Functional Liquid Crystal Polymer Surfaces with Switchable Topographies

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Surface coatings, as interfaces between functional devices and targeted objects, are critical in the performance of functional devices. Switchable topographies bring opportunities to regulate the functionality of surfaces, ranging from morphing and controllable friction to object lifting and debris removal. Various responsive materials have been investigated to develop switchable surfaces, among which liquid crystal (LC) polymers are attractive candidates due to their anisotropic properties. Herein, focus is put on recent reports of switchable surfaces made of LC polymers. The principle of actuation of LC polymer–based switchable surfaces is introduced, with following exemplary applications derived from these responsive surfaces in the field of surface morphing, switchable surface friction, and moving/lifting of objects. Finally, future possible applications of and challenges in using dynamic coatings with switchable surface topographies are discussed.

1. Introduction

In nature, creatures have evolved with various surfaces to tackle tasks, ranging from lotus leaves with delicate microstructures for self-cleaning to elusive skins of marine creatures secreting slippery mucus for defense.[1–6] Inspired by these biological examples in nature, scientists have developed artificial surfaces with special physical or chemical characteristics for impressive performance and functionality.[7–12] Switchable physical or chemical properties offer possibilities to regulate the function on demand with external stimuli.[13–18] Among various parameters, surface topography is a key physical factor that can affect the functions of surfaces. Surface morphing, also referred to as a switch in topographies, would affect the performance of surfaces. For example, a change in surface roughness would alter its friction coefficient,[19] while propagating waves on surfaces could be useful in the transportation of droplets.[20–22] Therefore, morphing surfaces and changing their topographies accordingly is desirable in practical applications to achieve certain functions. To date, various materials have been investigated to fabricate switchable surfaces with switchable topographies, such as hydrogels,[23–26] silicones,[17,25] and liquid crystal (LC) networks/elastomers.[31,26,27] The various materials that are known to deform their surfaces exhibit both unique advantages and shortcomings. With hydrogels, the shrinking/swelling mismatch is often used to induce shape change of the hydrogels.[28–31] As biocompatible materials, hydrogels are promising in biomedical applications.[32,33] Living cells can be even embedded in hydrogels to form morphed living composites.[32] However, hydrogels need the presence of water or other liquids to initiate local swelling differences to form the surface structures. For the systems made of silicones, poly(dimethylsiloxane) (PDMS) elastomers are often used as soft substrates to fabricate bilayer systems to form wrinkles on surfaces.[17] PDMS has been demonstrated to be a promising material in wearable devices, where PDMS-based switchable surfaces would be useful for instance in haptic applications.[34–36] However, the wrinkled structures are rather random and lack directionality. In LC polymers, LC mesogens are usually aligned in a certain order. Their advantage of anisotropic properties enables the possibility of programming deformation modes of LC polymer–based responsive surfaces. In this review, we will highlight the recent research progress in the development of responsive surfaces, especially those made of liquid crystalline polymers, and give a perspective on the future development of switchable surfaces.

2. Principle: LC Polymers and Anisotropic Deformation

LC polymers are materials where molecular entities are organized following the LC order, such as in nematic or smectic phases.[26,37] Most recently studied functional LC polymers can
be classified as liquid crystal networks (LCNs) or liquid crystal elastomers (LCEs).\textsuperscript{25,30} LCNs are usually glassy polymers with the glass transition temperature ($T_g$) higher than room temperature, while LCEs are elastomeric polymers with $T_g$ around or below room temperature. They are usually prepared either by cross-linking of an LC side-chain polymer or via a photoinduced polymerization of LC reactive mesogens (RMs)/oligomers and LC order is kept in the formed network. Usually, the LC order is quantitatively characterized using the order parameter $S$ with the equation

$$S = \frac{3 \cos^2(\theta) - 1}{2}$$

where $\theta$ is the angle between the LC molecular axis and the local LC director.\textsuperscript{39} Typically, the $S$ of nematic LCNs and LCEs is between 0.6 and 0.7, while that of the smectic polymers can be somewhat higher.

