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Blueprinting Photothermal Shape-Morphing of Liquid Crystal Elastomers

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20
21 **Denotes equal contribution

22
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24

25 Liquid crystal elastomers (LCEs) are an attractive platform for dynamic shape morphing due
26 to their ability to rapidly undergo large deformations. While recent work has focused on
27 patterning the director orientation field to achieve desired target shapes, this strategy cannot
28 be generalized to material systems where high-resolution surface alignment is impractical.
29 Instead of programming the local orientation of anisotropic deformation, we develop here an
30 alternative strategy for prescribed shape morphing by programming the magnitude of stretch
31 ratio in a thin LCE sheet with constant director orientation. By spatially patterning the
32 concentration of gold nanoparticles (AuNPs), uniform illumination leads to gradients in
33 photothermal heat generation and therefore spatially-nonuniform deformation profiles that
34 drive out-of-plane buckling of planar films into predictable three-dimensional (3D) shapes.
35 Experimentally realized shapes are shown to agree closely with both finite element
36 simulations and geometric predictions for systems with unidirectional variation in

1 deformation magnitude. Finally, we demonstrate the possibility to achieve complex
2 oscillatory motion driven by uniform illumination of a free-standing patterned sheet.
3
4 Morphing of two-dimensional sheets into three-dimensional shapes is a useful strategy to
5 dynamically alter the physical properties of materials, offering diverse applications in fields
6 ranging from biomedical devices to advanced manufacturing.^[1] Over the past decade, numerous
7 studies have focused on programming desired three-dimensional structures of soft materials
8 such as shape-memory polymers (SMPs)^[2,3] and gels^[4-7] by introducing spatial variations in
9 thermal expansion/contraction, swelling, or molecular order.^[8] A particularly useful class of
10 materials to achieve dynamic two-dimensional (2D) to three-dimensional (3D) shape
11 transformations are liquid crystal elastomers (LCEs), where the coupling between the
12 orientational ordering of polymerized mesogens and the conformation of a polymer backbone
13 can be leveraged for large, anisotropic deformations that are dictated by the director field.^[9,10]
14 Using oriented surface alignment layers^[11] or microchannels,^[12] director orientation can be
15 patterned with a resolution approaching 10 μm .^[13] A subsequent reduction of nematic ordering,
16 usually driven by heating, leads to local contraction along the director and expansion along the
17 transverse directions, driving out-of-plane buckling into 3D shapes that are ‘blueprinted’ by the
18 pattern of director orientation. However, while geometric methods allow for the deduction of
19 the necessary in-plane director orientation field to generate a desired profile of Gaussian
20 curvature,^[14-17] there are a number of practical drawbacks to this approach. First, prescription
21 of complex director fields requires significant processing, making high-throughput fabrication
22 and evaluation of designs challenging. Additionally, the surface alignment methods needed to
23 specify director orientation with high spatial resolution are only amenable to certain chemistries
24 due to the need for high mesogen content, and thus cannot be widely generalized to all LCE
25 systems. For example, while classical LCE systems based on siloxanes,^[18,19] as well as recently
26 developed systems that rely on simple and efficient ‘click’ chemistries,^[20] offer attractive

1 thermal and mechanical properties for shape-morphing systems, they typically only allow for
2 alignment of the director field with coarse spatial resolution such as through application of shear
3 stress^[21–23] or magnetic fields.^[24] To circumvent the need for a spatially-varying director
4 orientation, where the *direction* of deformation varies but the magnitude is constant, a potential
5 alternative method to drive shape changes is to instead locally prescribe the *magnitude* of
6 deformation within an otherwise homogeneous director field. While spatial variations in the
7 extent of deformation have been widely employed for shape programming of isotropic
8 gels,^[4,7,25–28] and briefly considered in seminal theoretical work on LC polymers,^[29] this
9 approach has yet to be experimentally realized in LCE systems. Furthermore, no theory for this
10 means of shape programming in anisotropic materials exists despite the potential generality of
11 this method to any LCE system that can be aligned into a monodomain with a unidirectional
12 director field.

