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Xu Deng (✉ dengxu@uestc.edu.cn)

University of Electronic Science and Technology of China <https://orcid.org/0000-0002-9659-0417>

Yao Tan

University of Electronic Science and Technology of China

Jinlong Yang

University of Electronic Science and Technology of China

Yong Li

Digital Media Art

Xiaomei Li

Max Planck Institute for Polymer Research

Qiao Wu

University of Electronic Science and Technology of China

Fanfei Yu

University of Electronic Science and Technology of China

Jiaxi Cui

University of Electronic Science and Technology of China

Longquan Chen

University of Electronic Science and Technology of China

Dehui Wang

University of Electronic Science and Technology of China <https://orcid.org/0000-0003-2444-7125>

Yue Fan

University of Electronic Science and Technology of China

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A Liquid-pressure-adaptive Superhydrophobic Surface

Yao Tan^{1†}, *Jinlong Yang*^{1†}, *Yong Li*^{1,2}, *Xiaomei Li*^{1,3}, *Qian Wu*¹, *Yue Fan*^{1,4}, *Fanfei Yu*¹,
*Jiaxi Cui*¹, *Longquan Chen*^{1,5}, *Dehui Wang*^{1,6}, *Xu Deng*^{1,7*}

† These authors contributed equally to this work

* Corresponding Author(s) E-mail: dengxu@uestc.edu.cn

1. Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

2. Digital Media Art, Key Laboratory of Sichuan Province, Chengdu 610021, P.R. China

3. Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

4. School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, P. R. China

5. School of Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

6. Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou 313001, P. R. China.

7. Shenzhen Institute for Advanced Study, University of Electronic Science and Technology of China, Shenzhen 518110, P. R. China

Abstract:

The dynamic application environments of superhydrophobic surfaces, such as in the manufacturing, chemical, and garment industries, require the fast adaptiveness of the surfaces to their surroundings. Despite the progress in materials and structural design of superhydrophobic surfaces, simultaneously achieving high superhydrophobic stability and low adhesion by traditional design is still challenging. Here, we demonstrate a liquid-pressure-adaptive superhydrophobic surface with self-adjustable solid-liquid stability and adhesion when reacting to the dynamic environmental requirements. To understand the underlying adaptive processes, we imaged the liquid impalement dynamics in three dimensions by confocal microscope and measured the stability and superhydrophobicity in varied systems. We envision our design strategy of liquid-pressure-adaptive superhydrophobic surfaces with dynamic anti-infiltration capability could guide the development of stable superhydrophobicity under complex wetting conditions.

Superhydrophobic surfaces have attracted great attention due to their unique attributes, including self-cleaning, antifouling, anti-icing, fluid drag reduction, and heat transfer.¹⁻¹⁰ The lyophobic nature of superhydrophobic surfaces is based on the premise of a stable air cushion in the structures.^{1, 11-13} The high proportion of air cushion helps to achieve low solid-liquid adhesion (high superhydrophobicity) but is fragile to vanish (low stability) under severe conditions, such as under high liquid pressure.¹⁴⁻¹⁷ Therefore, the balance between the stability and low adhesion of superhydrophobic surfaces in changing environments has become vital in real-world applications.¹⁸⁻²⁰ Researchers have invested much effort in optimizing the structure of superhydrophobic surfaces yet most of which are made of fixed air cushion proportion.²¹ That is, the solid-liquid contact area can't adjust according to the dynamic environment once the superhydrophobic surfaces are manufactured. Recently, smart surfaces with varied air cushion proportion have been demonstrated, either using soft materials under external stimuli

^{22, 23} or constructed by multiple-layer structures.²⁴ A better solution may be the development of superhydrophobic surfaces with adaptive topography in response to the forces applied by the liquid (*i.e.*, liquid pressure) and therefore the surface is capable to regulate the solid-liquid stability and adhesion when facing the dynamic environment.

To understand the coupling mechanism between superhydrophobicity and Cassie-Baxter state stability, we first revisit their response to the structural dimensions (Figure 1a), using a model superhydrophobic surface composed of micropillars with a characteristic length of pillar radius R and determined spacing D . The Cassie-Baxter model well describes the relationship between the solid-liquid contact area fraction $f(f = \pi R^2/D^2)$ and the superhydrophobicity, which is denoted as apparent contact angle (θ^*),

$$\cos \theta^* = f(\cos \theta_Y + 1) - 1 = \pi R^2(\cos \theta_Y + 1)/D^2 - 1 \quad (1)$$

where θ_Y is Young's contact angle. From Equation 1, we obtain the monotone decreasing of superhydrophobicity with R , as shown in Figure 1a. To design superhydrophobic surfaces with high performance, a small R is desired. On the other hand, the stability of the superhydrophobic state is calculated by breakthrough pressure P_θ from depinning, according to the discussion from Tuteja et al.²⁵

$$P_\theta = 2\pi R\gamma \sin(\theta - \varphi_{min}) / (D^2 - \pi R^2) \quad (2)$$

