Tunable Structural Color Surfaces with Visually Self-Reporting Wettability

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Functional materials with wettability of specific surfaces are important for many areas. Here, a new lubricant-infused elastic inverse opal is presented with tunable and visually “self-reporting” surface wettability. The elastic inverse opal films are used to lock in the infused lubricating fluid and construct slippery surfaces to repel droplets of various liquids. The films are stretchable, and the lubricating fluid can penetrate the pores under stretching, leaving the surface layer free of lubrication; the resultant undulating morphology of the inverse opal scaffold topography can reversibly pin droplets on the fluidic film rather than the solid substrate. This mechanical stimulation process provides an effective means of dynamically tuning the surface wettability and the optical transparency of the inverse opal films. In particular, as the adjustments are accompanied by simultaneous deformation of the periodic macroporous structure, the inverse opal films can self-report on their surface status through visible structural color changes. These features make such slippery structural color materials highly versatile for use in diverse applications.

1. Introduction

As a fundamental property of a solid surface, wettability plays a key role in addressing the problems related to energy, environment, resources, and health. Thus, designing a surface with a specific wettability becomes an important task. In this field, nature is a museum for arousing our inspiration. With four and a half billion years of stringent evolution and natural selection, many organisms have developed surfaces with special wettability properties in order to survive in their environments. The pitcher plant is endowed with a slick interior for capturing insects, with a surface microtexture suitable for locking in an intermediary liquid. Inspired by such organisms, scientists in insects, with a surface microtexture suitable for locking in an intermediary liquid. Inspired by such organisms, scientists have developed numerous functional surfaces with special wettability properties. Some of the most prominent examples are porous surfaces infused with a slippery liquid and designed to create a fluid–fluid interface between a low-surface-tension lubricant and immiscible liquids. This design even outperforms its natural counterparts and state-of-the-art synthetic surfaces in its ability to repel various simple and complex liquids. However, most such slippery surfaces have a constant wettability, whereas surfaces with the tunable interface interactions essential for many applications are rarely reported. In addition, present strategies for investigating the surface wettability usually require elaborate instruments, which are limited in outdoor applications where real-time monitoring of the wettability is needed. Thus, functional surfaces with tunable wettability capable of self-reporting are still sought.

In this paper, we present a new lubricant-infused elastic inverse opal with the desired surface features. Inverse opals are a type of 3D, periodically-arranged macroporous material that can be negatively replicated from colloidal crystal templates. This periodic structure gives rise to the interesting optical properties and vivid structural colors of the inverse opals. Because of their distinct function, responsive inverse opals have found many important applications as self-reporting sensors to measure various environmental changes. However, their potential value in the construction of functional slippery surfaces remains unexplored. Thus, we herein used elastic inverse opal films to lock in the infused lubricating fluid, and so constructed slippery surfaces for repelling droplets of various liquids. The films were stretchable, and the lubricating fluid could penetrate the pores under stretching, leaving the surface layer free of lubrication; the resultant undulating morphology of the inverse opal scaffold topography could reversibly pin droplets on the fluidic film rather than the solid substrate. This mechanical stimulation of the inverse opal films could be directly translated into dynamic adjustments of wettability and optical transparency. Because of the simultaneous deformations of the periodic macroporous structure during the adjustments, the inverse opal films could self-report their surface status as visible structural color changes, indicating that our slippery structural color materials could be highly versatile for a broad range of applications.

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2. Results and Discussions

In a typical experiment, the elastic inverse opal films were derived from colloidal crystal templates, as schematically described in Figure S1 (Supporting Information). In this process, the colloidal crystal templates with ordered array structures were obtained by self-assembling SiO₂ nanoparticles on glass slides using a vertical deposition method. To enhance the close-packed junction structures of the SiO₂ nanoparticles, the glass slides and the fabricated colloidal crystal arrays were treated with 400 °C sintering. The inverse opal structures were formed by filling the voids of the colloidal nanoparticle array templates with a polymer solution and evaporating the solvent to solidify the polymer. Polyurethane (PU) is a soft polymer with extraordinary extension and transparency and was used as the filling element. Thus, after etching the glass slides and their surface SiO₂ colloidal crystal templates with hydrogen fluoride (HF) overnight, free-standing PU inverse opal films with the desired elastic properties were achieved. The voids of PU inverted opal should have a slight shrinking after HF treatment because of the water surface tension during the drying process of the film.