For most practical applications, LC mesogens are macroscopically oriented along a local director, which can be uniaxial, splayed, bended, twisted, or helicoidal. When the order parameter of the cross-linked LC polymer is decreased, the system exhibits anisotropic deformation. In response to the reduction of the order parameter, a uniaxial LC polymer contracts along the LC director and expands in perpendicular directions, as shown in Figure 1a.\textsuperscript{40,41} The reduction of the order parameter can be induced by external stimuli, such as heat, light, humidity, and electric fields.\textsuperscript{16,27,42–52}

The order parameter reduction can be combined with programmed LC alignment to afford two kinds of stimulation: actuation of free-standing films with director variation in the film thickness direction and topographical deformation with director variation in the lateral direction. The director variation in film thickness direction is usually used to develop actuators that are capable of performing bending, twisting, or more complex motions in typically free-standing stripe-shaped films, which would be useful in developing soft robots.\textsuperscript{21,45,53–61} For instance, polymerizing an RM in a glass cell with a planar alignment layer on one side and homeotropic alignment layer on the opposite side, an LCN with a splay configuration can be harvested (Figure 1b-i, ii). Upon thermal stimulation and order parameter reduction, the splay-configured LCN film deforms from straight to curled, as shown in Figure 1b-iii at 29 °C to Figure 1b-iv at 150 °C.\textsuperscript{62} While in cases where the director variation is in the lateral direction with respect to the coating/film plane, surface topographical deformation occurs upon stimulation in the films either free-standing or attached on substrates, which will be the focus in following sections.

Based on the order parameter controlled anisotropic dimensional changes of microscopic domains, the bending of a film can also be induced by the introduction of lateral spatially varying director distribution into the LC polymer. For example, Ikeda and coworkers demonstrated the polarized UV light–triggered bending behavior of a free-standing polydomain LC polymer film (Figure 1c).\textsuperscript{43} Due to the high concentration of azobenzene moieties, the UV light could not penetrate the film. It is mostly absorbed by materials in the film surface. Azobenzene moieties that are aligned parallel to the light polarization undergo trans–cis isomerization and result in shrinkage of microscopic domains in the direction parallel to the light polarization. Due to the gradient of light absorption across the film thickness, the shrinkage deformation at the top is larger than at the bottom surface, leading to the bending behavior of the whole film.

3. Surface Morphing

Nonuniform LC director profiles can be precisely engineered by means of photoalignment methods using photosensitive

![Figure 1. a) Illustration of the anisotropic deformation of LCN upon order parameter reduction by stimulation. Reproduced with permission.\textsuperscript{40} Copyright 2018, Wiley-VCH. b) Application of the anisotropic deformation property in macroscopic actuation of a splay LCN film. i. LC director profile varies across the film thickness. When the order parameter is reduced, the planar side of the film would shrink whereas the homeotropic side would expand. ii. Cross-section SEM image of the splay LCN. Reproduced with permission.\textsuperscript{53} Copyright 2009, Springer Nature. iii. Splay LCN at 29 °C, iv. curled at 150 °C. Reproduced with permission.\textsuperscript{62} Copyright 2005, Wiley-VCH. c) Bending of the polymer film with polarized light. Reproduced with permission.\textsuperscript{45} Copyright 2003, Springer Nature.](image-url)
dyes/polymers. Complex director patterns are used to induce both the formation of curved surfaces and/or to induce surface morphing.\[63–65\] De Haan et al. developed LCN films with complex LC director patterns by using the photoalignment method.\[46\] Different alignment patterns have been generated using this method, including azimuthal, spiral, radial, ½ clockwise, ½ counterclockwise, and complex sun alignments. LC polymer films with defect patterns can be deformed into complex shapes with photothermal stimulation. For example, a film with a radial alignment deformed into an anticone shape upon stimulation (Figure 2a-i), caused by contraction along the radial direction and expansion along the azimuthal direction. With a similar mechanism, a film with azimuthal defect could be deformed into a cone shape upon photothermal stimulation (Figure 2a-ii). In addition to LCNs, lightly cross-linked LCEs were developed by White and coworkers, where the film was engineered with an array of defects to form a voxelated surface upon thermal actuation (Figure 2b).\[27\] The lightly cross-linked LCE is prepared by free-radical photopolymerization of acrylate end-capped oligomers synthesized via the Michael addition reaction of nematic diacrylates to a primary amine. Due to the elastomeric property, the actuation strain is large up to 55%. Except for heat, topographical features of LCE sheets can also be controlled with either light\[66\] or electrical stimulation.\[50,67,68\]