where γ is the surface tension of the liquid, ρ is the density of the liquid, θ is the equilibrium contact angle, and φ_{min} is the minimum local geometry angle. Detail derivation of Equation 2 can be found in the Supporting note. Large values of P_θ imply a robust air-liquid-solid composite interface, with a high energy barrier between the metastable composite interface (Cassie state) and a globally equilibrated wetted interface (Wenzel state). Otherwise, small values of P_θ imply that the composite interface cannot maintain its superhydrophobic stability against small infiltration pressure differentials across the liquid/vapor interface. For a surface with determined material and structure (*e.g.*, arrays of pillars), P_θ has a monotone

growth with the increase in R (Figure 1a). To determine the parameters of a superhydrophobic structure, such as R in our case, the trade-off between the superhydrophobicity and the stability should be evaluated.²⁶ Due to the coupling relationship between superhydrophobicity and stability, it is pseudo-logical in the traditional superhydrophobic surfaces design to balance the low adhesion and high stability of the solid-liquid interface. Compared to the determined solid fraction once fabricated, dynamic change of solid fraction in response to the liquid condition may be a better solution in advanced applications.^{27,28} A rational choice is to design a soft-hard integrated structure that can increase the stability at elevated liquid pressure (P). To design a superhydrophobic surface that reversibly produces programmed deformation against complex environments, both stimuli-responsive structure and supporting structure are necessary (Figure 1b). While the small deformation of the soft head at moderate conditions facilitates the superhydrophobicity, the increase in the R of the soft head at elevated P guarantees the stability of the surface (Figure 1a, b).

In this paper, we present a bilayer-structural liquid-pressure-adaptive superhydrophobic surface (LPASS), composed of rigid micropillar arrays with soft polydimethylsiloxane (PDMS) on the top (Figure 1c). We apply shape-deforming PDMS as stimuli-responsive top materials, facilitating the reversible deformations. The rigid micropillar array is designed at the bottom of the composite structure to produce the support for soft head. By using confocal microscopy, we quantified the pressure resistance, *i.e.* the variation of distance between two composite micropillars against pressure. We show that the stable Cassie state could be persisted by LPASS in the water droplet compression. Lateral force measurement demonstrated that the stability of the Cassie state was achieved without the sacrifice of superhydrophobicity. We envision that this rational design will help the surface intelligently and automatically adapt to dynamic fluidic conditions in various applications.

Results and discussions

Design of the liquid-pressure-adaptive superhydrophobic surface (LPASS). The LPASS is designed from rigid pillars, on top of which are decorated by a stress-deformable soft material (Figure 1c, Figure S1, the wetting properties of the materials listed in Table S1).²⁹ The rigid material provides the mechanical strength of the surface, while the soft head is responsible for the adaptive dynamic adjustment of the geometric structure. Micropillar arrays were fabricated by photolithography, followed by the enhancement of the mechanical rigidity by coating a silica shell and surface-free-energy reduction using fluorination. To generate the soft hemispherical top on the micropillars, a thin PDMS film was prepared on a cover glass by spinning coating and then transferred onto the top of the hydrophobic micropillars by a modified dip-coating technique (experimental section). To optimize the characteristics of LPASS, we first adjusted the diameter of the pillar to $d = 25 \mu\text{m}$ and spacing between two micropillars to $D = 100 \mu\text{m}$ to get a rigid superhydrophobic surface with determined dimensions (Figure S2). The high uniformity and regularity of the prepared surface are shown in a scanning electron microscopy (SEM) image (Figs 1d, Figure S3). It should be noted that the hemispherical PDMS (the green part) top on the micropillars (the blue part) also serves as a re-entrant structure, which could better stabilize the Cassie state for LPASS, compared to a simple array of micropillars with vertical walls.

The coupling mechanism between P and the deformation requires a quick-response elastic soft head with the deformation compatible with P_θ . The PDMS was selected because of its intrinsic hydrophobicity and tunable elasticity.^{30, 31} However, PDMS could be turned to be viscoelastic by using a low cross-linking degree structure. To determine the optimized cross-linker ratio that can be used in the LPASS, we used dynamic scanning to characterize the response of the internal structure of the PDMS materials to the external field, which exhibits a characteristic dynamic rheological response at low-frequency area, *i.e.*, long-term relaxation.⁶ The storage modulus G' and loss modulus G'' as a function of frequency for PDMS of several typical cross-linker ratios (from 5:1 to 75:1) are summarized in Figure 2a (the mechanical

