma. *Macromolecules* **1999**, *32*, 6800−6806.

(29) Yan, X.; Yao, J. M.; Lu, G. A.; Chen, X.; Zhang, K.; Yang, B. Microcontact Printing of Colloidal Crystals. *J. Am. Chem. Soc.* **2004**, *126*, 10510−10511.