13
14 While most LCE systems rely on uniform heating to trigger shape change, optically-driven
15 shape morphing is an attractive approach owing to the remote deployability, spatiotemporal
16 control, and dynamic reconfigurability offered by using light as a control stimulus. Furthermore,
17 light-responsive systems are particularly useful for programming deformation profiles, either
18 through spatiotemporally patterned light fields or flood illumination of materials containing
19 localized inclusions of photothermal or photochemical moieties.^[8] Programmed buckling in
20 response to both patterned and flood illumination has been widely exploited in gel^[30–32] and
21 shape-memory polymer systems.^[33–36] In contrast, work on liquid crystalline materials has
22 focused primarily on the use of spatially patterned light^[37–40] with a few exceptions including
23 azobenzene-containing LCEs with shapes blueprinted by director orientation^[41] and glassy LC
24 polymer cantilevers with coarsely patterned photothermal hinges.^[42]

25

1 Recently, we introduced a method to spatially pattern gold nanoparticles (AuNPs) in LCE
2 fibers^[43] and hydrogel sheets^[44] with high spatial resolution using UV-induced photoreduction
3 of gold salt.^[45,46] Following patterning, exposure to visible light induces localized photothermal
4 deformation that drives shape-morphing. In this work, we explore the utility of this method to
5 blueprint shape changes of thin LCE nanocomposite (LCENC) sheets with unidirectional in-
6 plane director fields in response to flood illumination. Specifically, we show that discrete
7 patterns of photothermal inclusions can generate a rich array of dynamic shape changes due to
8 buckling driven by nearly discontinuous changes of in-plane deformation. Furthermore, smooth
9 variations in deformation can be programmed via grayscale patterning of AuNP absorbance to
10 yield more complex shape changes. Finite element method (FEM) simulations are used to help
11 understand the shapes selected by these materials, in concert with an analytical model based on
12 the principles of Gaussian morphing^[4,47-49] that provides a general approach to the design of
13 axisymmetric shapes through unidirectionally varying stretch profiles.

14
15 To fabricate monodomain LCEs, 50 μm thick planar nematic films are synthesized following
16 the work of Ahn and co-workers (see Supplementary Information, **Scheme S1**).^[50] This
17 chemistry is employed due to its amenability to formation of monodomain samples with
18 relatively low nematic-isotropic transition temperatures (T_{NI}) and large thermomechanical
19 strains. Briefly, n-dodecylamine and 8-amino-1-octanol are mixed in a 1:1 molar ratio with the
20 diacrylate mesogen RM82 with an overall stoichiometry of acrylate:amine functionalities of
21 1.1:1, selected to afford a cross-link density that allows for large strains while maintaining
22 sufficient mechanical robustness. All reactants are melted in a vial with 1 wt% photoinitiator,
23 filled between two rubbed polyimide-coated glass slides, and oligomerized in an oven overnight
24 at 55°C. Following oligomerization, films are photopolymerized under UV light and the
25 resulting monodomain samples harvested. To impart photo-responsiveness, gold nanoparticles
26 (AuNPs) are produced by in-situ photoreduction of gold salt within the pre-formed LCE films

1 as previously reported.^[43] LCE samples are swollen with a solution of HAuCl₃, oleylamine, and
2 photoinitiator and exposed to UV light through a photomask to produce AuNPs via
3 photochemical reduction (**Figure 1A**). Because the degree of gold reduction is controlled by
4 the dose of UV light, the resulting absorbance of the nanocomposite can be spatially
5 programmed using grayscale photomasks (**Figure 1B**).^[26]