To obtain arbitrary control of surface patterns, Yang developed a photolithographic method using microchannels to spatially and arbitrarily control LC orientations with a (sub)micron resolution (Figure 2c-i).\[69\] This methodology could be combined with numerical calculations to design the direction of microchannels to afford the desired 3D shaped surface upon stimulation, with an example of a face texture emerging at thermal stimulation (180°C) from a flat surface (Figure 2c-ii).\[70\] With this methodology, the surface pattern can be designed arbitrarily and precisely. Another noted facile strategy to form an arbitrary pattern is by selectively patterning the LCE with photothermal dopants (e.g., gold nanoparticles) to morph the LCE film by photothermal actuation accordingly, even with flood light exposure.\[71\]

4. Ciliated Surfaces

Ciliated surfaces are ubiquitous in many biological organs with various functions, including cleaning and transportation.\[72–76\] Scientists have been inspired by these examples to develop functional surfaces with cilia for various purposes.\[55,77–84\] For instance, Toonder et al. developed an electroactive artificial array for microfluidic mixing.\[84\] The polyimide–Cr double-layered elastic cilia are in the curled state initially. When a voltage is applied between the Cr layer and indium tin oxide, the electrostatic attraction force induces the cilia rolling out and extending over the surface, while when the electrical stimulation is removed, the cilia roll back to the initial curled state by the stored elastic energy. This electroactive cilia array has been proven useful in inducing the fluctuation of liquids, for instance, low-viscosity silicone oil. Using light as wireless stimulation, Oosten et al. fabricated light-responsive artificial cilia using a facile method inkjet printing that can be controlled wirelessly and remotely.\[55\]

Two kinds of azobenzene derivatives are utilized to make the cilia sensitive to light with different wavelengths, including UV light and visible light, and obtain various deformation modes (Figure 3a). The light-sensitive artificial cilia are capable of inducing turbulence in water upon stimulation with light. Fiber arrays were

![Figure 2](https://example.com/image.jpg)

**Figure 2.** a) Photothermal actuation of films with radial and azimuthal alignment. Reproduced with permission.\[46\] Copyright 2012, Wiley-VCH. b) Photographs of LCE film with nine +1 topological defects between crossed polarizers. The director orientation varies azimuthally around the defect. Nine cones arise from the LCE defect array when heated and reversibly flatten upon cooling. Reproduced with permission.\[27\] Copyright 2015, The American Association for the Advancement of Science (AAAS). c) i. Designing a face-texture surface using both a metric tensor and curvature tensor by controlling the director fields on the top and bottom surfaces of the LCE sheet. ii. The LCE sheet takes the shape of a face when actuated at an elevated temperature (180°C). Reproduced with permission.\[70\] Copyright 2018, National Academy of Sciences.
demonstrated to be useful in transporting objects. For instance, fibers made of LCE with azobenzene moieties as the cross-linker could bend toward the UV light source (Figure 3b).[85] By changing the incident direction of the UV light, the bending direction of fibers is changed and becomes asymmetric by changing the lamp position to transport liquid and floating particles. A recent study also demonstrates its application as a light guide.[86] Compared to systems with two stable actuated and nonactuated states, oscillating systems with dynamic states would be more interesting and desirable.[21] Recently the application of magnetically responsive ciliated surfaces has been demonstrated by Toonder and coworkers in removing sand particles under the stimulation of a rotating magnetic field.[83] White et al. used a polarized multiwavelength Ar⁺ laser beam (457, 488, and 514 nm) to induce the oscillation of an azo-LCN with uniform alignment, by taking advantage of the fast isomerization of azobenzene moieties under the laser beam and the self-shadowing effect.[87] Notably, in these two examples, the systems work unattended without much human interference, using either the programmed magnetic field or static photonic field. A more general strategy was developed via the combination of the self-shadowing effect and photothermal effect.[53] Upon photoheating, a splay LCN undergoes bending; with the self-shadowing effect, the film oscillates in a static photonic field. A range of light with different wavelengths can be chosen by selecting proper photothermal dyes/reagents, ranging from UV light to NIR light.[53,57,71] From a broader perspective, this combinational method of photothermal effect and self-shadowing is also applicable to other responsive materials.[88,89] For instance, Zhao and coworkers demonstrated the application of the photothermal strategy in the design of sunflower-like biomimetic omnidirectional trackers (SunBOT), which applies to various kinds of responsive materials, ranging from hydrogels and polymers to LCNs.[88] The SunBOT is able to intrinsically detect and accurately track the direction of the incident laser with a large range of zenith angles from 20° to 150° (Figure 3c-i).

