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COMMUNICATION

Light-controlled quick switch of adhesion on a micro-arrayed liquid crystal polymer superhydrophobic film†

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A micro-arrayed liquid crystal polymer film, cross-linked in the nematic phase, was successfully prepared from an optimized azobenzene precursor and polydimethylsiloxane-soft-template-based secondary replication. Regulated by alternating irradiation of UV-visible light (365 nm/530 nm), the micro-arrayed film showed an ideal quick (<1 min) and reversible switch of superhydrophobic adhesion.

Many biological systems are distinguished by their special superhydrophobic adhesion properties, such as the superhydrophobic lotus leaf with ultralow water adhesion,[1–3] rose petals that are superhydrophobic but stick water to them,[4] and rice leaves and butterfly wings with anisotropic water adhesion.[5,6] These enumerated natural superhydrophobic adhesion properties originate from the cooperation of specific surface energy and elaborate surface micro/nano structures.[7] Researchers have found numerous inspirations from nature and developed plenty of artificial superhydrophobic materials with tailored adhesion properties, such as self-cleaning surfaces,[8–10] no-loss droplet transfers and so on.[11–15] Tuning the adhesion of water droplets on superhydrophobic surfaces has been demonstrated recently, however, most of them are achieved on different samples.[16] A great challenge still remains about how to reversibly control water adhesion on the same surface, which requires the precise coordination of surface chemistry response and surface roughness.[17] Recently, considerable interest in superhydrophobic surfaces has been focused on stimuli-responsiveness due to its significance in design of smart microfluidic devices.[18,19] Ichimura *et al.* have reported that the motion of liquids can be manipulated by light when a substrate surface is modified with a photoisomerizable azobenzene monolayer;[20] but this strategy is unfavorable for no-loss droplet transfer due to the lyophilicity of the surface. Besides, the surface is not applicable for water, the most commonly used liquid. It is well known that a superhydrophobic surface is ideal to reduce the mass loss in droplet transfer.[21,22] We have introduced a temperature control strategy that regulates the droplet adhesion on the same superhydrophobic surface;[23] however, temperature increment would drastically accelerate the evaporation of the water droplet, which is fairly disadvantageous for no-loss droplet transfer. Among diverse stimuli such as thermal, light, electricity *etc.*, light has dominant advantages such as non-contact, high accurate positioning and low thermal effect. So it is highly desirable to develop a superhydrophobic surface with light-controllable adhesion.

Herein, we designed and fabricated a light-regulated adhesion switch on a micro-arrayed azobenzene liquid crystal polymer (LCP) superhydrophobic surface, by which water droplets could be rapidly, precisely, and through no contact, locally controlled. Azobenzene LCP, a typical functional material combining photoisomerization, liquid crystallinity, and macromolecular properties together in one entity,[24] was selected as a candidate to fabricate a light-controlled smart surface with superhydrophobic adhesion. A micro-arrayed azobenzene LCP film cross-linked in nematic phase was successfully prepared from an optimized azobenzene precursor and polydimethylsiloxane (PDMS)-soft-template-based secondary replication. Regulated by alternate irradiation of UV–visible light (365 nm/530 nm), the micro-arrayed azobenzene LCP film showed an ideal quick (less than 1 min) and reversible switch of superhydrophobic adhesion based on the cooperative photoisomerization of the azobenzene mesogens aligned parallel in the surface region of the microposts.

Fig. 1 shows the azobenzene LC monomer (DA11AB) synthesized for the preparation of the photoresponsive superhydrophobic LCP film. DA11AB was designed to have three connected functional parts: (I) double acrylates at the two ends of the monomer provide the polymerization and cross-linking points; (II) azobenzene group in the middle of the monomer creates the photoresponsiveness and acts as a mesogen to form the LC phase; (III) the spacers with 11 methylenes link part (I) and (II) together and make the monomer substantially hydrophobic. However, DA11AB itself shows a very narrow nematic phase window (5 °C) and the temperature range (81–86 °C on cooling) is far away from room temperature (Fig. S1, ESI†). A wide and near room temperature nematic phase window is favored to guarantee the preparation and performance of the azobenzene LCP film. Thus, a no-azobenzene cross-linker (C9A) was introduced to