properties of these five PDMS samples measured at the frequency of 1 Hz are listed in Table S2). The higher the G' , the harder the elastic deformation. On the other hand, G'' indicates the speed of destruction and reconstruction of the material cross-linked network. The larger the G'' , the PDMS materials lose more energy under the action of shear, indicated by larger viscosity. The objective of the measurement is to select the optimized cross-linker ratio of PDMS that has the maximum elastic deformation. PDMS with a cross-linker ratio of 5:1, 10:1, 25:1, or 50:1 are more like elastic materials since each G' is larger than the corresponding G'' . However, the magnitude of G' with a cross-linker ratio of 5:1 reaches several thousands of kilo-Pascals, which is much larger than that exists in the hydraulic system. For PDMS with a cross-linker ratio of 75:1, G'' becomes larger than G' , indicating an insufficient deformation response. Since P_θ in our model rigid pillar-array arranged superhydrophobic surface is close to the magnitude of one kilo-Pascal (Supporting note), we optimized the cross-linker ratio of PDMS as 50:1 for the LPASS that possesses the largest elastic deformation. In the following sections, we focus on hemispherical PDMS tops with cross-linker ratios in the range between 10:1 (rigid) to 50:1 (soft) for comparison in their deformation response against P .

Mechanism of the dynamic ridge deformation in response to varied pressures. To investigate the deformation of the soft head under P , we performed laser scan confocal microscope (LSCM) measurements at different liquid pressures.^{32, 33} Figure 2b shows that the LPASS is at the Cassie state under water at different liquid pressures (Video S1), characterized by the trapping of an air cushion within the structure of surfaces. It is known that a transition from Cassie state to the completely wetted Wenzel state can be triggered by an increase in P . To investigate the capability of LPASS to stabilize the Cassie state, we increased P by controlling the height of the liquid column (Figure S4). To capture the internal details of the transition, by analyzing 3D stacks of LSCM images, we extracted the coordinates of the x-z section to acquire the height and shape of the wetting ridge (Figure 2b). The transition occurred when P reached 0.8 kPa for the LPASS with the cross-linker ratio of 10:1, 1.2 kPa for the

LPASS with the cross-linker ratio of 25:1, and 1.6 kPa for the LPASS with the cross-linker ratio of 50:1. It can be found that the LPASS with a greater deformation range can withstand about twice P_θ compared to that with a rigid head. The degree of deformation of the head can also be qualitatively observed in the confocal images. The largest horizontal stretch of the soft head under the same P is found for the LPASS with a cross-linker ratio of 50:1.

To explain this increased stability against P , we investigated the change of R with P by applying fluorescence intensity analysis (Figure S5). The deformation ratio of R in response to P is shown in Figure 2c. The horizontal stretch of the soft PDMS head is supposed to originate from two factors. The initial stretch of the soft PDMS head (R_γ') is assumed to be caused by γ which pulls the substrate at the contact line. Considering the small modulus of the PDMS, the effect of γ on the soft cap is inevitable, because γ is large enough to pull the soft PDMS at the range of modulus we use. Such surface-tension-induced deformation, *i.e.*, ridge at the three-phase contact line (TPCL), has been reported in literature for macroscopic droplets deposited on a soft substrate.³⁴⁻³⁶ Theoretical models have also been developed to predict the profile of the ridge.³⁵⁻³⁷ When the soft surface shrinks into a micro soft sphere that touches the water, the surface-tension-induced stretch also exists. Similar to macro drop-induced liquid ridge, we found that the incremental dimension also scales as $R_\gamma' \sim C_1 \gamma / G'$ (Supporting note, Figure S6). Here, C_1 is the geometry constrain that is related to initial dimension of the micro sphere.³⁸ The surface-tension-induced stretch is proportional to γ but inversely proportional to G' . We have confirmed this by using structure with different radii, liquid with different surface tensions and soft head with different moduli (Figure S7). When P is exerted on the soft head, the elastic PDMS further deforms in the lateral direction. As shown in Figure 2c, a clear increase in the deformation ratio can be found for the PDMS with a cross-linker ratio of 50:1, with 10% growth in R under the pressure of 1.6 kPa; while R of the rigid PDMS with a cross-linker ratio of 10:1 is almost unchanged under the applied pressures. The horizontal deformation induced by the

pressure (ΔR_p) is estimated using a classical stress-strain model for a confined sphere of elastomer under compression. ΔR_p is estimated to scale as $\Delta R_p \sim C_2 P / G'$ (Supporting note). Here, C_2 is a parameter of geometry constrain. A close to linear correlation is identified by fitting the experimental data (Figure 2c), which verifies the feasibility of the model. As a combination of the effect of surface-tension-induced and liquid-pressure-induced stretch of soft head, P_θ of LPASS with a cross-linker ratio of 50:1 (~1.6 kPa) is almost twice higher than that of LPASS with a cross-linker ratio of 10:1 (~0.8 kPa). To confirm that the increase in P_θ originates from the increase in R , we further prepared a control surface composed of the rigid head (cross-linker ratio of 10:1) with the $R=17.5 \mu\text{m}$ and $D=75 \mu\text{m}$. The control surface has a f close to that of LPASS with a cross-linker ratio of 50:1 at its greatest deformation. A similar P_θ can be found in the control surface and the LPASS with a cross-linker ratio of 50:1 (Figure 2c). It can be concluded that the LPASS with a cross-linker ratio of 50:1 can self-adapt the radius of the soft head efficiently in response to P that protects the air cushion from destruction. It is worth mentioning that the deformation of PDMS is reversible under pressure, measured from 10 repeatable compression cycles under 10 kPa pressure (Figure S8), and the recovery occurs immediately, measured from the recovery time (Figure S9).