Figure 3. a) Printed light-driven cilia flaps in the water medium. The cilia respond to light of different wavelengths due to different azobenzene moieties in the LCN. Reproduced with permission.[55] Copyright 2009, Springer Nature. b) LCE fiber arrays bend toward the light source under UV light (365 nm) exposure. Reproduced with permission.[85] Copyright 2016, Wiley-VCH. c) Artificial phototropism of the SunBOT and the underlying mechanism. i. Gold nanoparticles–poly(N-isopropylacrylamide) SunBOT in water detects and tracks the incidence angle of the laser. ii. The underlying mechanism of the feedback loop of phototropism using the photothermal effect. Reproduced with permission.[88] Copyright 2019, Springer Nature.
The underlying mechanism of this artificial phototropism originates from the self-shadowing effect and photothermal effect (Figure 3c-i,ii). The photothermal effect first induces shrinkage at the side near the incident light and the pillar bends toward the incident light. When the bending reaches the incidence angle of the laser, the self-shadowing effect causes the tip to block light from illuminating the bent hinge, and the temperature of the hinge decreases. This slightly lower temperature than the transition temperature leads to the slight unbending of the hinge until the exposure of the hinge to the light and reaching the equilibrium state. Interestingly, this principle applies when the cross-linking density is relatively high and the response is slow. For systems with a lower cross-linking and faster response, the system exhibits an out of equilibrium oscillation,[89] which is similar to the photoinduced oscillators developed by White et al. and Gelebart et al.[93,87]

5. Switchable Topographies of Coatings Adhered on Substrates

5.1. Shear Stress–induced Topographical Deformation

In addition to free-standing LC polymer films, the surface topography of coatings adhered to substrates can be altered with stimuli. The most distinguishing characteristics between coatings and free-standing films lie in the restriction of lateral deformation in coatings. As the coatings are firmly fixed on rigid substrates, the deformation can only escape in the thickness direction, and lateral deformation is prohibited, manifesting as the surface topographical deformation of coatings. The first demonstration of a topographical deformation was performed on an LCN coating consisting of isotropic and chiral nematic domains.[43] Upon heating (200 °C), the chiral nematic domains expand in the direction along the helix axis, with larger amplitude in cholesteric domains than isotropic domains, generating protrusions in the cholesteric areas. In addition, neighboring domains can be programmed with different alignment to introduce shear stress into the system. Liu et al. used a localized electric field to transform part of an originally planar orientation into homeotropic alignment and obtained coatings with alternatively aligned cholesteric and homeotropic orientations.[90] Azobenzene moieties were incorporated in the system to make it light-sensitive. Using order parameter reduction induced by the trans–cis isomerization of azobenzene, the homeotropic areas shrink in height and create lateral stress absorbed by the adjacent planar areas, elevating the planar areas (Figure 4a). Multidomain configurations can also be induced by self-assembly.[40,91–93] For instance, chiral dopants in the LC mixture are capable of inducing the formation of fingerprint texture on the substrate with homeotropic polyimide, due to the cooperation of the twisting force from chiral dopants and vertical anchoring force from polyimide.[93] LC mesogens adopt a helicoidal arrangement with alternatively aligned homeotropic and planar orientations. With azobenzene moieties in LCN and UV light illumination, the homeotropic orientation would shrink in the z-direction, while the lateral expansion–induced shear stress is absorbed by the adjacent planar domains. This lateral stress contributes additionally to the expansion of planar areas in the z-direction together with the order parameter reduction (Figure 4b). With light as stimulus, the topographical deformation is triggered remotely and wirelessly.

