1. Introduction

Several animals and plants ingeniously developed anisotropic micro- or nanostructures to facilitate smart functions. \[1\] Prominent examples include butterfly wings\[2\] and rice leaves\[3,4\] featuring directional superhydrophobicity, or slippery peristomes of Nepenthes pitcher plants.\[5\] These natural prototypes inspired the development of artificial surfaces with unidirectional wetting properties allowing the transport of liquid droplets.\[6,7\] Another interesting case is the frictional anisotropy of snake scales\[8–11\] enabling snakes to locomote efficiently, even on slippery or inclined surfaces. While some snakes use the edges of their ventral scales to climb even trees,\[10\] many snakes feature oriented micron-sized fibrils with nanoscale steps causing anisotropic friction along their body (Figure 1a).\[11–18\]

Embedding this anisotropic frictional capability in engineered surfaces promises great potential for applications which demand frictional anisotropy. Consequently, several artificial surfaces have been designed and fabricated through replicating the arrangement of snake scales on metal\[19,20\] or by mimicking the micro-fibril structure with polymers,\[21,22\] metals\[23,24\] or even ceramics.\[25\] And indeed, frictional anisotropy was demonstrated on these snake-inspired, micro-structured surfaces.

Here, we go a step further and present a smart surface which can reversibly switch between isotropic and anisotropic friction or even tune the frictional anisotropy (Figure 1b). For that purpose we utilize the unique properties of shape memory polymers (SMPs)\[26,27\] which “memorize” a predefined so-called permanent shape. Once this permanent shape is defined, they can be manipulated into nearly any arbitrary, so-called temporary shape in a programming process. Afterward, they switch back to the memorized permanent shape in a recovery process if triggered by an external stimulus such as heat or light.\[28–32\] Recent studies also reported on SMPs with recovery triggers such as electric\[33\] and magnetic\[34\] excitations as well as humidity.\[35,36\] This intrinsic material property of SMPs together with the possibility to structure their surface down to the nanoscale provides great potential for the development of smart surfaces with switchable functionality. So far, SMPs have been successfully prepared with various microstructures including elements for optics,\[37–39\] medicine,\[40\] wetting control,\[41–43\] and reversible adhesion.\[44–47\]
Our smart surface is fabricated by replicating the micro-fibril structures found on the ventral scales of the Chinese cobra (Naja atra) into a SMP foil. The magnitude of friction anisotropy on the surface can be controlled by tuning the height of nano-steps at the fibril tips during recovery. The step height as well as the induced frictional anisotropy at the nano-steps during the recovery process are characterized in situ by atomic force microscopy (AFM). The long-term stability of the height of the nano-steps was monitored at four different stages of the recovery process. The reusability is proven by the analysis of flattening/recovery cycles. Finally, the resulting smart surface is utilized for the unidirectional transport of single microspheres made from polydimethylsiloxane (PDMS). Further experiments showing the simultaneous transport of many PDMS microspheres and sand particles demonstrate the potential for dry self-cleaning of technical surfaces.

2. Results and Discussion

2.1. Snake Inspired Surface with Switchable Topography

As outlined in Figure 1 we use the ventral scales of snakes as an inspiration to fabricate a smart surface from a SMP whose surface can be switched from a flat to a nano-stepped configuration. Figure 2 summarizes the whole process.
switched between the flattened and structured topography by cyclically conducting the flattening and heating processes.

2.2. In Situ Characterization of Topography and Friction Anisotropy by Atomic Force Microscopy

AFM allows the in situ characterization of the restoring process of the SMP foil. Figure 3a–c shows the respective AFM images during the transformation from a flattened to a recovered, structured surface at the same location of a SMP foil. The bottom panels display the topographical line sections along the red, dashed arrows in the upper AFM images. A roughly flat topography is observed over the 10 µm scan range in Figure 3a. The edges of the steps are still observable, but their heights are less than 6 nm. After heating the sample on a hot plate for 10 s, the topography at the same position changes significantly as shown in Figure 3b. The line section across the same fibrils already shown in Figure 3a reveals that the step heights increase to more than 30 nm. Further heating causes a complete recovery of the surface after 200 s (Figure 3c). The step heights of the same fibrils as shown in Figure 3b increase to almost 60 nm. Furthermore, it is interesting to note that the overall shape of the fibrils remains unchanged during this recovery process while their length and width reduce slightly.