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† Electronic supplementary information (ESI) available: Experimental section, characterization methods, DSC curves and POM images of DA11AB and the mixture of DA11AB and C9A, and POM images of the cut-off azobenzene LCP microposts. See DOI: 10.1039/c2sm07471k
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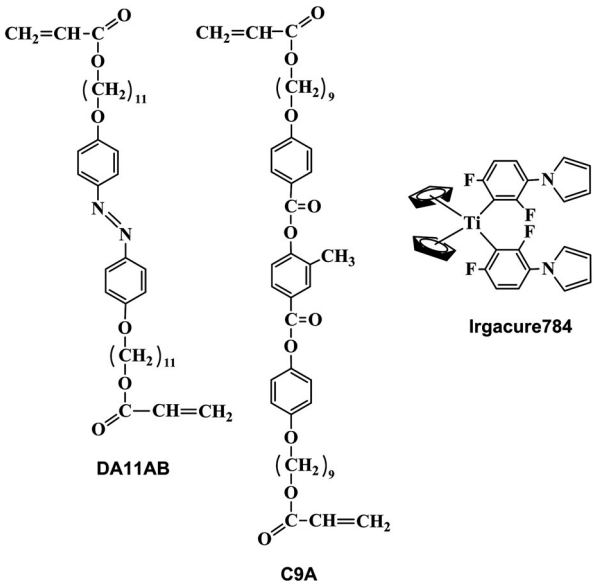

Fig. 1 Chemical structures of LC monomers (DA11AB and C9A) and photoinitiator used to prepare the azobenzene LCP film. The molar ratio of DA11AB and C9A in the mixed precursor was 1 : 4.

blend with DA11AB to achieve a wider temperature range of the nematic phase (40–103 °C on cooling), by which the nematic phase window of the mixed precursor was successfully enlarged from 5 °C to 63 °C, having a lower limit temperature for the nematic phase (40 °C) near to room temperature (Fig. S1, ESI†).

It is well-known that surface chemical composition as well as a suitable micro/nanoscale rough surface cooperatively create superhydrophobicity.[7,22,25–29] To introduce uniform and quantitatively controllable surface roughness to the azobenzene LCP film, PDMS-soft-template-based secondary replication was utilized (Fig. 2a). Benefiting from the wide and near-room-temperature nematic phase window of the mixed precursor used to prepare the azobenzene LCP, the melt monomers were easily and sufficiently filled into the microgaps of the soft template and the cross-linked azobenzene LCP film was well replicated (Fig. 2b–d). According to the parameters of our former studies,[1–3,23] two sets of square-arrayed 10 μm square posts with space 5 μm (D5) and 15 μm (D15) were chosen. Fig. 2e and Fig. S2 (ESI†) show the polarizing optical micrographs of the cut-off microposts. It is clear that the edges of the microposts are luminous (Fig. 2e) and show a 45° in-plane-rotating on–off alternation (Fig. S2, ESI†), denoting that the azobenzene mesogens are aligned parallel to the surface region of the microposts in the nematic phase. The uniform alignment of the azobenzene mesogens becomes the basis of a cooperative photoisomerization that further determines a sufficient polarity change of the film surface for the following adhesion regulation by alternate UV-visible light irradiation.

The static contact angles (CAs) on the flat azobenzene LCP film are shown in Fig. 3a and demonstrate that the as-prepared flat film shows intrinsic hydrophobicity. The lower CA to water in *cis* state is consistent with the light-induced increasing of the surface polarity, since in the excited *cis*-configuration, the higher dipole moment leads to an increase of local polarity of the polymer chain. The dynamic sliding angles (SAs) of 3 μL water droplets on the flat azobenzene LCP film in both *trans* and *cis* states are greater than 90°, *i.e.* the water droplets are firmly stuck on the surface of the flat film in any tilt angles. As Fig. 3b and Fig. 3c show, with the introduction of surface roughness, the CAs of both micro-arrayed LCP films of MA-F0208-D15 and MA-F0208-D5 are greatly increased into the superhydrophobic region (CA > 150°). The change of surface roughness influences not only the wettability but also adhesion. Caused by the great decrease of the gas–solid interfacial ratio, the droplet adhesion on MA-F0208-D15 obviously becomes smaller than the case of the flat azobenzene LCP film.