Topographical deformation can also be achieved via an electric field, which is a desired stimulus for the facile integration of responsive materials into devices with existing electronic techniques for practical applications. For instance, Feng et al. used an array of interdigitated electrodes to provide an in-plane alternating electric field to actuate the fingerprint LCN coating (Figure 4c).[89] With electrical stimulation, LC mesogens respond by oscillating with a small amplitude in the alternating electric field, causing the reduction of the order parameter and topographical deformation. In addition to this macroscopic deformation with a typical height at the scale of hundreds of nanometers, the surface was observed to oscillate chaotically with minor amplitude. The electrically induced topographical deformation and surface oscillations are promising for cleaning tilted surfaces without water, an application which is of special interest to clean surfaces in rural and dry areas, such as solar panels in the desert. Since intrinsically the homeotropic orientations in the fingerprint LCN coating decrease while the planar orientations increase in height, the topographical deformation mode depends on the initial state of relative height between homeotropic and planar areas. Feng et al. developed methods using the dichroism of a dichroic photoinitiator and dye to control the relative height between homeotropic and planar orientations, based on controlled material diffusion during polymerization.[94] Dichroic molecules align with the LC host and exhibit larger light absorption in planar areas than homeotropic areas. Therefore, for system I with the dichroic photoinitiator, the photoinitiation and polymerization rates in planar areas is faster than in homeotropic areas. Monomers diffuse from monomer-rich homeotropic areas to monomer-depleted planar areas, and the planar areas will be higher than homeotropic areas after polymerization (Figure 4d-i). For system II with dichroic dyes, on the contrary, the polymerization is inhibited in planar areas due to the larger light absorbance of the dichroic dye and smaller photoinitiation of the isotropic photoinitiator. Correspondingly, monomers diffuse from planar to homeotropic areas, resulting in higher homeotropic areas than planar areas (Figure 4d-ii). These two kinds of coatings exhibit different modes in stimulation: In system I, the surface corrugation is enhanced as planar areas go further up and homeotropic areas go further down; in system II, however, the surface corrugation is inverted as initially lower planar areas would be elevated and initially higher homeotropic areas shrink in height during stimulation.

In addition to the self-assembly method, photoalignment is an alternative method to form programmed textures. Hendrikx et al. prepared LCN coatings (Figure 5a-i) using a photoalignment method.[95] The domains were engineered with orthogonal planar orientations, leaving a defect line in between. As azobenzene monomers were incorporated in the LCN, the order parameter would be reduced upon UV illumination. Upon the reduction of the order parameter, for the domain with alignment parallel to the defect line, the LCN domain contracts in the direction parallel to the defect line and expands perpendicular to the defect line, generating pushing lateral stress to the neighboring domains, elevating the areas near the defect line. On the contrary, the neighboring
domain with the orthogonal alignment absorbs the lateral stress and exhibits the opposite deformation, becoming depressed (Figure 5a-ii). The deformation amplitude could be amplified using a compliant elastomer instead of a rigid glass as the base for the LCN (Figure 5a-iii).

Except for the binary “On” or “Off” states of surface topographical actuation, Hendrikx also demonstrated surface oscillations using illumination with green light (455 nm) and polarized UV light (365 nm). The polarization direction of the UV light was constantly rotated, which was realized with computer-aided mechanical rotation of the polarizer.

To prepare complex microscopic defect patterns, Wei and coworkers developed a plasmonic method to program microscale defect patterns into LCNs. With the developed microscopic defect patterns, Lavrentovich et al. demonstrated their topographical deformation with thermal stimulation. The radial defect turns into depression upon thermal stimulation due to the activation force pushing materials away from the defect center and toward the periphery (Figure 5b); in contrast, the center of the circular defect becomes elevated at high temperature as a result of the activation force pushing materials to the defect center. With the photoalignment method, the LC alignment pattern can be freely programmed, enriching the application scenarios of switchable surfaces.

5.2. Free Volume Generation–Induced Topographical Deformation

Except for shear stress between domains with spatially varying LC directors, extra free volume is also generated in the actuation process. The concept of free volume was first used by Eisenbach...
et al. to elaborate on the influence of the polymer matrix on the azobenzene isomerization kinetics. Free volume is required in azobenzene isomerization to allow segmental movements of polymers and the conformation rearrangement of the polymer chains neighboring the azobenzene moieties. Liu et al. found that density decreases due to the generation of free volume when the LCN is illuminated with UV light, as shown by the density measurement experiments in salt water (Figure 6a-i). With UV illumination, the azobenzene-containing LCN film at the bottom floats to the top of the water surface, indicating a decrease in the LCN density and formation of extra free voids inside the LCN. The generation of free volume manifests as the surface topographical deformation of a chiral-nematic coating with part of the coating being illuminated using a photomask. Further studies have revealed that the generation of free volume is largely enhanced by the oscillation of the LC polymer network using the dynamic trans–cis–trans isomerization of azobenzene by the illumination of 365 and 455 nm light with proper light intensity regulation (Figure 5a-ii). Later Liu et al. used an alternating electric field to trigger the oscillation of an LCN. An AC electric field was applied to the LCN coating via interdigitated electrodes (Figure 6b-i). The LC mixture had a net positive dielectric constant and the LCN was of homeotropic alignment. Dynamic disorder is introduced into the LCN with the electrical actuation by exerting oscillatory stress on the LCN, thereby creating molecular voids and extra free volume. In the in-plane alternating electric field, the electric torque exerted on mesogens at the electrode gap areas is larger than electrode areas, triggering more free volume generation and thus surface protrusions at the electrode gap areas (Figure 6b-ii–iv). When the LCN is excited by the electric field at its resonance frequency, a maximal free volume creation is

