

Intelligent Surfaces Thermally Switchable between the Highly Rough and Entirely Smooth States

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Electronic Supplementary Information

Abstract Reversible switching from a highly rough surface to another entirely smooth surface under external stimuli is crucial for intelligent materials applied in the fields of anti-fogging, self-cleaning, oil-water separation and biotechnology. In this work, a thermal-responsive liquid crystal elastomer (LCE) surface covered with oriented micropillars is prepared via a facile two-step crosslinking method coupled with an extrusion molding program. The reversible change of topological structures of the LCE surface along with temperature is investigated by metallographic microscope, atomic force microscopy and optical contact angle measuring system. At room temperature, the LCE sample is filled with plenty of micropillars with an average length of 8.76 μm , resulting in a super-hydrophobic surface with a water contact angle (WCA) of 135°. When the temperature is increased to above the clearing point, all the micropillars disappear, the LCE surface becomes entirely flat and presents a hydrophilic state with a WCA of 64°. The roughness-related wetting property of this microstructured LCE surface possesses good recyclability in several heating/cooling cycles. This work realizes a truly reversible transformation from a highly rough surface to an entirely smooth surface, and might promote the potential applications of this dynamic-responsive LCE surface in smart sensors and biomimetic control devices.

Keywords Intelligent surface; Liquid crystal elastomer; Switchable topological structure

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INTRODUCTION

Many organisms, such as shark,^[1] gecko,^[2,3] water strider^[4] and lotus leaf^[5] have evolved microstructured surfaces with powerful functions after aeon of the struggle for survival. These microstructures on the surfaces endow organisms with special abilities like color change,^[6,7] anti-reflective coating^[8] and hydrophilic/hydrophobic properties,^[5,9,10] which have attracted scientific attention in developing a series of bionic functional materials.^[11,12] As a representative example, lotus leaf possesses super hydrophobicity and strong self-cleaning ability, owing to the micron-sized papillae structure and hydrophobic epicuticular wax on the surface.^[13,14] Various materials mimicking the superhydrophobic and self-cleaning surfaces of lotus leaf have been developed and applied in many fields.^[15,16]

Nowadays, scientists are no longer content with constructing traditional fixed hydrophobic surfaces,^[17,18] but prefer to fabricate biomimetic stimuli-responsive surfaces with reversible hydrophilic/hydrophobic properties for the wider application prospects.^[19,20] The change of microstructure on the surface often plays a vital role in the switching of wetting

properties. To date, there are two basic strategies to construct dynamic responsive surfaces with switchable hydrophilic/hydrophobic abilities. One typical method is to fabricate the surfaces from stimuli-responsive polymers or inorganic nanomaterials and change the chemical properties of the surface to realize the switching between the hydrophilic and hydrophobic states.^[21–27] For example, Jiang and colleagues first invented a photo-responsive ZnO nanorod film whose wetting properties could be switched between the hydrophilic and hydrophobic states by being exposed to UV light or in the dark.^[21] Jiang^[22] and Zhang^[23,24] respectively reported thermal and pH responsive surfaces by modification with thermal-sensitive poly(*N*-isopropylacrylamide) and pH-sensitive 2-(11-mercaptoundecanamido)benzoic acid. However, limited by the special chemical structures and reaction conditions, these surfaces and reversible chemical switchings were always nondurable, time consuming and costly, which seriously hindered their practical applications.

In recent years, another strategy has attracted more and more scientific attention, that is, to adjust the physical properties of the surfaces, such as roughness, by directly changing the topological microstructures of the surfaces under external stimuli,^[28–35] thereby achieving the reversible switching between the hydrophobic and hydrophilic states. For example, Han's group reported an elastic polyamide film with a

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triangular net-like structure which could realize reversible wettability by biaxially extending and unloading the film.^[28] Wu and Keller constructed several microstructured thermal-responsive surfaces covered with magnetic-aligned nematic elastomer micropillars by using a replica molding technique, the surface roughness changes between the high and low states induced by temperature variation could result in a reversible switching of the wetting properties of the microstructured surfaces.^[29,30] Li's group reported a switchable superhydrophobic surface comprised of a dense array of magnetorheological elastomer micropillars, where the wettability could be reversibly switched by an on/off magnetic field.^[31] Liu and Broer reported a series of electro-responsive oscillating surfaces, which could exhibit fluid-like dynamic topographies under alternating electric field.^[32–35] However, the previously reported microstructured surfaces always required some complicated preparation techniques, driving equipment or driving methods. More importantly, most of the previous reported reversible surfaces could only switch between the high and low roughnesses, as schematically illustrated in Fig. 1(a), and could not become utterly flat under external stimuli, resulting in a relatively narrow adjustment of the water contact angle (WCA) and plaguing their application potentials in the fields of anti-fogging materials, self-cleaning films, oil-water separation, and biotechnology, etc. Thus, development of smart surfaces switchable between the highly rough and entirely smooth states still remains challenging.