The microstructures of the colloidal crystal templates and the resultant PU inverse opal substrates were characterized by a scanning electron microscope (SEM), as shown in Figure 2. It can be observed that the mono-disperse SiO₂ nanoparticles on the film surface were closely packed to a face-centered cubic structure (Figure 2a), which contributed to a perfectly ordered latex arrangement. This high degree of regularity was also reflected in the fast Fourier transform (FFT) images (the inset of Figure 2a). The inverse opal was obtained by using PU to fill the void spaces of the SiO₂ nanoparticles and then removing the nanoparticles. The top-view SEM images of the PU inverse opal film are shown in Figure 2b. The film consisted of well-ordered macropores with void sizes of about 240 nm (10% shrinkage compared with the sphere diameter of 260 nm). This macroporous structure would not only provide sufficient room for liquid adsorption but also contribute to the rough surface and the special wettability properties of the film.

As the PU polymer had extraordinary extension capacity, the PU inverse opal films were expected to be endowed with the same feature. This was confirmed by stretching the films to different lengths. The top-view SEM images of the inverse opal under moderate stretching are shown in Figure 2c,d. The well-ordered 3D nanoscale pore structure of the inverse opal changed from nearly spherical to elliptical. These elliptical pores displayed a certain volume enlargement against orientation, which indicated the inverse opal's potential as a useful substrate for the infusion of liquid. Obviously, the further the inverse opals were stretched, the bigger the volume of orientation of the films that appeared. However, it was found that the continuous nano-structure of the inverse opal could be damaged by excessive stretching. Thus, after a series of tests on the structural colors, liquid infusion, and film strain tolerance, we set the stretching ratio limit to under 50% compared with the orientation for further research.

To impart a slippery surface to the PU inverse opal film, lubricating fluids, such as perfluorinated oil (DuPont Krytox 103, refractive index is 1.300), were infused into the 3D nanoscale pore structure of the inverse opal and even overcoat
the surface of the films. Because of the amphiphilicity of the PU polymer, fully filling the inverse opal of the lubricating fluid was easy to achieve through the application of a vacuum. The excess lubricating liquid on the surface of the inverse opal films was removed by the centrifugal force of the spin-coating apparatus. After this treatment, only a thin layer of lubricating fluid was locked on the surface of the inverse opal films. As the selected lubricating fluid usually had low surface energy and was chemically inert, the surface of the inverse opal films was physically smooth to the molecular scale and repelled immiscible liquids of virtually any surface tension.

This was confirmed by recording the wettability of surfaces of the inverse opal films by droplets, as shown in Figures S2 and S3 (Supporting Information). It was found that the water droplet contact angle on the surface of the perfluorinated oil-filled inverse opal films became 85° from their original 100° without oil filling (Figure S2a,b, Supporting Information), and the oil contact angle (for silicone oil) become 15° from their original 40° (Figure S2c,d, Supporting Information). Besides the changed contact angle, filling the inverse opals with the chemically inert perfluorinated oil also led to significant changes in the sliding angle of the droplets on the surfaces of the films (Figure S3, Supporting Information). It could be observed that the droplets were pinned on the inverse opal films or were absorbed into the porous inverse opal structure when the films were not filled with perfluorinated oil. Thus, the sliding angle hysteresis of the droplets on this situation tended towards infinity. However, with the presence of the perfluorinated oil, the sliding angle hysteresis of both water and silicone oil was effectively eliminated. Therefore, the lubricating fluid-infused inverse opal films provided an ideal slippery surface.

The stretchability of the liquid-infused PU inverse opal films provided a promising means to dynamically manipulate the mobility of both oil and water droplets on their surfaces. Generally, the oil-lubricated PU inverse opal films showed distinct deformation-responsive properties under uniaxial mechanical stretching. This response can be quantitatively predicted by relating the induced strain force change to the substrate deformation. Thus, with orthogonal stretching, the pore volume of the inverse opal structures was enlarged and a negative pressure field built up in the film, which caused the retreat of the fluid coating the film surface into the pores. This process should make the inverse opal films recover their rough surfaces as with the unfilled structure (the surface roughness of the PU films under stretching is discussed in the Supporting Information). However, when the stretching force was removed, the shape of the inverse opal pores changed from ellipsoidal back to spheroidal, and their volume also returned to the previous condition. Accordingly, the oil-lubricated flat surface forms again as the liquid moved outward until it reached the equilibrium state. In this liquid-infused inverse opal system, the flat, smooth liquid interface in the relaxed state serves as the lubricating layer that allows drops to slide freely, whereas the undulating morphology of the stretched film reversibly halts the moving droplets by pinning them on the fluidic film rather than the solid substrate. Thus, the inverse opal was expected to provide a dynamic gas–liquid–solid interface that could be reversibly varied between a liquid-lubricated and a textured surface in response to mechanical stimuli (stretching) sensed by the elastic substrate.