We further clarify the contribution of γ and P on the elevation of P_θ , by measuring P_θ on LPASS with different structural sizes (corresponding to different initial P_θ). From Eq. 2 and Eqs. S3-S5, we can roughly predict the theoretical P_θ from P . Figure 2d shows the change of P_θ with P for LPASS with cross-linker ratio of 50:1 at three different sizes (the results for LPASS with other cross-linker ratios are summarized in Figure S10). Surface-tension-induced enhancement of P_θ (area colored in orange) keeps constant with the variation of P , while pressure-induced enhancement of P_θ (area colored in green) has a monotone increase with P . With the reduction of the dimension, namely higher initial P_θ , it is found that the regulation of pressure-induced deformation and therefore the P_θ becomes more significant. Table S3

summarizes the ratio of the enhanced P_θ from γ and P for LPASS with different modulus and sizes. The pressure-induced deformation contributes more on the stability with the reduction of the size. We also measured P_θ for LPASS at three different sizes, the results confirm the enhanced stability when the initial P_θ increases.

To explain the increased stability against P , we also imaged and analyzed the transition process of the water-air interface (Video S2). The interface is captured in the reflection mode (Figure 2e). By analyzing 3D stacks of the confocal image, we extracted the coordinates of the interface and thus the local height of the air cushion. The interface is curved under P (inset in Figure 2e), in accordance with those reported in the literature.³⁹ Cassie-to-Wenzel transition correlated parameters, namely the minimum height $h_{\min}$ and the microscopic contact angle θ_{CL} , are extracted from the curved interface. In general, the transition to the Wenzel state can be triggered either by sagging, when the $h_{\min}$ reaches zero, or depinning, when θ_{CL} reaches the advancing contact angle of the material that the TPCL slides down. The abrupt of $h_{\min}$ indicates the depinning mechanism occurs for all samples. Nevertheless, the transition was found to be mitigated in the LPASS, reflected by the gradual change of both $h_{\min}$ and θ_{CL} . When increasing the pressure in the liquid, the pressure-dependent deformation of the PDMS sphere narrows the gaps between each pillar, allowing the contact line to bear higher P before moving downside. These findings imply that the LPASS not only increases the critical impalement pressure, but also slows down the transition. It should be mentioned that asymmetry geometry or defects of the soft cap could reduce the stability, similar to the conditions in rigid superhydrophobic surfaces. By revisiting the stability equation (Eq. 2), we can find that asymmetry could reduce the value of either R or $\sin(\theta - \varphi_{\min})$, and therefore yield a reduction in P_θ . Since the soft PDMS cap is generated under the constrain of surface tension, it tends to form sphere at the top of the pillar, which could mitigate the asymmetry to some extent, compared to the asymmetry of original rigid structure. Also, enclosed structures like cavities could prevent the local failure caused by asymmetry to the whole surface.

The balance between the stability of superhydrophobicity and the lateral adhesion force on the LPASS. To test the stability of the as-prepared LPASS, we performed a series of infiltration experiments with a drop interacting with the surface. First, we probed the transition of wetting states by pressing a droplet against LPASS (Figure 3a). Here, we used a micro-nano structured superhydrophobic plate with P_θ much higher than the model LPASS to press the droplet that can trigger the Cassie to Wenzel wetting transition. Using a force sensor underneath the LPASS, we monitored the vertical force exerted by the droplet as it was squeezed (Figure 3b). Cassie and Wenzel states can be distinguished from the vertical force by a sudden change in the force curve during compression (insert images in Figure 3b). The insert in Figure 3b summarizes the critical forces of the LPASS with different cross-linker ratios at the Cassie to Wenzel state transition. The critical force in the LPASS with a cross-linker ratio of 50:1 was found to be over twice higher than that with a cross-linker ratio of 10:1. This is in accordance with the P_θ measurement. The force measurement confirms that the ability of automatic adjustment of solid-liquid contact area of LPASS facilitates the stable Cassie state.