6
7 The as-synthesized films are monodomain with a constant director orientation (**Figure S1**) with
8 an order parameter of $S \approx 0.6$ as measured by wide-angle X-ray scattering (WAXS),^[51] with a
9 glass transition temperature of $T_g \approx -4$ °C, a broad $T_{NI} \approx 100$ °C, and an elastic modulus parallel
10 to the director of $E \approx 9$ MPa (**Figure S2**). We note that introduction of AuNPs does not
11 significantly affect the thermal or mechanical properties of the films, as evidenced by DSC,
12 TGA, and tensile tests (**Figure S2**). Upon uniformly heating above 40 °C, samples reversibly
13 contract along the director and expand in the perpendicular directions, ultimately contracting to
14 60% of their initial length along the director when heated to 120 °C (**Figure 1C**). To probe the
15 effect of photothermal heat generation on deformation, films are placed on a hot plate at a
16 defined temperature and exposed to 200 mW cm⁻² of light with wavelength 530 nm. The length
17 at each temperature is recorded to define a stretch ratio, $\lambda = l_{final}/l_{initial}$ where $l_{initial}$ is defined
18 as the length along the director at room temperature. As shown in **Figure 1C** for the case of
19 maximum light absorbance, a photo-induced temperature change of $\Delta T \approx 20$ °C (**Figure S3**) is
20 observed. We note that in principle this temperature change could be substantially greater and
21 is limited by the intensity of the incident light source. Photo-deformation is maximized when
22 samples are held at 80-90 °C due to the proximity to T_{NI} ; thus, all subsequent experiments are
23 conducted at an ambient temperature of 85°C. Because AuNP absorbance determines the
24 magnitude of temperature change upon photothermal heating, control of light dose during
25 photoreduction can be used to systematically program the resulting photo-deformation. As

1 shown in **Figure 1D**, the stretch λ due to photothermal heating can be programmed from 0.77
2 – 0.92 by controlling the transparency of the photomask to UV light from 0% black (nearly
3 transparent to UV light) and 100% black (nearly opaque) during patterning. This introduces the
4 possibility to locally control photo-deformation—and thus shape transformation—through
5 judicious design of photomasks.

6
7 To connect the patterned photothermal heat generation to shape transformation, we develop
8 FEM simulations and a geometric model. In the FEM simulations, LCE sheets are modeled
9 using the neo-classical free energy density^[52,53] implemented into Abaqus as a user subroutine
10 UMAT. A stretch-temperature relation, fit to the experimental measurement (**Figure 1C**), is
11 introduced into the free energy to describe the temperature-dependent anisotropy of LCEs (see
12 **Experimental Section** and **Supporting Information**). Once a temperature field corresponding
13 to a specific design of photothermal patterning is prescribed, the equilibrium shape is solved by
14 FEM in Abaqus.

15
16 To model these shape changes geometrically, we turn to the principle of Gaussian
17 morphing,^[48,49] previously exploited for isotropic systems, and apply it to the anisotropic case
18 considered here. In this model, the in-plane deformation due to photothermal heat generation
19 defines a ‘target metric’ that describes how the distance between points in the flat sheet should
20 change upon deployment to generate a shape of defined curvature. We consider the case of
21 sheets with uniform orientation of the director along the u axis (**Figure 1A**), where the
22 magnitude of stretch λ is constant along u and varies as a function of v . Thus, the metric tensor
23 is given by

$$24 \quad \mathbf{g} = \begin{bmatrix} \lambda^2(v) & 0 \\ 0 & \frac{1}{\lambda(v)} \end{bmatrix} \quad (1)$$

1 Crucially, in this case, the local magnitude of stretch varies while the direction is constant,
 2 similar to the case of isotropic gels^[4,7,25–28] and equibiaxially-strained thermoplastics^[35,54] but
 3 distinct from the case of a director field with patterned orientation but uniform magnitude of
 4 stretch.^[11,17] Using Gauss’s *theorema egregium* (see **Supplementary Information** for a more
 5 detailed discussion), the Gaussian curvature can be calculated from the metric tensor by

$$6 \quad K = -\frac{1}{\sqrt{\lambda}}(\sqrt{\lambda}\lambda')' = -\frac{2}{3\sqrt{\lambda}}(\lambda^{3/2})'' \quad (2)$$

7 Thus, by solving Equation 2 for a desired curvature profile $K(v)$, a corresponding stretch profile
 8 $\lambda(v)$ can be computed. Finally, using an experimentally-determined calibration curve of stretch
 9 vs grayscale, a photomask can be generated to pattern the necessary photothermal profile is
 10 patterned into the nematic sheets (see **Supporting Information** for additional detail).