To demonstrate this tuning function, we analyzed the dynamical wettability of the films’ surfaces by monitoring the liquid droplets on the slippery surface with or without stretching (Figure 3). The droplets slid down the liquid-infused inverse opal substrate, but stopped and were held in place when the substrate was stretched. However, as soon as the stretching ceased, the droplets began to slide again (Figure 3). Thus, the changes in mobility correlate with the reconfiguration of the film under reversible stretching, as recorded in Movie S1 (Supporting Information). There was no droplet residue left on the

![Figure 3. Dynamic control of droplet mobility on a tilted surface: a) Scheme showing the control mechanism: a droplet of test liquid changes from sliding to pinning under stretch as the film surface reconfigures from flat to rough; b) process of a silicone oil droplet sliding on the film surfaces without stretching; c) process of the droplets pinning on the film surfaces with i–iii) stretching and iv) the droplet sliding down when the strain was relaxed. The scale bar is 1 cm.](wileyonlinelibrary.com)
film surface after the droplets slid away upon release from pinning; this was consistent with the lubricating film remaining continuous rather than allowing the oil to wet and foul the underlying solid.

The lubricant volume fraction on the inverse opal substrate is a very important parameter during the construction of the slippery surface. Too low a fraction would not fill the pore structures of the films, and the resultant film could not form a slippery surface, while the wettability tuning feature was lost when the lubricant volume fraction was high enough (Supporting Note S1, Supporting Information). Thus, with a series of tests, we confirmed the effective fraction of the lubricant in the inverse opal substrate and investigated the wettability performance of a few films under different uniaxial strains (Figure 4a). The droplets on the film showed decreasing gradient sliding angles with increasing lubricant area ratios (3.5–4.5 μL cm⁻²). In addition to the infused lubricant, we also investigated the effects of the slippery surface on different droplets (Figure 4b).

Six kinds of hydrocarbon oils with different surface energies were selected for comparing the sliding angles as a function of strain: namely, hexane (18.43 mN m⁻¹), heptane (20.14 mN m⁻¹), octane (21.6 mN m⁻¹), decane (23.7 mN m⁻¹), dodecane (25.4 mN m⁻¹), and hexadecane (27.3 mN m⁻¹). It was found that the sliding angle of oils with lower surface tensions had a sharp increase when a small strain was applied to the film. For example, the sliding angle of hexane increased from 7° to 17° with a gradual strain change from 0% to 10%. However, this strain change had no discernible effect on hexadecane, which required nearly 40% strain to reach a sliding angle of 17°.

Besides the reversible wettability, the liquid-infused PU inverse opal films also had tunable optical transparency and structural colors. As described above, the liquid on the surfaces of the films would retreat into the bottom pores, leaving a larger area of unfilled open pores on the surfaces of the films. This construction would scatter more light at the liquid-air interface and lead to the tunable optical transparency of the films. We confirmed this feature by gradually stretching the liquid-infused PU inverse opal films. It was found that increasing the strain resulted in lower light transmission through the film until it finally became opaque, and the light transmission recovered when the strain was relaxed (Figure S4, Supporting Information). Thus, the sensitivity of the liquid-infused PU films to inverse opal structural deformation enables fine tuning of the transparency over a continuous, wide range in response to stimuli.

Because of the periodic arrangement of the pores, the elastic PU inverse opals should have a photonic band gap (PBG) (Figure S5, Supporting Information). This would lead to certain wavelengths or frequencies located in the PBG being tunable by stretching the PU films to a rational length. Thus, the elastic films should display vivid tunable structural colors and characteristic reflection peaks. However, because of the high transmittance of the film material, only weak reflection peaks could be detected (Figure S6, Supporting Information, the contrastive reflection spectra of the film before and after infiltration of the perfluorinated oil are given in Figure S7, Supporting Information), while their structural colors were not obvious under normal circumstances. To solve this problem, we increased the contrast ratio of the film materials by placing them on a black background plate. Figure 5 shows the reflectance spectra and the structural colors of the inverse opal films under uniaxial stretching. The changes in the films' colors can be observed clearly by the naked eye, and the corresponding reflectance spectra could be recorded with a spectrometer. It is noteworthy that the film materials could be imparted with shiny structural colors under any background when using carbon black nanoparticles (with the size of 2–50 nm) dispersed in PU solution as their pregel materials, as shown in Figure S8 and Movie S2 (Supporting Information). This improvement made the films more versatile for different application.