We also analyzed the growth process of the single fibril step marked by the black arrow in Figure 3a–c. Figure 3d displays seven height measurements taken during the complete heat induced recovery process as a function of time. The data points are close to a straight line if plotted on a logarithmic time scale. The same result is observed at other steps of micro-fibrils (see Figure S2a, Supporting Information). This confirms that the height increases exponentially with heating time at a fixed temperature, as already described in refs. [37,48].

AFM has the advantage that the frictional forces at the nano-steps can be measured simultaneously with the topography during the recovery process. Figure 3e shows the friction loops of the AFM tip scanning the fibril steps up (trace direction) and down (retrace direction) along the position marked as a red, dashed line in the topography images in Figure 3a,c, respectively. As frequently observed, there is a significant frictional peak marked by arrows at the nanoscale step edges for upward scans and a smaller one for downward scans.[13,17,49] A comparison of the two friction loops reveals also that the frictional peak for the upward scans is much higher for the structured (Figure 3c) than for the flattened surface (Figure 3a). For downward scans, however, the frictional peaks for the two cases are almost equivalent. Consequently, there is a large difference between upward and downward scans for the structured surface leading to a frictional anisotropy. For the flattened surface,
however, the anisotropic effect is almost negligible. This outcome is in agreement with other studies showing that frictional anisotropy of snake scales can be detected by AFM \cite{13,17}, tribometry \cite{50} as well as by classical friction experiments with an inclined plane \cite{51,52}.

Figure 3f displays the frictional anisotropy at the second fibril step (marked by the black arrow in the AFM images) as a function of its corresponding step height during the recovery process from (a) to (c). A nearly linear relationship is observed. The initial frictional anisotropy on the temporarily flattened surface (Figure 3a) was close to one (1.35) and finally increased to 3.84 after full recovery (Figure 3c). Additional measurements of the frictional anisotropy at two other micro-fibril steps are plotted in Figure S1b, Supporting Information. All data points fit to a straight line. This outcome proofs that the frictional anisotropy increases linearly with the height of the nano-steps which in turn can be controlled via the heating time of the SMP foil.

This result suggests that the frictional anisotropy can be set through the step-height which can be controlled by stopping the recovery process at the dedicated value. Thus, we produced several samples, stopped their recovery at various states, stored them under controlled conditions well below $T_{\text{switch}}$ and analyzed their topography weekly over a time span of three months. The step heights stayed constant within the experimental error for 12 weeks (see Figure S3a, Supporting Information). Additionally, we analyzed the step heights during eleven consecutive flattening and recovery cycles and observed...
no degrading within the experimental error (see Figure S3b, Supporting Information). Furthermore, it might be interesting to note that the optical transmittance of the polymer foils is about 90% in the visible range for flat as well as for the structured surface (see Figure S4, Supporting Information) because the overall height of the nano-steps is one order of magnitude smaller than the visible wavelengths.

2.3. Drift of Microparticles through Random Vibrations

As already outlined in Figure 1b it is the goal of our study to utilize the snake inspired surfaces for the transport of microparticles. The approach is based on the fact that a small particle on top of a laterally vibrated surface with frictional anisotropy experiences a net force acting in the direction of lower friction. A simplified but instructive model is presented in Figure S1, Supporting Information.