To determine whether the superhydrophobicity is changed in LPASS, we use a precise lateral adhesion force measurement rather than the apparent contact angle measurement.⁴⁰ Since the lateral force is an accumulation effect of the adhesion of singular cap, we are able to predict the deterioration of the superhydrophobicity from lateral force measurement. The lateral adhesion force between a water droplet and the surface was measured using a soft wire positioned in the center of droplet, calculated from the deflection of the wire when moving the sample surface at a constant speed (Video S3, Figure S11a, insert in Figure 3c). As a representative example of a force curve, Figure 3c shows a typical static regime, a transition regime, and a kinetic regime. This is in accordance with the results measured from rigid superhydrophobic surfaces in the literature.²⁶ When moving the test substrates horizontally, the force gradually increased until a maximum value of 78 μN . This maximum force corresponds to the threshold force that triggers the water droplet to slide. The force subsequently decreased to a constant level of approximately

38 μN , which was around 50% of the maximal force. We attribute the presence of a higher threshold force compared to the force required for continuous motion to the accumulation of required force to depinning the TPCL on a single cap along the contact line of the droplet. The force to detach the liquid from single cap is largely dependent on the contact area and the accumulated force eventually results in a difference of apparent front and receding contact angles and drop width.²⁶ However, the highly dynamic interaction between the liquid and solid for a moving droplet makes it difficult track the deformation on a singular pillar. The measured static force and kinetic force at a series of moving velocities are summarized in Figure S11b. Typical static force and kinetic force at moving velocity of $0.51 \text{ mm}\cdot\text{s}^{-1}$ are selected and plotted in Figure 3d. A slight increase in the lateral adhesion was found for static force measured from LPASS with the increasing cross-linker ratio. This could be attributed to the aforementioned deformation of the soft head by surface tension. Clear deterioration of the superhydrophobicity was found in the control surface as the static force was increased by almost 50%, originated from the significant increase in the solid fraction.

To show the balance between the stability of superhydrophobicity and the lateral adhesion force on the LPASS, we demonstrate the utility of LPASS for a continuous process of a droplet impacting and fast droplet shedding on an inclined surface. Drop impact is a highly dynamic process with varied pressure applied on the surface, which requires the surface to bear the critical maximum pressure with sufficient solid fraction. Fast droplet shedding after droplet impact, however, necessitates a low adhesive force with a small solid fraction. We first confirmed the rebound of drop impacting on a horizontally placed LPASS (Figure S12). Similar to drop impacting on rigid superhydrophobic surfaces, complete rebound was found under certain conditions. Impact phase diagram as a function of cross-linker ratio (Figure S12b) shows that the largest Weber number ($We = \rho D_{\text{droplet}} v^2 / \gamma$) range in which the drop can fully rebound is found on the LPASS with a cross-linker ratio of 50:1. Here, D_{droplet} is the diameter

of the impacting droplet and v is the velocity of impact. The impact phase diagram indicates that the stability of the surface against drop impact increases with cross-linker ratio. By extracting the contact time (τ) in the full rebound regime, the data collapses into a line, following the scaling law of $\tau \sim (\rho D_{\text{droplet}}^3 / \gamma)^{\frac{1}{2}}$ with the fitting coefficient of 1.0145. The results are consistent with theoretical analysis on rigid superhydrophobic surfaces, suggesting that the soft cap hardly influences the dynamics of the drop impact.⁴¹ Based on the analysis of drop impact on horizontally placed LPASS, we investigated the impact process on tilted surfaces. Figure 3e shows time-lapsed images of water droplet collision on the LPASS with different cross-linker ratios under a tilt angle of $\alpha = 15^\circ$ at We ($We = \rho D_{\text{droplet}} (v \cos \alpha)^2 / \gamma$) of 46.2 (Video S5). The water droplet undergoes rebounding and then falling with trajectories indicated by the dashed red line. For the LPASS with a cross-linker ratio of 50:1, the water droplet can complete rebound from this surface with a sequence of rebound at a speed close to $0.27 \text{ m}\cdot\text{s}^{-1}$. But for the LPASS with a cross-linker ratio of 25:1 and 10:1, only partial rebound was found, followed by rolling off the surfaces at a speed of $0.15 \text{ m}\cdot\text{s}^{-1}$ and $0.09 \text{ m}\cdot\text{s}^{-1}$, respectively. The partial rebounding indicates the breakdown of Cassie state during the impact that increases the solid-liquid adhesion significantly. Droplet impact on the control surface was also conducted. Despite the complete rebounding, the droplet can only rebound once because of the large dissipation of kinetic energy induced by the high adhesion between the surface and droplet, resulting in a sliding velocity ($0.11 \text{ m}\cdot\text{s}^{-1}$) apparently smaller than that of LPASS with a cross-linker ratio of 50:1.

The impact phase diagram of LPASS with varied cross-linker ratios is summarized in Figure 3f. The complete rebound is reflected by open symbols while filled symbols denote the partial rebound. Complete rebound of the droplet requires the superhydrophobic surface a high infiltration pressure. It can be found in Figure 3f that the softer the head, the higher We the surface can bear, exhibiting the efficiency of the soft head in protecting the surface from

infiltration during the droplet impact. Despite the instantaneous increase in solid fraction at the impact area, the solid fraction in the rest part of the surface remains small with low adhesion to the water droplet. As a result, the shedding velocity of LPASS with varied cross-linker ratios in the complete rebounding regime collapses into a master curve, revealing that the shedding velocity is irrespective of the stiffness of the soft head (also seen in Figure S12c). Though the control surface also preserves the high infiltration pressure during the drop impact, the shedding velocity is significantly small than that of LPASS because of the large solid fraction. The enhanced water droplet bouncing and sliding on LPASS is ascribed to the composite interfaces that can perceive the changes in external pressure and adapt its solid-liquid area accordingly.