Figure 5. Topographical deformation caused by the lateral stress in planar domains. a) i. Graphical illustration of the LCN coating consisting of domains with orthogonal alignments on top of a compliant polymer layer. Topographical deformation of LCN coatings with ii. rigid glass and iii. A compliant polymer layer as the substrates. Reproduced with permission.[96] Copyright 2018, Wiley-VCH. b) i. PolScope image of a flat LCN coating with radial defects at 30 °C, which maps the optical retardance and director orientation. ii. Surface depressions developed by the radial defects upon heating. iii. PolScope image of a flat LCN coating with circular defects at 30 °C. iv. Surface elevations developed by the radial defects upon heating. Adapted with permission.[97] Copyright 2018, Springer Nature.
observed. Surface oscillation during electrical stimulation has also been revealed with laser speckle imaging in further studies.[103,104]

The aforementioned two strategies of shear stress and free volume-induced topographical deformation have their respective characteristics. The strategy based on shear stress is more universal and can be used to program the surface structure arbitrarily by controlling the alignment configuration of LC polymers, while the strategy based on free volume depends on precise light actuation of the responsive moieties of LC polymers in the case of a light trigger or an optimized field frequency and the presence of dielectrically responsive molecules in the case of electrical actuation. In the latter case, the design of the electrode structure determines the shape of the structures being formed.

6. Application of Switchable Surfaces

Switchable surfaces are useful in many potential applications. In this section, we will focus on systems made of LC polymers, with a brief introduction to some noted examples made of other materials.

6.1. Lifting/Moving Solid Objects

Switchable surfaces are capable of moving or lifting objects on top. With cross-linked networks of fingerprint texture, the fingerprint texture direction could not be rotated but topographical deformation and surface oscillation are induced by an alternating electric field.[40] Feng et al. demonstrated the removal of discrete sand grains from an active area with the topographical deformation of a fingerprint LCN coating, while the sand grains at the nonactive area without an electrode remained intact (Figure 7a). Macroscopically, the topographical deformation was demonstrated to work for the sliding down of sand from the tilted panels (Figure 7b), which would be promising in dry removal of dust from optical elements in rural areas where water is precious or not available. The switchable surface topology could also control the placement of microparticles with designed valleys on the surfaces. To form valleys in the stimulated state, a linear singular (LS) director pattern was programmed into the LCN (Figure 7c).[105] Across the LCN coating thickness direction, there are right- and left-handed twist profiles of the LC director separated by the disclination line. Upon UV illumination, the azobenzene transforms to the cis-bend configuration, resulting in the order parameter's reduction and triggering the formation of valleys along the disclination line. Driven by gravity, the microparticles are re-placed in the valleys. Similarly, the alignment pattern can also be programmed to be circular with concentric singular disclinations to collect the microparticles in a circular pattern. Notably, all these particle placement processes are conducted in a water medium, which would aid to alleviate or even eliminate the electrostatic interaction between microscale particles and the coating surface.

Switchable surfaces can also perform macroscale work in lifting loads.[27,69,106] For instance, upon heating, LCE-based voxelated films with a defect array could lift a load 147 times heavier than the weight of the LCE film with a stroke of $\approx 3000\%$ when actuated by heating at 175 °C (Figure 8a).[27] To enhance the capability to lift loads, White et al. developed multilayered laminated LCE films with thickness up to 300 μm by laminating layers of LCE (50 μm thick) with the LC oligomer as both the LCE and adhesive.[104] With four layers of LCE, the film with a 2 × 2 array of +1 topological defect was capable of lifting a load over 1100 times its weight (Figure 8b). Three stacked LCE films were capable of achieving a stroke over 6 mm with a load 120 times the weight of the films on top.
Figure 7. a) The topographical deformation of the fingerprint LCN coating remove discrete grains from active areas on a tilted stage. b) The sand was cleaned from the electroactive fingerprint LCN coating on a tilted stage with the aid of topographical deformation. Reproduced with permission.\textsuperscript{[40]} Copyright 2018, Wiley-VCH. c) Placement of particles using responsive topographies. i. Director representation of assembled cells consisting of the LS configuration. ii. 3D topographical image of the actuated coating with LS configuration. iii. Microparticles assemble at the topographically low disclination sites. Reproduced with permission.\textsuperscript{[105]} Copyright 2020, ACS.