Figure 4 visualizes the directional drift of small particles transported due to this effect on several samples. A ventral scale of the Chinese cobra served as reference and is compared with three artificial surfaces: An originally structured SMP, a flattened one, and a recovered one. All examined surfaces were sputter-coated with a thin homogeneous silver layer to increase visibility of the microparticles under the light microscope and to achieve similar surface properties for all samples. Furthermore, the metallic layer avoids possible triboelectric effects. After placing a PDMS microsphere on each surface, we vibrated the surfaces with a small vibration motor and recorded the particles’ movement with an optical microscope.

Figure 4a demonstrates the drift of a PDMS microsphere on the vibrated snake scale. The left image displays the starting position of the sphere. The SEM image in the inset shows the surface structure and indicates the orientation of the micro-fibrils pointing from top to bottom. With the onset of the vibrations, the microparticle starts to tremble in all directions, but due to the frictional anisotropy of the snake scale, the movement in bottom direction is slightly easier. Consequently, it performs small random jumps in all directions, but the overall drift is largest along the micro-fibril structure to the bottom of the image. The center and right optical image reveals the position of the sphere after 11 and 14 s. The complete path is plotted by data points in the graph on the right. Within 43 s the drift in y-direction is about 5.5 mm while the random movement in x-direction does not exceed 0.5 mm.

The overall phenomenon is also observed on the structured SMP foils. Putting other PDMS microspheres on the originally structured (Figure 4b) and recovered SMP foil (Figure 4d) we observe a clear drift of each particle along the direction of the micro-fibrils (to the bottom in our presentation) due to the vibration of the surfaces. The respective travelling distances in y- and x-direction on these two surfaces are 4.3 and 0.26 mm (time span 20 s) and 4.75 and 0.45 mm (time span 41 s), respectively. We would like to point out that the overall movement is a stochastic path due to the random mechanical vibrations. Furthermore, we used microspheres with slightly different diameters in Figure 4. Consequently, the overall drift velocities cannot be compared directly. The net drift, however, is unidirectional and the significant travel distance is only observed on the structured surfaces. Repeating the experiment on a completely flat surface or a flattened SMP foil results in a trembling of the respective sphere under observation but the overall long-term drift is negligible as demonstrated by the photographs and the plot in Figure 4c. Videos of the experiments summarized in Figure 4 are available in the Videos S1–S4, Supporting Information.

2.4. Dry Self-Cleaning with Snake Scale Inspired Surfaces

From the above presented experiments, we conclude that the surface structure of snakes can be copied to artificial surfaces which exhibit the same frictional anisotropy as snake scales. Moreover, this anisotropy can be switched on and off if replicated into a shape memory polymer. As a result, small particles can be artificially forced to drift in a predefined direction if the surface is mechanically excited by small vibrations.

This forced drift can be also applied to clean such a snake inspired surface from microparticles like dust or dry soil. Figure 5 shows such dry self-cleaning experiments. In order to demonstrate that the orientation of the micro-fibrils determines the direction of the drift, we placed two uniform samples of structured SMP foils in opposite direction on top of the vibration motor, that is, the micro-fibrils point to the left for the left surface and to the right for the right one. Consequently, the frictional anisotropy of the two samples points in opposite directions.

Figure 5 summarizes the drift experiments conducted with this set-up. As a control experiment, we first placed two microspheres close to the center of the two samples and started the random vibration. As expected, they drift in opposite direction and reach the left and right borders of the two samples within 7 s (left column of Figure 5 and Video S5, Supporting Information). In order to demonstrate that piles of similar microparticles are also transported unidirectionally, we placed several microspheres and sand grains in the stitching of the two surfaces (middle and right column of Figure 5 and Videos S6, S7, Supporting Information). After the start of the random vibration, the complete area is cleaned within 65 and 105 s for the microspheres and sand grains, respectively. In general, we observed that different types of particles which differ in size and material drift at different velocities. We therefore conclude that the cleaning process for the sand grains took longer time than for the microspheres. This feature opens the opportunity to separate particles through their different drift rate.