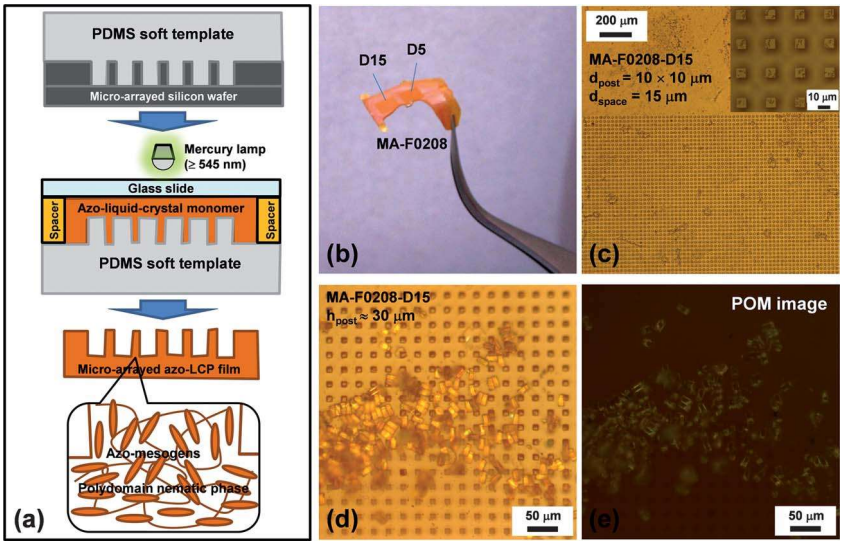

Fig. 2 The micro-arrayed azobenzene LCP film (MA-F0208, in nematic phase) prepared by PDMS-soft-template-based secondary replication. (a) Schematic illustration of the preparation process. (b) Optical photo of MA-F0208 with two patterned areas named as D15 and D5. (c) Large-area optical microscopic image and local amplified image (inset) of MA-F0208-D15. The patterns of D15 and D5 are all square-arrayed square posts with the post width of 10 μm. The spacings between two nearest posts for D15 and D5 are 15 μm and 5 μm, respectively. (d) Optical microscopic image of the cut-off microposts. The height of the posts is about 30 μm. (e) Polarizing optical micrograph of the cut-off microposts with the same position in (d).

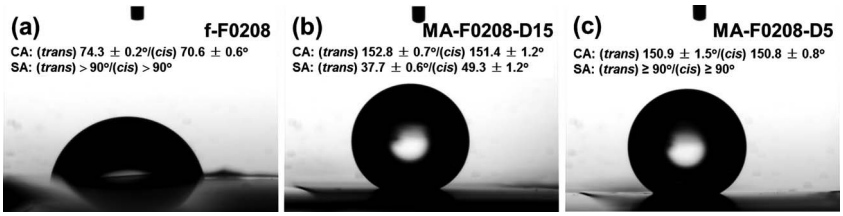

Fig. 3 Photoresponsive CA and SA results of (a) flat azobenzene LCP film and (b, c) micro-arrayed azobenzene LCP films (MA-F0208-D15 and MA-F0208-D5) with a 3 μL water droplet. The time for UV light irradiation (365 nm, 120 mW cm^{-2}) was 6 s and 30 s for visible light (530 nm, 30 mW cm^{-2}).

Moreover, by alternating irradiation of UV-visible light, the superhydrophobic adhesion on MA-F0208-D15 can be effectively and quickly regulated (SA in *trans*, 37.7 ± 0.6°; SA in *cis*, 49.3 ± 1.2° with 3 μL water droplets). It also should be noted that the CAs of MA-F0208-D15 and MA-F0208-D5 do not have a distinct difference before and after the UV light irradiation. It means that the change of the wetting behavior (embodied by CA values) is very tiny, while the change on the adhesive force (embodied by SA values) is significant after the UV light irradiation. The adhesive difference should result from the distinct change of polarity when the azobenzene LCP converts between the *trans* and *cis* isomers. For MA-F0208-D5, although the water droplets stay in a superhydrophobic state, the SAs in *trans* and *cis* states are both greater than 90°, thus the adhesion change induced by photoisomerization cannot be reflected.

MA-F0208-D15 has shown the above-mentioned SA response by light irradiation, but it still could not achieve "rolling" and "pinning" of water droplets since the larger *cis*-SA (49.3 ± 1.2°) is less than 90°. As we know, SA is directly related to water droplet size.[30,31] Generally, a bigger droplet leads to a smaller SA on a certain surface. It is found that a photo-controllable switch was successfully achieved with a 2 μL water droplet (Fig. 4a). In general, there are two wetting states that exist, *i.e.*, the liquid–solid–air composite state and the wetted liquid–solid state when a liquid droplet settles on a hydrophobic surface, which represents two adhesion states of the low adhesion and the high adhesion.[22,27,28,32,33] After UV light (365 nm) irradiation for 6 s, the azobenzene mesogens at the surface of MA-F0208-D15 transfer to a *cis* state and the adhesion increases because of the growth of surface polarity (Fig. 5). In this case, the surface shows a higher SA (a high water adhesion) and the 2 μL water droplet in the superhydrophobic state is pinned on the surface (Fig. 4a). Subsequently, after the visible light (530 nm) irradiation for 30 s, the azobenzene mesogens at the surface return to a *trans* state and the surface reverts to the lower adhesive superhydrophobic state (Fig. 5), thus the 2 μL water droplet could roll off from the surface when the substrate was tilted above 67.7° (Fig. 4a). Such a quick and reversible switch of superhydrophobic adhesion was very well retained after many cycles by the alternate irradiation of UV and visible light. The repeatability and stability of the micro-arrayed azobenzene LCP film are satisfying as a boon of cross-linking, which offers the rubber elasticity to the LCP film (Fig. 4b).