Figure 8. a) A flat LCE polymer sheet was morphed to the voxelated state upon heating to 175 °C, which could be used to elevate objects on top. Reproduced with permission.\textsuperscript{[27]} Copyright 2015, The American Association for the Advancement of Science (AAAS). b) A multilayer LCE film with a defect array exhibits enhanced capability to lift a load that is 1100 \times its weight upon thermal stimulation. Three stacked LCE films were capable of achieving a stroke over 6 mm with a load 120 times the weight of the films. Reproduced with permission.\textsuperscript{[106]} Copyright 2018, Springer Nature.
6.2. Switchable Friction

Surface topography and roughness are important factors influencing surface friction. By changing the surface structures, the friction can be altered accordingly. For instance, Liu et al. used the alternating homeotropic/cholesteric patterns introduced in Figure 4a to form striped-patterned surface protrusions via UV light stimulation (Figure 9a-i). With surface protrusions, the friction coefficient was changed accordingly. The surface friction could be affected not only by the surface corrugation itself but also by the relative orientation of ridges at the two coatings in contact with each other. When the ridges are parallel and interlock with each other in motion, the static friction coefficient is largely enhanced; for the case that the motion is parallel to the ridges, the surface friction is only slightly increased. When the ridges’ orientations are orthogonal, the surface friction is even reduced by a reduced contact area (Figure 9a-ii). Feng et al. demonstrated the enhancement of surface friction using a polydomain system with simultaneously applied UV light and electrical stimulation. The surface topography can be changed by independently applied UV light or electric field; the surface changes from a flat to corrugated state, creating interlocking joints on the surfaces, which increase the surface static friction coefficient and critical sliding angle (Figure 9b-i–iii). When electrical and UV light stimulation is applied simultaneously, the deformation amplitude and static friction coefficient are greatly enhanced, rendering the object held at the angle of 90° (Figure 9b-iv). Interestingly, the surface topographical deformation and surface friction property are related to not only the applied stimuli but also the stimulation history (Figure 9b-v, vi), due to the promoted cis–trans isomerization of azobenzene by the electrothermal effect in the presence of electrical stimulation.[107]

Figure 9. a) Light-controlled surface friction using switchable LCN coating patterning. Reproduced with permission.[19] Copyright 2014, The Royal Society of Chemistry. b) Electrical and light control of surface friction using dual-responsive LCN coating. Reproduced with permission.[93] Copyright 2020, Wiley-VCH.
This example demonstrates the possibility of programing logic gates into switchable surface topographies using multistimuli responsive systems.

6.3. Functional Coatings Made of Other Responsive Materials

In the previous sections, we have reviewed the development and potential applications of switchable surfaces made of LC polymers. Beyond this classification, there are also many interesting reports of switchable surfaces made of other materials. In this section, we will briefly introduce some relevant examples.

A noted exemplary application is the manipulation of water droplets. The wetting behavior of surfaces is closely related to surface structures. By patterning the surface with polygonal posts made of SU-8, the droplets deposited on top adopt different shapes due to the anisotropic wetting,\(^\text{108}\) ranging from octagonal to hexagonal, depending on the geometry of the posts. With the anisotropic wetting behavior depending on the surface structure, the liquid wetting can be switched between isotropic and anisotropic by changing surface structures.\(^\text{109}\) The surface can also be engineered between adhesive/nonadhesive states by switching the surface between a low-adhesive Cassie state and an adhesive flat state.\(^\text{110}\) Another strategy to manipulate droplets on the surface is to combine the concept of slippery liquid–infused porous surface (SLIPS)\(^\text{8}\) with switchable surface topographies.\(^\text{111–114}\) Surfaces were switched between a slippery state overcoated with a lubricant and a rough state free of lubricant, which could be triggered by mechanical stretching or electrical stimulation.\(^\text{111–113}\) Magnetic fields can also be used to trigger the pop-up of the surface made of iron/poly(dimethylsiloxane) (Fe/PDMS) gel infused with silicone oil to increase the surface friction and manipulate droplets in air or bubbles underwater.\(^\text{114}\)