Applications of LPASS. We first confirmed that the LPASS can also bring a stable Cassie state in the liquid system other than interaction with the droplet. To measure the infiltration pressure, we constructed a microfluid system that is similar to that we reported previously. In this system, the LPASS constitutes the upper inside wall of a microchannel with 80 μm in height, 20 mm in width, and 50 mm in length (Figure 4a). To compare the superhydrophobic stability between different cross-linker ratios of LPASS, we used confocal microscopy to measure the critical flow rate before impalement. At the critical velocity, the water-air interface disappeared gradually along the flow direction (Figure 4b, Video S6). The critical flow rate was measured to be $443.3 \pm 12.5 \mu\text{L} \cdot \text{min}^{-1}$ for LPASS with a cross-linker ratio of 50:1, $246.7 \pm 12.5 \mu\text{L} \cdot \text{min}^{-1}$ for the LPASS with a cross-linker ratio of 25:1, and $150 \mu\text{L} \cdot \text{min}^{-1}$ for the LPASS with a cross-linker ratio of 10:1. As the fluid in the microchannel was driven by pressure, the higher fluid rate resistance indicates the stronger ability to sustain the superhydrophobic state. Our results prove that the LPASS contributes to the stable superhydrophobic state under water, demonstrating that the soft PDMS hemisphere on the top of LPASS yields a prolonged superhydrophobic state.

Except for micropillar structured model superhydrophobic surfaces, we demonstrate the universality of our method. Despite the different formula to calculate the P_θ , such as in

superhydrophobic surfaces with structures of stripe or cavity, the deformation of soft cap regulated by liquid pressure always facilitates the balance between stability and superhydrophobicity of the surface. We demonstrated the soft head can be coated on a stripe-structured superhydrophobic surface (Figure 4c). Such micro-stripes not only assure anisotropic solid–liquid interfacial interaction, but also have a reentrant cross-sectional profile to enhance stability. The maximal force applied on a drop to induce Cassie-Wenzel transition on LPASS with different cross-linker ratios was listed in Figure 4c. The results are similar to the compression effect produced on LPASS with arrays of micropillars. It is not unexpected that the forces applied on LPASS with arrays of micro-stripes are larger than those on the LPASS with arrays of micro-pillars due to the higher solid fraction.

Furthermore, through structural adjustments, we demonstrated that a pressure-induced switch of superhydrophobicity on LPASS can be achieved (Figure 4d, Figure S13). For a LPASS with a spacing of 15 μm ($f = 19.6\%$), the deformation of the soft head at elevated pressure is enough to close the liquid-air surface that totally prevents the liquid from impaling into the air cushion. Although this method for increasing stability is based on the sacrifice of superhydrophobicity ($\theta^*=121^\circ$), the concession is inevitable and acceptable in industrial production.

In summary, we proposed a liquid-pressure-adaptive superhydrophobic surface design strategy that can automatically adjust its structure driven by surrounding applied pressure to achieve a dynamic balance between superhydrophobic stability and solid-liquid adhesion. By employing 3D LSCM and theoretical considerations, we quantified the surface-tension-induced and pressure-induced deformation and explained the underlying mechanism. The designed surface is expected to have broad significance for industrial productions, breaking the limitation of maintaining the stability of the solid-liquid interface while keeping low adhesion, which is conflicting with the traditional logic of superhydrophobic design. Such liquid-pressure-based morphological change of soft superhydrophobic surface can well protect itself by resetting the

topological structure. We envision that this reasonable design will help the superhydrophobic surface intelligently and automatically adapt to fluid changes in various applications.

Methods

Fabrication of liquid-pressure-adaptive superhydrophobic surfaces. The rigid micropillar arrays were fabricated from negative photoresist (SU-8 2025, Microchem, USA) by photolithography. To increase the mechanical rigidity, a silica shell (20-40 nm in thickness) was coated on the SU-8 surface by chemical vapor deposition (CVD) of tetraethoxysilane (Sigma Aldrich, 98%) catalyzed by an aqueous ammonia solution (TCI, 28%). To reduce the surface energy of the surface, the micropillars were chemically functionalized with trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (Sigma Aldrich, 97%) by CVD. The SU-8 pillar is self-fluorescent and can be excited with a 405 nm laser. Polydimethylsiloxane (PDMS, the mixture of Sylgard 184 elastomer kit and curing agent) was used to create the soft hemispherical top on the micropillars. A thin film of PDMS was first coated on a cover glass by spinning coating (8000 rpm for 20 s). The film was then transferred onto the top of the fluorinated pillars by a modified dip-coating technique. Specifically, the surface with micropillars was placed reversely upon the PDMS film and pressed until a full contact. After the surface was peeled off and partially cured in a dryer at the temperature of 75 °C for 2 hours. The PDMS was designed with different cross-linker ratios (from 5:1 to 75:1).