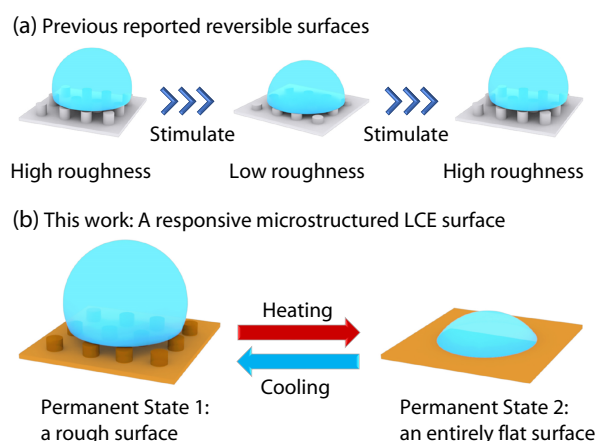


Fig. 1 (a) Previous reported dynamic responsive surfaces with switchable high and low roughnesses. (b) A microstructured LCE surface with switchable roughness and smoothness described in this work.

As a classical two-way shape memory material, oriented liquid crystal elastomer (LCE) materials could reversibly perform a large shape deformation from one permanent state (State 1: mesomorphic state) to another permanent state (State 2: isotropic state) during the LC-to-isotropic phase transition, and have been widely applied in many fields, such as artificial materials, soft actuators, and so on.^[36–40] It inspired us that if a microstructured LCE film had a highly rough surface in one permanent state (State 1) and an entirely flat surface in the other permanent state (State 2), it could reversibly and fast deform from the permanent State 1 to permanent State 2. In other words, this microstructured LCE surface could achieve a

fast reversible transformation from a rough state to another smooth state (Fig. 1b), rather than the conversions between the high and low roughnesses as previously reported in all the pioneering work.^[29–35]

Herein, a facile two-step crosslinking method coupled with an intermediate extrusion molding program was designed and used to fabricate a dynamic responsive LCE surface covered with oriented LCE micropillars. Unlike the previously reported methods of using a magnetic field to induce the ordered alignment of LC molecules to further obtain ordered LCE micropillars,^[29,30] a silicon substrate filled with micropores was used as the mould to extrude the flat pre-crosslinked LCE film to obtain regular LCE micropillars on the surface. The mesogens inside the micropillars were forced to arrange orderly along the longitudinal axis and further fixed in the second crosslinking stage.

The key logic of this design was that the pre-crosslinked, entirely flat LCE film although stayed at polydomain mesomorphic state microscopically, possessed the nearly identical topological appearance of the isotropic state macroscopically, and thus could be regarded as the permanent State 2, whereas the further extrusion molding programming and the final second crosslinking treatment would mechanically align the surface mesogenic molecules to form micropillars, and solidify the resulting highly roughed LCE film as the permanent State 1 (Fig. 1b). Thanks to the two-way shape memory effect of LCE material, the thermal-induced LC-to-isotropic transition would consequently drive the microstructured LCE surface to transform from the permanent State 1 to permanent State 2 reversibly.

Benefitting from the large reversible shrinking/expanding deformation of the LCE micropillars along the longitudinal axis during the LC-to-isotropic phase transition, the topological microstructure of the surfaces could significantly change along with the temperature, resulting in broad adjustments of the surface roughness and the corresponding WCA. The microstructured surface and the micropillars were observed by scanning electron microscopy (SEM) to obtain characteristic parameters, including the diameter, length and spacing of these LCE micropillars. Besides, the reversible change of the microstructured LCE surface from roughness to smoothness was monitored in real-time by metallographic microscope (MM) and atomic force microscopy (AFM) during the heating/cooling process. At last, the WCA of the microstructured LCE surface as a function of temperature was elucidated, showing a significant reversible switching between the hydrophilic and hydrophobic states.