3. Conclusion and Outlook

To conclude, we developed a smart surface with anisotropic frictional properties inspired by the micro-fibril structure of snake scales allowing to transport microparticles through small random vibrations. As the smart surface is fabricated from a shape memory polymer it can be switched between a flattened and a micro-fibril structured topography with nanoscale steps upon heating and flattening. Accordingly, the frictional properties of the surface change from nearly isotropic to
anisotropic along the fibril direction. Since the frictional anisotropy increases linearly with the step height, it can be controlled by interrupting the recovery process at any intermediate step height. The SMP foils show excellent long-term stability and reusability. The anisotropy of the surface can be utilized for the unidirectional transport of microparticles through random vibration of the samples. The simultaneous transport of complete layers of microspheres or sand particles demonstrates dry self-cleaning.

The presented approach is different to previous studies where various actuation mechanisms ranging from sound\cite{53,54} to magnetic\cite{55,56} or UV light stimulation\cite{57} were utilized for the directional transport of micro-objects such as liquid droplets,\cite{56} microspheres,\cite{54,55,57} a polymer sheet,\cite{54} and a hydrogel rod.\cite{53} However, most of them were achieved by surface anisotropy due to a ratchet like surface or flexible microstructures impacting the micro-objects on top of the respective surface. In the case presented here, the height of the surface structures is

Figure 4. Movement of PDMS microspheres with slightly different diameters on a vibrated a) ventral scale of Chinese cobra, b) original structured, c) temporarily flattened, and d) recovered SMP foil. The photographs in the first three columns show the time-lapse of the microsphere drifting on the different substrates. The SEM images in the insets indicate the orientation of micro-fibril structures on the surfaces. They point always toward the bottom. The dashed circles in (a, b and d) represent the original position of the microspheres. The line charts in the last column mark the tracked trajectory of the microsphere travelling on the corresponding substrate for many seconds. The microsphere drifts in the direction of the fibrils (downward in this representation) in (a, b and d) but no drift was observed in (c) on the flattened SMP foil. About 30 data points were plotted for each trajectory, the time intervals between the data points are not alike. All surfaces were sputter-coated with a 10 nm silver layer to increase visibility (see experimental section).
well below 100 nm while their periodicity is some \(\mu m\). Consequently, the polymer foils have a high transmittance and appear transparent to the naked eye.

Due to these favorable optical properties, we speculate that snake scale inspired surfaces might be applied for the dry self-cleaning of technical surfaces. Possible applications include photovoltaic modules which are installed in extreme dry areas with many sun hours. Here, the lack of rain coincides with numerous sun hours but at the same time the removal of dust and dry soil is an issue.\cite{58} Cleaning with water needs costly manpower or robots and might cause other issues.\cite{58} In such a case, the dry self-cleaning through mechanical vibrations seems a promising approach.

Nonetheless, further studies are necessary to exploit the limits of the directional transportation through frictional anisotropy as well as optimized parameters for the respective technical application. The distance between the nanosteps and their height will influence the magnitude of the directional transport through frictional anisotropy. As soil and dust are not alike worldwide further tests in the field are necessary to evaluate the applicability of dry self-cleaning, that is, it might be necessary to use dedicated topography parameters for each region.

Further applications might include sorting particles by different drift rate. Since the average drift rate correlates with the frictional anisotropy, particles with different tribological properties might be separated through the presented mechanism.