Synthesis strategy of perylenediimide (PDI)-conjugated PDMS-NH₂ for fluorescent visualization. The synthesis of the PDI-conjugated silicone oil has been reported previously.⁴² The mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (2 g, 0.05 mmol) and PDMS-NH₂ (20 g, 8 mmol) in 20 ml DMF was stirred at 150 °C for 10 days under continuous purging with N₂ gas. After cooling to room temperature (25 °C), the mixture was washed with water and then filtered through Teflon membrane (pore size: 0.2 μm). The solvents (water and DMF) were removed under vacuum to produce a red solution that was directly dissolved in silicone

oil. The PDI-conjugated silicone oil was joined in the cross-linking stage of PDMS to make it with fluorescent properties and can be excited with a 488 nm laser.

Rheology measurement of PDMS samples. The mechanical properties of various PDMS samples were measured using the DMA tester (Q850 DMA, TA Instruments) in the compression mode at 0.1-100 Hz with an amplitude of 100 μm for 2 minutes. The temperature of the test chamber is set 25 $^{\circ}\text{C}$. The test samples were prepared using a ceramic mold with 10 mm diameter and 4 mm depth. Freshly mixed PDMS solutions (cross-linker ratios of 5:1, 10:1, 25:1, 50:1 and 75:1) were used to fill the mold, followed by degassing in a vacuum desiccator and curing in an oven at 75 $^{\circ}\text{C}$ for 2 hours.

Infiltration pressure measurement. The infiltration pressure was measured in a micro channel with three-layer sandwich structure.⁴³ The upper layer was a 1 mm thick microscope slide (25 mm x 60 mm) with two micropores at both ends (diameter: 1 mm). The test samples were attached at the bottom of the surface. The lowest layer of the construction was a microscope coverslip made of borosilicate glass (25 mm x 60 mm) with a thickness of 170 μm . The channel in the middle layer was created by two rectangular strips (2 mm x 50 mm) of PMMA (polymethyl methacrylate) film (SHENGJILI, China) with a thickness of 3 mm at both sides of the lowest layer. The two micropores on the upper slide were used to connect with the inlet and outlet tubing. To guarantee the waterproof, the three-layer construction, as well as the inlet and outlet tubing, was sealed by adhesive polymer (DEVCON, 5 minutes epoxy, 14265). The change of applied pressure ($P = \rho gh$) is realized by closing the outlet pipe and changing the liquid level (h) of the water storage container connected with the inlet pipe.

The change of wetting ridge in response to the applied pressure was visualized via the Laser scanning confocal microscopy (NIKON A1, 20 $\times$ /0.85 dry objective). The height of the wetting ridge is determined according to the fluorescence intensity of the solid-liquid interface. The image resolution was about 1.24 μm and 1.0 μm in the horizontal and vertical directions, respectively, except for areas closer than about 10% of the distance to the edges of the pillars

(fluorescence mode). Dyed water with Rhodamine B (Sigma Aldrich, 99%) of $1 \text{ mg}\cdot\text{mL}^{-1}$, which can be excited with a 605 nm laser, was injected into the chamber as the liquid.

Lateral adhesion force measurement. The lateral adhesion force was measured by a cantilever-based force sensor.⁴⁴ During testing, a $5 \text{ }\mu\text{L}$ water droplet was suspended at the end of a microneedle (diameter: 0.09 mm, length: 70 mm) as the force sensor and kept adhered throughout the process. The tested surfaces were placed below the water droplet at a controlled speed (from $0.17 \text{ mm}\cdot\text{s}^{-1}$ to $1.7 \text{ mm}\cdot\text{s}^{-1}$). The above process was recorded by a high-speed camera (Photron, Fastcam SA5) with a frame rate of 70 fps and analyzed by Tracker. The lateral adhesion force was linearly proportional to the deflection of the microneedle, and can be calculated by the elastic deflection according to the end-loaded cantilever beams deflection equation ($F_l = k\delta$, in which, F_l is lateral adhesion force, k is effective spring constant, and δ is elastic deflection).

Critical force measurement at impalement. The critical force at impalement was measured using a high-sensitivity microelectromechanical balance system. A $5 \text{ }\mu\text{L}$ droplet was placed on the sample surface, which was placed on the balance. To measure the impalement pressure of the droplet exerted on the surface, a candle soot templated superhydrophobic plate with extra-high infiltration pressure was slowly moved down to the droplet such that it contracted the water droplet and then moved down at the constant speed of $0.02 \text{ mm}\cdot\text{s}^{-1}$. During this process, the balancing force gradually increased until the droplet occurred impalement and then the droplet was withdrawn with the same speed.