11
 12 Using this patterning method, we first investigate the effect of discretely patterned deformation
 13 profiles on the buckling of nematic sheets using a bi-strip geometry, where one-half of a square
 14 sheet is patterned with a stripe of AuNPs such that the photoactive region bisects the length of
 15 the sheet with the long axis of the stripe parallel to the director (**Figure 1A**). For the case where
 16 the lateral dimensions of the square film are much greater than the thickness (here,
 17 width/thickness = 200), heat dissipation by convection limits thermal broadening across the
 18 interface between the photoactive and non-photoactive regions (**Figure S3B** and **Supporting**
 19 **Information**). In addition, despite a through-thickness gradient in heat generation due to the
 20 strong absorption of light by the nanoparticles that is necessary to generate appreciable
 21 temperature changes, the thin nature of these films ensures that the resulting temperature
 22 distribution is nearly constant through the thickness of the film (**Figure S3C**). For the simple
 23 case of a discrete photothermally-heated stripe, the equilibrium in-plane length is almost
 24 discontinuous across the stripe interface as the photoactive region contracts along the director
 25 and the energetic cost of this step-change in deformation is relieved by buckling out-of-plane.

1 For square films with side length $l = 10$ mm, the films preferentially roll about an axis
2 perpendicular to the photothermal interface to form a bottleneck shape upon illumination as
3 shown in **Figure 1E**, where the non-heated and heated regions adopt different radii of curvature
4 that are smoothly connected over the interfacial region as predicted by FEM. We note that films
5 tend to roll with the direction of curvature away from the light. This suggests that while small
6 asymmetries in heating through the thickness inevitably exist due to the decay in light intensity,
7 this is not the dominant factor in biasing the buckling direction of the film, since a higher
8 temperature at the surface of the film facing the incident light should prefer curvature toward
9 the light source. This shape transformation is analogous to the case of isotropic hydrogel bi-
10 strips with two discrete regions of cross-link density.^[55] This shape transformation can be
11 rationalized as follows: while a discontinuous target metric encodes divergent positive and
12 negative Gaussian curvature on either side of the interface, the non-zero thickness of a real
13 sheet, and the corresponding bending energy cost to deform it, causes the curvature to be
14 smoothed out across the interface into regions of finite Gaussian curvature with opposite signs.
15 The resulting shape consists of two zero- K regions on either end of the sheet, smoothly
16 connected by a neck that contains regions of both positive and negative Gaussian curvature,
17 wherein stretching energy (i.e. deviations from the discontinuous target metric) balances the
18 overall bending energy of the sheet.

19
20 To probe the utility of this method to program a wider variety of shapes, a series of additional
21 patterns are investigated. For example, illumination of a square sheet with a centered
22 rectangular inclusion with the long axis oriented parallel to the director results in a saddle-like
23 shape that is symmetric about the axes parallel and perpendicular to the director that bisect the
24 center of the film (**Figure 2A**). Placement of a photothermal region in one quadrant of the film
25 drives bending about an axis diagonally bisecting the sheet, resulting in a wrinkled hyperbolic
26 surface (**Figure 2B**). Finally, inclusion of a large square in the center of the sheet drives rolling

1 about an axis perpendicular to the director and wrinkling along the edges of the sheet (**Figure**
2 **2C**). These deformations are similar to those observed in nematic sheets with polydomain
3 inclusions^[56] and isotropic gels with local photothermal inclusions^[44] and again result from a
4 balance of stretching and bending energies as the films attempt to accommodate the
5 discontinuous target metric.

6
7 Remarkably, a simple change in the direction of the film edges with respect to the director and
8 photothermal inclusions leads to more complex behavior. When nanoparticles are patterned in
9 half of the film with the interface between the photoactive and non-photoactive region
10 extending diagonally between opposing corners of a square film at a 45° angle to the director
11 (**Figure 2D**), flood illumination from directly above the film drives wrinkling as observed for
12 the other striped case (**Figure S4**). However, when the sheet is illuminated from a 30° angle
13 with respect to the substrate along the edge parallel to the director, the film is observed to
14 oscillate continuously between two buckling modes (**Figure 2E-G**, **Videos S1-2**, and
15 **Supporting Information**). Initially, the film adopts a geometry such that the edge of the film
16 along the director curls about an axis perpendicular to the director, denoted as Mode 1. However,
17 the shape slowly evolves over a few seconds to become a full wavelength wrinkle (Mode 2)
18 that quickly snaps back to Mode 1 after several seconds as evidenced by the nearly
19 discontinuous change in film edge displacement when tracked from a 60 fps video (**Figure 2F**),
20 with a characteristic snapping time of ≈ 0.1 s. This cycle then repeats for the duration of
21 illumination. Inter-snap times range from 1.2 to 11.8 seconds, with an average time of 3.8
22 seconds. While oscillation due to self-shadowing effects^[37,42,57-59] and snapping between two
23 bistable shapes^[60,61] has been reported previously in nematic beams, cyclic oscillation via
24 photoinduced snapping has only been reported in one other case,^[62] to our knowledge. We
25 hypothesize that this phenomenon is driven by self-shadowing, where slight changes in the
26 incident light intensity due to deformation toggles the equilibrium between buckling modes.