Generally, the main reflection peak position λ of the inverse opal materials can be estimated by Bragg’s equation for a normal incident beam, λ = 2d sinθ, where d_{111} is the interplanar distance of the (111) diffracting planes and n_{average} is the average refractive index of the materials (Supporting Note S2, Supporting Information). With the stretching of the inverse opal films, their diffracting planes would be decreasing gradually, which could cause a blueshift in the peak position and structural colors. This process was confirmed in Figure 5. It can be observed that the stopband of the liquid-infused PU inverse opal films has an obvious blueshift (152 nm) from the initial state of 650 to 500 nm, with 0% to 50% longitudinal stretching. The initial color of the film was red before stretching and changed to orange, yellow, green, and blue during the stretching (Figure 5a–c indicated the 20%,

Figure 4. a) Comparison of sliding angle (silicone oil) as a function of strain on the inverse opal substrate with different amounts of infused lubricant; b) tuning the oil sliding angle as a function of strain for test droplets of different interfacial tensions.
35%, and 42% stretched film with their reflection peaks at 626, 548, and 510 nm, respectively. Because of the elasticity of the PU polymer, the stretching of the liquid-infused inverse opal films is reversible. Following the release, the reflectance peak underwent an obvious redshift back to its initial state. Figure S9 (Supporting Information) plots the reversible conversion of the stop-band position of the film under stretched state and released state for 20 cycles. It was clear that the shifts in peak positions were also repeatable and reversible. As the tuning of the wettability and the adjustment of structural colors and reflection peaks in the films were simultaneous, the elastic PU inverse opal films could self-report their surface status through visible visualized structural color changes. These features make our slippery structural color materials promising candidates for many sensor applications.

3. Conclusion

In summary, we presented a new slippery structural color film with tunable and self-reporting surface wettability. The film was composed of a PU inverse opal structure, which could be used to lock in the infused lubricating fluid and construct the slippery surfaces to repel droplets of various liquids. As the PU polymer had good elasticity, the lubricating fluid could infiltrate the pores when the films were stretched, causing the slippery surfaces to recover their undulating inverse opal scaffold topography and pin droplets on the fluidic film rather than the solid substrate. Thus, dynamically tuning surface wettability could be effectively achieved by using this mechanical stimulation. In particular, as the adjustments to wettability were accompanied by simultaneous deformations of the periodic macroporous structure, the inverse opal films could self-report their surface status through changes in their visible optical transparency and structural colors. These features make such slippery structural color materials highly versatile for use in diverse applications.

4. Experimental Section

Fabrication of PU Inverse Opal: Free-standing PU inverse opals were fabricated using a sacrificial template method. The opal templates were obtained by assembling a latex suspension of SiO$_2$, synthesized by our group, with a concentration of about 0.5 wt% and a latex diameter of 300 nm, at invariant temperature and humidity by a vertical deposition method. N,N-Dimethylformamide solution containing 20 wt% PU was infused and polymerized in the voids of the silica colloidal crystals. The PU was infiltrated into the SiO$_2$ opal templates by a dip-coating method. The molecular weight of PU was about 168 000. The composite films were dried at 60°C followed by HF etching for 1 h to obtain the inverse opals.

Liquid Lubrication and Stretch Slippery Test: Krytox 103 was added to the substrate and uniform coverage was achieved by tilting. The thickness of the overcoated layer can be controlled by the fluid volume given a known surface area of the sample. The stretching of the membrane was carried out by a uniaxial stretcher vernier caliper. The evolution of the distance between the arms was measured during the experiment, which was further used to calculate the strain of the membrane.

Characterization of Optical and Sliding Property: SEM images were obtained from a field emission scanning electron microscope (FE-SEM, HitachiS-3000N, Japan). In situ reflectance spectra were collected by a fiber optic spectrophotometer (Ocean Optics, Inc., HR 2000 256 UV–vis–NIR). Color photos and video were taken on a digital camera (Canon5D Mark II, Japan). Water contact angles were obtained by a JC2000D2 contact angle measuring system at ambient temperature. Contact-angle hysteresis was measured by increasing and decreasing the droplet volume while taking screenshots and extracting the advancing and receding contact angles. Sliding angles were measured on a customized tilting stage with a droplet volume of 20 mL. All contact angle values specified in the text were averaged over at least ten individual measurements.
Supporting Information

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

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