EXPERIMENTAL

General Considerations

Polymethylhydrosiloxane (PMHS) and Karstedt catalyst were purchased from Aladdin Inc. The LC monomer 4-methoxyphenyl-4-(1-buteneoxy) benzoate (MBB) was synthesized by following the experimental procedure of previous work.^[41] The crosslinker 4,4'-(((oxybis(ethane-2,1-diyl)) bis(oxy)) bis(ethane-2,1-diyl)) bis(oxy)) bis(vinylbenzene) (4OBV) was a new compound, and its precursor ((oxybis(ethane-2,1-diyl))bis(oxy)) bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) was synthesized by following the experimental procedure of previous

work.^[42] All the detailed synthetic protocols, instrument descriptions, and NMR data are included in the electronic supplementary information (ESI).

Preparation of the Microstructured LCE Surface

The fabrication process was divided into three main stages, including the first crosslinking stage, extrusion molding program and the second crosslinking stage. Typically, **PMHS** (51 mg, containing 0.85 mmol Si—H groups), **MBB** (202.6 mg, 0.68 mmol) and **4OBV** (33.8 mg, 0.085 mmol) were dissolved in 2.0 mL of toluene, which was then ultrasonicated for 10 min to ensure a homogeneous dispersion. The mixture was then cast into a polytetrafluoroethylene (PTFE) rectangular mold (2.0 cm long × 2.0 cm wide × 1.5 cm deep). After adding 2.5 μL of Karstedt catalyst into the above mixture, the PTFE mold was ultrasonicated for 15 s to remove the air bubbles, and then heated in an oven at 60 °C for 4 h, to accomplish the first crosslinking stage. After cooling to room temperature, the pre-crosslinked LCE film sample was carefully removed from the PTFE mold and further cut into a square-shaped film (1.5 cm long × 1.5 cm wide, the thickness was *ca.* 1.0 mm). A silicon substrate template filled with ordered micropores (23 μm diameter × 10 μm deep × 16 μm spacing) was tightly pressed on the flat surface of the pre-crosslinked LCE film, and the combination was sandwiched between a glass sheet and a PTFE sheet (10 cm long × 10 cm wide × 0.5 cm thick). A 100-gram heavy weight (pressure: *ca.* 4.36 kPa) was put on the top of the glass sheet to squeeze the LCE surface into the micropores of the silicon substrate template. The whole system was carefully transferred into a vacuum oven to remove the air at room temperature for 24 h. After the removal of air *via* vacuum, the sample was then heated to 50 °C under reduced pressure for another 24 h to complete the second crosslinking stage. After cooling back to room temperature, the LCE film sample was carefully removed from the silicon substrate, and the desired microstructured surface covered with vertical-oriented micropillars was achieved on the LCE film.

Preparation of the Flat Unoriented LCE Film

The mixture containing **PMHS** (51 mg, containing 0.85 mmol Si—H groups), **MBB** (202.6 mg, 0.68 mmol) and **4OBV** (33.8 mg, 0.085 mmol) and toluene (2.0 mL) was ultrasonicated for 10 min to ensure a homogeneous dispersion. The solution was then cast into a PTFE rectangular mold (2.0 cm long × 2.0 cm wide × 1.5 cm deep). After adding 2.5 μL of Karstedt catalyst into the above mixture, the PTFE mold was ultrasonicated for 15 s to remove the air bubbles, and then heated in an oven at 60 °C for 24 h to accomplish the crosslinking stage to provide a flat LCE film. After cooling back to room temperature, the flat LCE film was carefully removed from the PTFE mold and then cut into a square-shaped film (1.5 cm long × 1.5 cm wide, the thickness was *ca.* 1.0 mm). The flat crosslinked unoriented LCE film was prepared.

RESULTS AND DISCUSSION

Owing to the relatively low LC-to-isotropic phase transformation temperature of polysiloxane-based LCE system,^[11,43] we chose **PMHS** as the polymer main chain and a typical nematic monomer **MBB** as the mesogen (Fig. 2a). Furthermore, we designed and synthesized a new divinyl-terminated crosslinker

4OBV containing oligoethyleneglycol (OEG) units to increase the hydrophilicity of the surface, because the OEG groups of **4OBV** could combine with water to form hydrogen bonds, which would further reduce the WCA and enhance the hydrophilicity of the surface in the smooth state.