1 Though our FEM methods are unable to capture dynamic behavior at this time, we find that if
 2 a strain profile is imposed that is consistent with a high light intensity on the edge of the film
 3 and with less stretch in areas where the light would be blocked during shape evolution, Mode
 4 2 is predicted, suggesting that self-shadowing is capable of driving a transition in buckled
 5 geometry, and hence the oscillatory snapping behavior observed here (See **Figure S5**,
 6 **Supplementary Information** for more detail). Films of other geometries do not demonstrate
 7 oscillatory behavior when exposed to similar oblique illumination conditions (**Figure S6**).
 8 While further study is warranted to fully understand the underlying mechanics of this
 9 phenomenon, this behavior suggests that localized deformation can be leveraged for non-
 10 equilibrium behavior and impulsive motion upon judicious design of photo-induced buckling
 11 instabilities and illumination conditions.

12
 13 Next, we explore the utility of smoothly-varying spatial gradients in absorption to introduce
 14 continuous in-plane stretch profiles into nematic sheets, which provides opportunities to
 15 program shapes with arbitrary Gaussian curvatures. As a proof-of-concept, we first investigate
 16 the ‘forward’ problem, i.e. defining a stretch profile and evaluating the match between
 17 experiments, FEM simulations, and geometric predictions for the resulting 3D shape. As a
 18 convenient test case, we use stretch profiles of the following form to program square sheets:

$$19 \quad \lambda(\xi) = \lambda_{min} + (\lambda_{max} - \lambda_{min}) \exp\left(-\frac{1}{2}\left(\frac{2\xi-1}{d}\right)^2\right), \quad (3)$$

20 where $\xi = \frac{v}{w} \in [0,1]$, λ_{min} and λ_{max} are the minimum and maximum experimentally
 21 accessible stretches, respectively, and d is a dimensionless parameter that controls the spatial
 22 extent of variations in λ (**Figure 3A**). Indeed, as predicted by **Equation (2)**, as d is reduced,
 23 the resulting curvature increases in magnitude and becomes concentrated in a smaller region.
 24 Using the corresponding metric tensor, given by **Equation (1)**, theory and FEM (**Figure 3B-**
 25 **D**) predict buckling into candy wrapper-like shapes, with a ridge of positive Gaussian curvature

1 in the middle of the sheet that smoothly progresses along ν to valley regions of negative
2 Gaussian curvature that evolve to zero Gaussian curvature at the edges. To investigate these
3 shape transformations experimentally, samples are patterned using photomasks generated in
4 Matlab from a calibration curve of stretch versus percent black (see **Supplementary**
5 **Information** for photomasks and additional details). Experimental results (**Figure 3E**, **Figure**
6 **S7**) match the predicted deformations, with greater curvature and a tighter characteristic radius
7 of curvature of the ridge as d decreases. We find that the Gaussian curvatures observed by FEM
8 (**Figure 3B**) are in very good agreement with the ones predicted by **Equation (2)**, and
9 furthermore that the realized 3D shapes correspond closely to those from geometric predictions
10 (see (**Figure 3C**) and **Supporting Information**). This striking agreement demonstrates the
11 robustness of the shape morphing concept developed here and suggests its potential for
12 generalization to other chemistries and materials.