Micro-flow measurement. Micro-flow measurement adopted the same chamber as that used in infiltration pressure measurement. Differently, the inlet tubing was connected to a Syringe Pump (NE-500, OEM, America) to pump water and staying on the same level with outlet tubing which was opened and connected to a container. The critical flow rate was determined by the confocal microscope. Reflection mode was used to scan the water-air interface in the

microfluidic channel. Under the continuous increase of the input flow rate, the wetting state is determined according to the change of the water-air interface.

Droplet impact and rolling experiment. A water droplet (10 μL) impacted on the LPASS at a releasing height ranging from 0.5 mm to 10.5 mm and the tilt angle of the surface is 0° (experiment on horizontal surfaces) or 15° . The droplet rolling dynamics were recorded by a high-speed camera (Photron, Fastcam SA5) with a frame rate of 10,000 fps and analyzed by Image J. All experiments were conducted in an ambient environment at room temperature (25°C) and relative humidity of 40%.

Relaxation time measurement of PDMS samples. The relaxation time of various PDMS samples were measured using the DMA tester (Q850 DMA, TA Instruments) in the stretch mode. A PDMS sample was stretched and produced about 20% strain, followed by sudden removal of the stress to make the PDMS sample automatically relax for 5 minutes. The strain was recorded during the process. The temperature of the test chamber is set 25°C . The test samples were prepared using a ceramic mold with 12 mm length, 6 mm width and 2 mm thickness. Freshly mixed PDMS solutions (cross-linker ratios of 10:1, 25:1 and 50:1) were used to fill the mold, followed by degassing in a vacuum desiccator and curing in an oven at 75°C for 2 hours.

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Author Contributions:

Y.T., J. Y. and X.D. conceived the research and designed the experiments. X.D. supervised the research. Y.T., Y.L., X.L, Q.W., Y.F., F.Y., J.C., L.C. and D.W. carried out the experiments. All authors analyzed and interpreted the data and wrote the paper.

Additional information

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Figure 1. Design of the LPASS. (a) Influence of characteristic length on superhydrophobicity and stability. (b) Schematic showing the principle of the adaptive radius of the soft head in response to the infiltration pressure ($R_2 > R_1$, $P_2 > P_1$). (c) Self-adaptive superhydrophobic surface manufactured from rigid micropillars with a soft head. (d) False colored SEM images showing the high regularity of the LPASS. The green part indicates the PDMS cap and the blue part is SU-8 photoresist.

Figure 2. Dynamic anti-infiltration mechanism. (a) Mechanical properties of five different cross-linker ratios PDMS samples from rheological measurements at 0.1–100 Hz. (b) Confocal images showing the horizontal elongation of the PDMS hemisphere with different rigidities in response to the infiltration pressure. (c) The change of the hemisphere radius with the increase in the infiltration pressure. The control surface was made from a rigid head with $R=17.5 \mu m$ and $D=75 \mu m$. (d) Correlation between breakthrough pressure and the applied liquid pressure. The color area represents the contribution of the surface tension (orange) and liquid pressure (green) to the enhancement of infiltration pressure. (e) Confocal image of the reflection from the water-air interface and its x-z cross-section along the white line. We extract the microscopic contact angle θ_{CL} and the minimum height of the air cushion h_{min} normalized by the initial minimum height h_{min0} (Pressure=0 kPa).

Figure 3. Stability and lateral adhesion of the LPASS. (a) Schematic of the experimental setup that measures the infiltration force by compressing a droplet. A water droplet is pressed vertically on the LPASS, the loading force on which is measured by a high-sensitive force balance. (b) Critical force exerted on the water droplet when impalement happened on the LPASS with different rigidities of the hemisphere head. (c) Measurement of the static and kinetic lateral adhesion force on the test surfaces. (d) Comparison of static and kinetic lateral adhesion forces of a water droplet (3 μL) moving on the LPASS with different rigidities of the hemispherical heads. (e) Selected snapshots show the partial rebound and the full rebound of a droplet impacting on the LPASS under the same Weber number ($We = 46.2$) with rigid and soft hemisphere heads, respectively. (f) Impact phase diagram of water droplets impinging on LPASS with rolling velocity as a function of We .

Figure 4. Applications of the LPASS. (a) Schematic of the stability measurement of LPASS in a micro-flow channel. Reflection mode of confocal microscopy is used to confirm the impalement of the water-air contact line. (b) Impalement ability of LPASS with different rigidities of the hemisphere head. The continuous black color area, the yellow color area, and the discrete black circle area correspond to the impaled district the solid-liquid interface, the liquid-air interface, and the solid-liquid interface, respectively. The yellow color in the black circle indicates the reflection artifacts. (c) The SEM images and schematics of elongated LPASS and the critical force exerted on the water droplet when impalement happened on the different LPASS samples. (d) Conceptual diagram of the switching effect realized by LPASS.

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