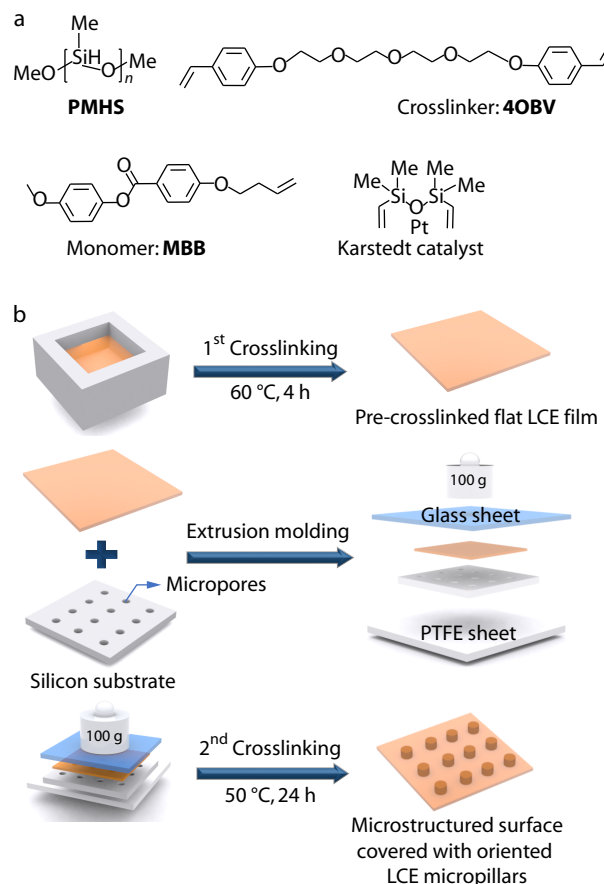


Fig. 2 (a) Molecular structures of **PMHS**, monomer **MBB**, crosslinker **4OBV** and Karstedt catalyst; (b) Schematic illustration of the fabrication process of the microstructured LCE surface covered with oriented micropillars.

To prepare the microstructured LCE surface, a two-step crosslinking method coupled with an intermediate extrusion molding program was carried out (Fig. 2b). As described in the experimental section, a PTFE mould filled with **PMHS**, **MBB**, **4OBV**, Karstedt catalyst and toluene was ultrasonicated and further heated in an oven at 60 °C for 4 h to accomplish the first crosslinking stage to provide a flat LCE film. Before performing the second crosslinking protocol, we cut the obtained polydomain flat LCE film into a square-shaped film, and pressed it into the micropores of the silicon substrate template in a vacuum oven to build vertical-oriented micropillars on the LCE surface. The sample was then heated to 50 °C under reduced pressure for 24 h to achieve the second full-crosslinking purpose, to provide the desired microstructured LCE surface covered with vertical oriented micropillars.

The thermal and mesomorphic properties of the LCE film were investigated by differential scanning calorimetry (DSC) and one-dimensional (1D) temperature-varied wide-angle X-

ray scattering (WAXS) experiments. As shown in Fig. 3(a), the DSC curves of the LCE film presented an enantiotropic mesophase during the heating and cooling cycles. A glass transition temperature of 6.3 °C and a typical LC-to-isotropic phase transition temperature (T_{iso}) of 58.6 °C were observed. As displayed in Fig. 3(b), during the heating process, the WAXS curves of the LCE film only presented one diffuse peak in the wide-angle region and no peak in the low-angle region, demonstrating the existence of a nematic phase in the LCE film. When the temperature rose above T_{iso} , the diffuse peak in the wide-angle region became weaker, indicating an LC-to-isotropic phase transformation of the LCE film, which was consistent with the DSC results. All these data proved that the LCE film had a nematic phase in the temperature range of 6.3–58.6 °C, and a relatively low nematic-to-isotropic phase transition temperature of ca. 58.6 °C.