Switchable surface topographies are used to develop switchable optical elements. Films with switchable surface topographies can be switched between transparent and translucent states thanks to the light scattering of microstructures.\(^\text{17,25,115–118}\) Other applications of switchable surfaces include biomedical applications, such as regulating the cell adhesion, spreading, shaping, proliferation, migration, and differentiation.\(^\text{15,119–122}\)

7. Conclusion

Switchable surfaces are useful in many applications. In this review, we gave a retrospective of the principle, fabrication, and applications of switchable surfaces, especially those made of LC polymers. The intrinsic anisotropic properties of LC polymers enable researchers to more freely regulate the surface structures and deformation behaviors. Despite impressive progress in the development of functional coatings using LC polymers, several aspects still need to be fully explored. First, most of the previously reported switchable surfaces are stimulated by harmful UV light or very high temperatures (i.e., >100 °C) that are not suitable for some practical scenarios. Novel LC polymers should be developed to be responsive to ambient stimuli, such as visible/NIR light, ambient thermal stimulation, or electric fields of low strength.\(^\text{123,124}\) Second, systems that are sensitive to multiple stimuli are attractive, as multistimuli sensitivity enables the possibility of programing complex response behavior into logic gates and endowing the system with smart functions.\(^\text{93,125,126}\)

Third, continuous and autonomous surface oscillation in a stimulation field without much human interference would be desirable. Similar to the oscillating hydrogel induced by the Belousov–Zhabotinsky (BZ) reaction\(^\text{127}\) and the oscillation of LC actuators in a static photonic field,\(^\text{21,128}\) oscillating waves propagating in either lateral direction or vertical direction (to the coating thickness) are very interesting and useful, for example, in transporting of objects\(^\text{20}\) and cleaning of surfaces.\(^\text{40}\) Another point is that the unique characteristics of LC polymers, for instance, the difference in surface energies endowed by various alignments of LCs, could be combined with surface topographies to find more applications in biomedical applications, for example, aligning the cell alignment directions and cell adhesion.\(^\text{15,129,130}\)

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

liquid crystal polymers, particles mitigation, responsive cilia, switchable surface topographies

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[1] Y. T. Cheng, D. E. Rodak, C. A. Wong, C. A. Hayden, Nanotechnology 2006, 17, 1359.
[2] K. Autumn, A. M. Peattie, Integr. Comp. Biol. 2002, 42, 1081.
[3] G. Huber, H. Mantz, R. Spolenak, K. Jacobs, S. N. Gorb, E. Arzt, Proc. Natl. Acad. Sci. 2005, 102, 16293.
[4] A. Malshe, K. Rajurkar, A. Samant, H. N. Hansen, S. Bapat, W. Jiang, CIRP Ann. 2013, 62, 607.
[5] B. T. Clarke, Biol. Rev. 1997, 72, 365.
[6] L. D. Graham, V. Glattauer, Y. y. Peng, P. R. Vaughan, J. A. Werkmeister, M. J. Tyler, J. A. M. Ramshaw, Biological Adhesives, (Eds: A. M. Smith, J. A. Callow), Springer, Berlin 2006, p. 207.
[7] M. Sitti, R. S. Fearing, J. Adhes. Sci. Technol. 2003, 17, 1055.
[8] T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, Nature 2011, 477, 443.
[9] Y. Liu, L. Moevius, X. Xu, T. Qian, J. M. Yeomans, Z. Wang, Nat. Phys. 2014, 10, 515.
[10] D. Wang, Q. Sun, M. J. Hokkanen, C. Zhang, F.-Y. Lin, Q. Liu, S.-P. Zhu, T. Zhou, Q. Chang, B. He, Q. Zhou, L. Chen, Z. Wang, R. H. A. Ras, X. Deng, Nature 2020, 582, 55.
[11] S. Wang, K. Liu, X. Yao, L. Jiang, Chem. Rev. 2015, 115, 8230.
[12] Q. Sun, D. Wang, Y. Li, J. Zhang, S. Ye, J. Cui, L. Chen, Z. Wang, H.-J. Butt, D. Vollmer, X. Deng, Nat. Mater. 2019, 18, 936.
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