In conclusion, by designing of the surface chemical composition and morphology of the micro-arrayed azobenzene LCP film, a light-controlled quick and reversible switch of superhydrophobic adhesion was successfully realized. There are several superiorities in such light-regulated interfacial systems: (I) compared with heating and chemical stimuli, light has little influence on the microfluidic environment, *e.g.* undesired high temperature or introduction of chemical contaminants; (II) non-contact and localized control makes possible a high-precise operation. (III) The stimuli-responsive speed of the surface adhesion switch is greatly enhanced into ten-second grade, which will facilitate a real-time continuous control of microfluids. (IV) The cross-linking state of the film guarantees a satisfying stability for practical application in microfluidic systems. This work will shed light on and promote the design and practical application of smart interfaces with superhydrophobic adhesion switches.

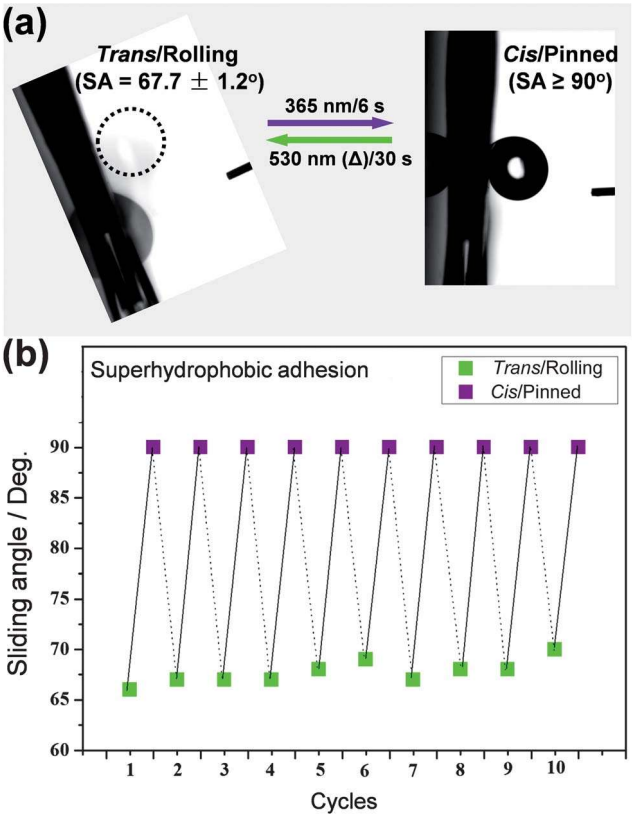

Fig. 4 Light-controlled quick and reversible switching of superhydrophobic adhesion between rolling and pinning on MA-F0208-D15 with a 2 μL water droplet. (a) Microscopic profiles of the rolling and pinned water droplets. (b) 10-Cycle measurement of the superhydrophobic adhesion switching by alternating irradiation of UV and visible light (365 nm/530 nm). The dotted line shows the initial shape of the water droplet, which indicates the superhydrophobicity of the surface. The droplet rolled out of the patterned area and settled on the flat region of the azobenzene LCP film, the CA thus appears rather low.

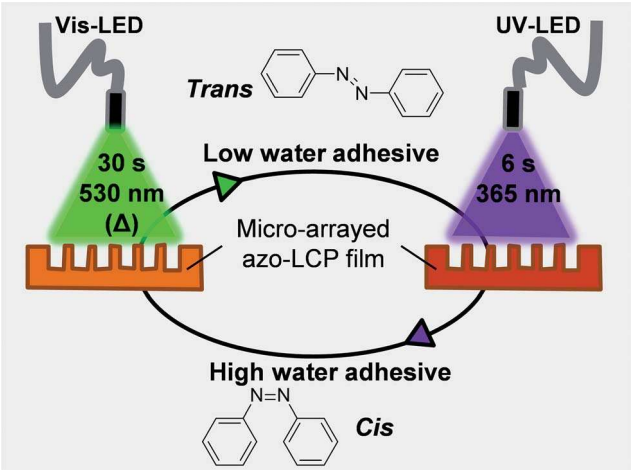

Fig. 5 Top-irradiation mode for the adhesion switch. The green light (530 nm, 30 mW cm^{-2}) makes the azobenzene LCP in the film into the *trans* state, thus the film surface shows a relatively low water adhesion. Reversibly, the UV light (365 nm, 120 mW cm^{-2}) changes the azobenzene LCP into the *cis* state and the surface of the film shows a relatively high water adhesion. The time for UV and visible light irradiation was 6 s and 30 s, respectively.

Acknowledgements

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