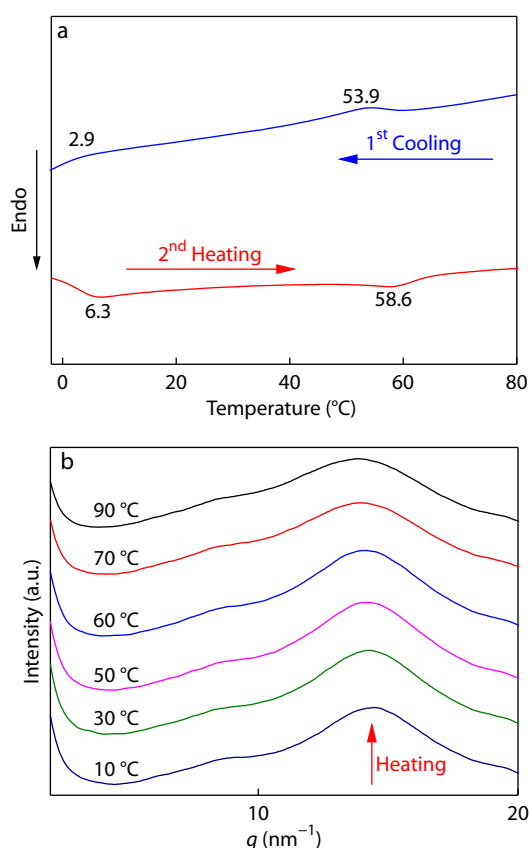


Fig. 3 (a) DSC curves of the LCE film during the first cooling and second heating scans at a rate of 10 °C/min under nitrogen atmosphere; (b) 1D-WAXS patterns of the LCE film during the heating process.

SEM technique was used to investigate the topological structures of the silicon substrate and the microstructured LCE surface. Regular holes with an average diameter of ca. 22.79 μm and a spacing of 15.74 μm could be observed on the surface of the silicon substrate, as displayed in Fig. 4(a). SEM images (Figs. 4b–4d) recorded from vertical, oblique, and horizontal directions of the microstructured LCE surface demonstrated that these micropillars had regular cylindrical shapes at room temperature. After calculation, the average

length of these micropillars was about 8.76 μm , the diameter was 22.73 μm , and the spacing was 15.91 μm . These data were consistent with the micropore sizes of the silicon substrate template, proving a successful negative pressure molding process.

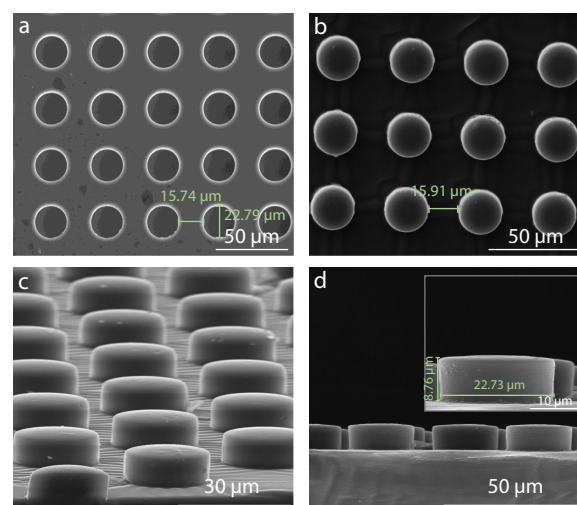


Fig. 4 SEM images of (a) the silicon substrate surface, and the microstructured LCE surface in (b) vertical, (c) oblique, and (d) horizontal directions.

To continually monitor the topological structure changes of the micropillars during the heating/cooling cycle, MM and AFM experiments were performed to observe the dynamic responsive LCE surface. Benefitting from the real-time imaging system of MM and the three-dimensional modeling of AFM, the *in situ* shape changes of the micropillars and roughness change of the microstructured LCE surface could be recorded and analyzed. As shown in Fig. 5(a) and Video S1 (in ESI), during the heating process, the oriented micropillars on the LCE surface gradually became shorter and disappeared at last, while the microstructured LCE surface could become entirely flat. At room temperature, the shape of the micropillars was intact, and the boundary was clearly visible. In the early heating stage, the topological structure of the surface had no significant change in view. When the temperature continued to rise above the T_{iso} , the micropillars began to contract along the longitudinal axis, and the boundary of the micropillars became blurred. Finally, all the micropillars disappeared, and the microstructured LCE surface became entirely flat at 75 °C. After cooling back to 25 °C, the microstructured LCE surface could revert to its original state and grow with micropillars again. This reversible change of the microstructured LCE surface between the roughness and smoothness was observed in the next several heating and cooling cycles.