4. Experimental Section

Nickel Shim Fabrication: To replicate the micro-fibril structures of snake scales into SMP surfaces via hot embossing, robust nickel shims with negative patterns of the nano-stepped micro-fibrils were fabricated. For that, molted ventral scales of *N. atra* (provided by Guillaume Gomard) were cut into rectangles with a size of \(10 \times 7\) mm and then blown with pressurized air for around \(5\) s to clean them from possible contaminations. The scales prepared in this way were glued with Norland Optical Adhesive 88 (Norland Products, Inc. USA) onto...
a 4-inch silicon wafer and evaporated with 8 nm of chromium (adhesive layer) and 40 nm of gold (conductive plating base). Subsequently, the substrate was masked with nonconductive tapes leaving a circular plating window with a diameter of 85 mm defining the final Ni-shim size. After that, the masked substrate was mounted to a special plating holder and immersed into the standard electroplating system with a boric acid containing nickel sulfamate electrolyte ($T = 52 ^\circ C$, pH 3.4–3.6).\(^{[39]}\) During the plating process, the current density was gradually increased from 0.1 to 1 A-dm$^{-2}$ to slowly fill the micro-structured areas. This process results in a defect-free, stiff homogenous nickel layer with a thickness of about 600 µm, which could repeatedly endure forces of several tens of kilo-Newton in the following hot embossing process. Next, the silicon wafer was removed by dissolving it in 30% KOH solution and the snake scales together with the glue were eliminated from the thick nickel layer using chloroform in an ultrasonic bath (at 40 °C for 30 min). Finally, the obtained Ni-shim with negative micro-fibril structures was mechanically cut into a disk with 78 mm diameter and cleaned by oxygen plasma (STP2020, R3T, Germany) for 60 min at 22 °C, 800 W, 450 mTor.

Defining and Manipulating the Topography of the Smart Surface: The shape memory polymer used in this study was the thermally triggered, cycloaliphatic polyester urethane block copolymer distributed as Tecoflex EG-72D (Lubrizol Corp., USA). Its permanent shape could be defined while synthesizing or redefined after fabrication by melting when the temperature was over the transition temperature $T_{\text{switch}}$. To program a temporary shape, the temperature should be higher than the switching temperature $T_{\text{switch}}$ of the SMP but below its transition temperature $T_{\text{hard}}$. Cooling the polymer after deformation, the temporary shape was obtained and will be stable as long as the temperature was below $T_{\text{switch}}$. The recovery process happened only if the polymer was heated to (or close to) $T_{\text{switch}}$. Then, it would continuously recover back to its original permanent shape. In previous studies\(^{[37,62]}\) with the same SMP, the temperatures $T_{\text{hard}} \approx 150 ^\circ C$ and $T_{\text{switch}} = 40–70 ^\circ C$ were determined.

The hot embossing technique was applied to structure the SMP with an enhanced hot embossing machine based on a commercial system from Jenoptik\(^{[36,63]}\). First, to define the permanent shape, the nano-step structure of the Chinese cobra’s ventral scale was replicated into the SMP surface with a previously produced Ni-shim. For that, the shim was pressed into a foil of the SMP with an embossing force of 12 kN at a temperature of $T = 155 ^\circ C$. After cooling the foil down to room temperature, the original structured, permanent state of the smart surface was obtained. To program a temporary topography, the previously structured SMP surface was hot embossed again but with a flat shim (used as mold) with an embossing force of 8.5 kN and a temperature of $55 ^\circ C$. Subsequent cooling resulted in a flat, unstructured temporary shape (or surface). Finally, placing this flat SMP foil on a hot plate ($55 ^\circ C$) released the inner forces and the surface recovered to its structured, permanent state again. The last two steps count as one flattening and recovery cycle of the SMP which could be repeated many times (see refs. [37,62] and Figure S2b, Supporting Information).

Characterization Methods: The topography of the snake scales, the negative structures on the Ni-shim, and the structured and flattened SMP sample were imaged by SEM (SUPRA 60 VP, Carl Zeiss AG, Germany). Sample surfaces were sputter-coated with a 10 nm thick silver layer beforehand. Microscopic friction at the nano-steps of micro-fibril scales together with the glue were eliminated from the thick nickel layer using chloroform in an ultrasonic bath (at 40 °C for 30 min). Finally, the obtained Ni-shim with negative micro-fibril structures was mechanically cut into a disk with 78 mm diameter and cleaned by oxygen plasma (STP2020, R3T, Germany) for 60 min at 22 °C, 800 W, 450 mTor.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.