13
14 To truly program shape transformation, the inverse problem – i.e., computing the stretch profile
15 $\lambda(\nu)$ that leads to a desired 3D shape upon actuation – needs to be solved. While the
16 corresponding differential geometry has been developed for isotropic gels with differential
17 swelling^[4,5,47] and nematic sheets with varying director orientation,^[14,17] we are not aware of
18 previous solutions for the anisotropic case of varying stretch magnitude with a homogenous
19 director orientation. As a first step, we focus here on shapes with constant negative and positive
20 Gaussian curvature, with the appropriate stretch functions obtained by numerically solving
21 **Equation (2)** within the constraint of the stretches achievable in our system and constructing a
22 polynomial fit to the solution (see **Supporting Information** and **Figure S8** for details). The
23 target negative and positive curvature, calculated stretch profiles, and simulated curvature
24 generated by FEM are shown in **Figure 4A, D**. The calculated stretch profiles prescribe high
25 deformation in the center of the sheet and low deformation at the edges parallel to the director
26 field in the case of constant negative Gaussian curvature and the opposite – low deformation in

1 the middle and high deformation at the edges – for the case of constant positive Gaussian
2 curvature. The simulated curvatures from FEM match the target constant curvatures quite well
3 in the center portions of the films but deviate at the edges, presumably reflecting an elastic
4 ‘boundary layer’^[63] that lowers the bending energy for a non-zero thickness sheet. The
5 corresponding samples are prepared using photomasks generated from the calculated stretch
6 profiles (see **Supplementary Information**) and experiments show buckling of LCE sheets into
7 a saddle-like shape and a shallow spherical cap-like shape for negative and positive Gaussian
8 curvature, respectively, matching the predictions of the accompanying FEM simulations and
9 geometric models (**Figure 4B-C, E-F** and **Figure S9**). Interestingly, FEM predicts that a non-
10 axisymmetric saddle shape should be lower energy than the observed axisymmetric shape in
11 the case of constant negative Gaussian curvature (**Figure S10**). However, the non-axisymmetric
12 shape is not observed experimentally, possibly due to imperfections in sample fabrication or
13 kinetic selection of the axisymmetric shape. We note that the observed shapes are analogous to
14 those experimentally realized in LCEs with patterned axisymmetric director fields about a +1
15 defect.^[16]

16
17 In summary, we have demonstrated a method combining experiments, FEM simulations, and
18 geometric predictions to program photoactive shape morphing from monodomain LCE sheets
19 with a unidirectional director by spatially controlling photothermal heat generation.
20 Discontinuous metrics introduced via localized photothermal inclusions are shown to drive
21 buckling into both static shapes and autonomously oscillating forms. Furthermore, we
22 developed a new theory based on Gaussian morphing to encode smoothly-varying stretch
23 profiles to rationally approach the design of targeted shapes. We anticipate that this fabrication
24 method is generalizable to a variety of chemistries that are incompatible with methods to
25 spatially pattern in-plane director fields, opening up new opportunities for shape morphing in a
26 variety of liquid crystalline polymer materials.

1 **Experimental Section**

2

3 *Materials:* 1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82) was
4 purchased from Synthon Chemicals and used as received. 8-amino-1-octanol and *n*-
5 dodecylamine were purchased from Tokyo Chemical Industries. 2,2-dimethoxy-2-phenyl-
6 acetophenone (Irgacure 651), oleylamine, and gold(III) chloride trihydrate (HAuCl₄) were
7 purchased from Sigma Aldrich.

8

9 *LCE Fabrication:* The procedure of Ahn and co-workers^[50] was followed with slight
10 modification. RM82, dodecylamine, and 8-amino-1-octanol were combined in a molar ratio of
11 1.1:0.5:0.5 with 2.5 wt% of Irgacure 651 in a vial and melted at ≈ 85 °C and vortexed repeatedly.
12 Following evacuation to remove air bubbles, the molten mixture was infiltrated via capillary
13 action into alignment cells composed of two glass slides coated with Elvamide polyimide
14 (DuPont), rubbed with a velvet cloth, and set to 50 μm thickness with glass spacers. Samples
15 were placed in an oven at 55 °C to oligomerize overnight, subsequently cured with UV light
16 (10 mW cm^{-2}) for 30 min and harvested by soaking in warm water and gently opening the
17 alignment cells with a razor blade.