AFM characterization was further performed to quantitatively analyze the shape change of the micropillars with the temperature. As measured in SEM images (Fig. 4), the average length of the micropillars on the LCE surface at room temperature was about 8.76 μm , which was beyond the AFM height measurement range (no more than 5 μm). According to the MM images (Fig. 5a), the length of the micropillars gradually became shorter along with the temperature in-

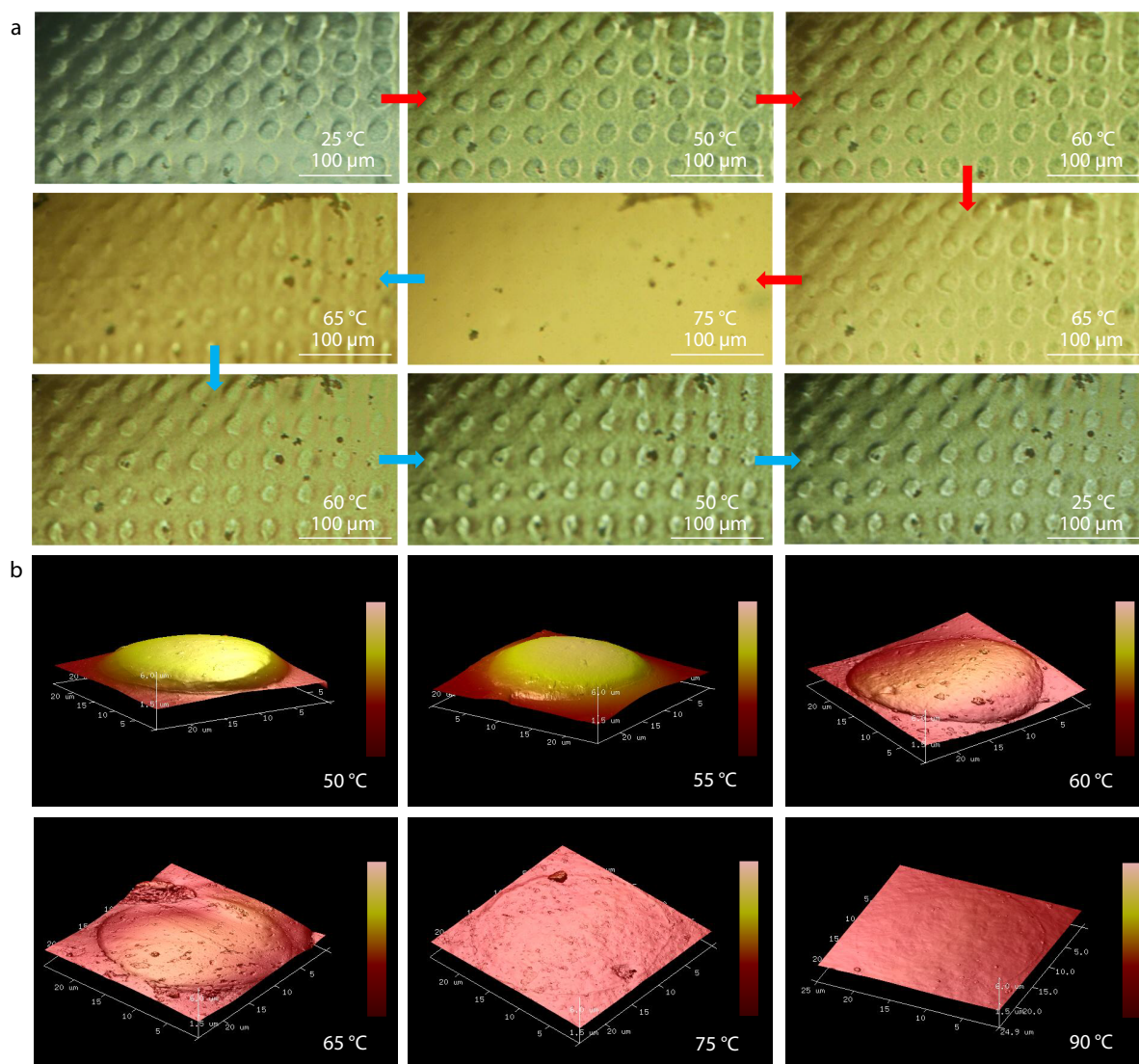


Fig. 5 (a) MM images of the LCE surface captured in the vertical direction during the heating/cooling cycle; (b) AFM images of the microstructured LCE surface at 50, 55, 60, 65, 75 and 90 °C, respectively.

creasing. At 50 °C, the length of micropillars was successfully measured by AFM to be *ca.* 4.26 μm , as shown in Fig. 5(b). When the temperature was further increased to 90 °C, the micropillars almost disappeared, and the length reached the minimum value of 0.09 μm . In order to evaluate the variation trend of micropillars length more intuitively, the average length of the micropillars as a function of temperature was further measured in the temperature range between 50 °C and 90 °C. As plotted in Fig. S6 (in ESI), the length of micropillars exhibited a decrease from 4.26 μm to 2.53 μm in the temperature range of 50–58 °C. When the temperature rose above 60 °C, the length dramatically decreased and reached *ca.* 0.14 μm at 75 °C, indicating that the surface was entirely flat. As the temperature increased from 75 °C to 90 °C, the average length of the micropillars further decreased to 0.09 μm .

In addition to the height variation of the micropillars, the dimensions of the microstructured LCE film as a function of temperature were further measured in a temperature range between 25 and 90 °C. The thickness variation as a function of

temperature is given in Fig. S7 in ESI. At room temperature, the dimensions of the LCE film were *ca.* 1.53 cm long $\times$ 1.58 cm wide $\times$ 826 μm thick. When the temperature further rose up to 90 °C, the dimensions of the LCE film reached *ca.* 1.48 cm long $\times$ 1.52 cm wide $\times$ 931 μm . These data indicated that during the heating process, the microstructured LCE film performed a shrinking deformation in horizontal direction, and an expansion in the normal direction, which caused the increase in the film thickness.

As reported in previous studies,^[29,30] a continuous change of the topological structure would induce a change in the physical properties of the surface, such as wetting. Herein, the change of WCA along with temperature was measured by an optical contact angle measuring and contour analysis system (Shanghai Fangrui Instrument Co., Ltd.) to evaluate the relationship between the surface roughness and the hydrophilic/hydrophobic properties of the surface covered with oriented LCE micropillars. In order to avoid the influence of solvent evaporation on the experimental results, the micro-

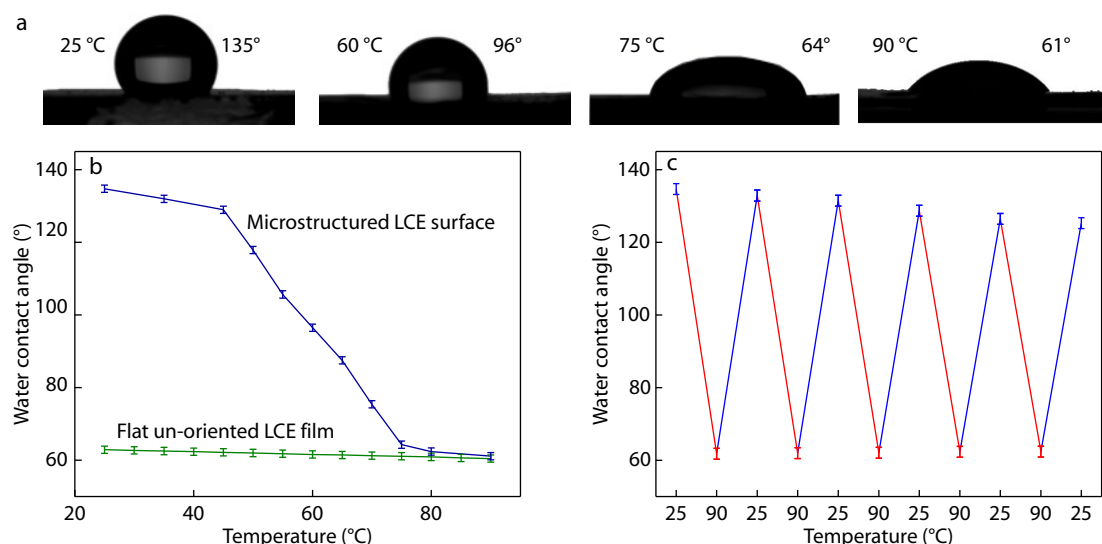


Fig. 6 (a) The images of the water droplets on the surface of the LCE film at 25, 60, 75 and 90 °C and corresponding WCAs; (b) The changes of WCAs of the microstructured LCE surface and flat unoriented LCE film as a function of temperature; (c) Cyclic measurement of the WCA of the microstructured LCE surface switching between 25 °C and 90 °C.

scopic images were captured when the water droplets dropped on the film surface for 5 s, and the WCA data were further calculated automatically. After each measurement, the old water droplet was wiped away, and a new water droplet was put on the same place of the same surface at the next temperature point. As shown in Figs. 6(a) and 6(b), as the temperature rose from 25 °C to 90 °C, the shape of the water droplets on the microstructured LCE surface changed from a large hemisphere to a small hemisphere, indicating a conversion from the hydrophobic state to the hydrophilic state of the LCE film. The change in WCAs of the microstructured LCE surface as a function of temperature was plotted in Fig. 6(b). At room temperature, the LCE film with micropillars on the surface had a WCA of 135°. According to the Cassie model, the WCA of the microstructured LCE surface should be 145°, with the formula: $\cos\theta^* = f_{SL}(\cos\theta + 1) - 1$,^[44] in which θ^* was the WCA of the surface at room temperature, f_{SL} was the area fraction of the liquid droplet in contact with the surface, θ was the WCA of the flat surface (here $f_{SL}=0.13$, $\theta=64^\circ$). The measured WCA value θ^* was slightly less than theoretical calculation, which demonstrated that the surface covered with oriented LCE micropillars was in the Cassie state, and the upper part of the micropillars was somewhat wetted. In the early stage of the heating process, the WCA performed a gentle decrease from 135° to 128°. As the temperature continued to rise above T_{iso} and reached 75 °C, the WCA sharply dropped to 64°. In the subsequent heating process from 75 °C to 90 °C, the WCA slightly dropped to the minimum value of 61°, implying a hydrophilic state of the flat LCE surface without micropillars. The variation of the WCA with the temperature increasing was similar to the contraction trends of the oriented LCE micropillars recorded in the MM and AFM images, indicating that the change of hydrophilic/hydrophobic properties was correlated with the variation of surface topological structure and roughness.

In addition, a flat cross-linked unoriented LCE surface was also prepared as a control experiment. As shown in Fig. 6(b)

and Fig. S8 (in ESI), the WCA data of the flat unoriented LCE film slightly decreased from 63° to 61° when the temperature changed from 25 °C to 90 °C, whereas the WCA data of the dynamic-responsive LCE surface significantly changed from 135° to 61°. These contrasting data proved that the WCA variation of the dynamic-responsive LCE surface was indeed due to the change of the surface topological structure, rather than the temperature variation.

Cyclic measurements of the WCA switching between 25 and 90 °C were further performed to evaluate the stability and recyclability of the microstructured LCE surface. As displayed in Fig. 6(c), during the first heating process, the WCA of this microstructured LCE surface clearly decreased from ca. 135° at 25 °C to ca. 61° at 90 °C. After cooling back to room temperature, the WCA recovered to 133°, which was close to its original value of 135°. After several heating/cooling cycles, a very slight change of WCAs was recorded. The microstructured LCE surface remained a hydrophilic state at high temperature and a hydrophobic state at room temperature, indicating a good reversibility of roughness-related wetting property. Based on all these experimental data, including the SEM, MM, AFM, and the wetting properties, it was clear that the microstructured LCE surface prepared in this work could realize a truly reversible transformation from a highly rough state to another entirely flat state owing to the disappearance of the oriented LCE micropillars under external stimuli, which was quite different from the changes between the high and low roughnesses reported in previous studies.^[29–35]

CONCLUSIONS

In summary, taking advantage of the two-way shape memory effect of LCE material, we successfully prepared a thermal-responsive polysiloxane-based LCE surface covered with oriented LCE micropillars *via* a facile two-step crosslinking method coupled with an extrusion molding program. The changes in the length of the micropillars and the roughness of

the surface during the heating/cooling process were continuously observed by SEM, MM and AFM. The physical properties of the microstructured LCE surface, such as wetting, could be efficiently tuned by changing the surface roughness. At room temperature, the micropillars had an average length of 8.76 μm , an average diameter of 22.73 μm and a spacing of 15.91 μm , so that the film surface was highly rough and exhibited a hydrophobic state with a WCA of 135°. As the temperature increased, the micropillars gradually shortened and disappeared at 75 °C, meanwhile the surface became entirely flat and presented a hydrophilic state with a WCA of 64°. In addition, the roughness-related wetting property of this microstructured LCE surface possessed a good recyclability in several heating/cooling cycles. This work realized a truly reversible transformation from a highly rough surface to an entirely smooth surface, and endowed this stimuli-responsive microstructured LCE surface with potential applications in smart sensors and biomimetic control devices.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2617-9>.

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