18

19 *Photopatterning of Nanocomposites:* Stock solutions of HAuCl₄ (11.8 mg, 0.035 mmol) in
20 acetone (0.3 mL), oleylamine (59 mg, 0.22 mmol) in toluene (0.5 mL), and Irgacure 651 (56.2
21 mg, 0.22 mmol) in toluene (0.5 mL) were freshly prepared. To prepare the gold nanoparticle
22 precursor solution, 200 μL of HAuCl₄, 400 μL of Irgacure 651, and 200 μL of oleylamine stock
23 solutions were sequentially added to a vial and diluted with 800 μL of toluene. Films were
24 swelled in gold solution, blotted on filter paper to remove excess solution, and sandwiched
25 between a glass slide and a photomask. Photomasks were prepared in Matlab and Adobe
26 Illustrator, fabricated via inkjet printing (HP LaserJet 500) on plastic transparency films (Apollo

1 Laser Printer Transparency Film), and glued on glass coverslips. Samples were exposed to 30
2 mW cm⁻² of light with 365 nm wavelength (Thorlabs) for 10 s, developed in acetone for 60 min
3 to remove unreacted gold salt, and dried.

4
5 *Instruments and Measurement:* UV-vis spectra were recorded on a fiber optic spectrometer
6 (Ocean Optics Flame). To evaluate photoactuation, samples were placed on a hot plate covered
7 with filter paper to prevent sticking and heated to 85 °C. All actuation experiments were
8 performed with a 530 nm LED (LEDSupply) generating an intensity of 200 mW cm⁻² and shape
9 transformations were recorded using a camera (Nikon 5500). Displacement data during
10 oscillation was extracted from recorded videos recorded at 60 fps using Tracker software (Open
11 Source Physics). Because the time-scale of snapping is similar to that of the frame rate, blurring
12 of images prevented the use of some frames for tracking analysis during snapping.

13

14 *FEM Simulations*

15 In the finite element simulations, thin LCE sheets are modeled with the same geometry as that
16 in the experiments, i.e. a square shape with a width-to-thickness ratio of 200. We model these
17 LCE sheets by using the neo-classical free energy density^[52,53] implemented into Abaqus as a
18 user subroutine UMAT (see **Supporting Information** for details). The ratio of the bulk
19 modulus to the shear modulus K/μ is set as 500, which indicates that the Poisson's ratio is 0.499
20 and thus the sheets are nearly incompressible. A stretch-temperature relation (**Figure 1C**), fitted
21 to the experimental measurement, is introduced into the free energy to describe the temperature-
22 dependent anisotropy of LCEs (see **Supporting Information**)

$$23 \quad \lambda = 0.6 \sqrt{1 + 1.778 \frac{120-T}{60}}, 60^\circ\text{C} \leq T \leq 120^\circ\text{C}.$$

24 Although in experiments the stretch is defined with respect to the length at room temperature,
25 in FEM simulations the lengths below 60 °C and above 120 °C are treated as those at 60 °C and

1 120 °C, respectively, because the difference is negligible. The above stretch-temperature
2 relation indicates that the nematic LCEs start to deform at 60°C and continuously deform until
3 120°C, yielding a maximum stretch of 0.6 parallel to the director. Using the above equation, the
4 stretch patterns in the experiments are converted into temperature distributions, which are
5 assigned to the LCE sheets as predefined fields. The element type is three-dimensional hybrid
6 quadratic brick with reduced integration (Abaqus type C3D20RH). We performed a mesh
7 refinement study to ensure that there are at least three elements along the thickness and that the
8 aspect ratio of a single element is no greater than 5. As a result, approximately 3×10^4 elements
9 are involved in each finite element model. The LCE sheets in all the simulations have free
10 boundary conditions, except the case shown in **Figure 4B**, in which symmetric boundary
11 conditions about $u/w = 0.5$ is applied. Artificial damping is introduced into the static general
12 procedure such that the sheets can snap to a stable equilibrium state when loss of stability occurs.
13 The damping factor in the simulations is determined based on the dissipated energy fraction,
14 which is set as 1×10^{-5} , a value that can suppress instabilities without having a significant effect
15 on the solutions.

16

17 **Supporting Information**

18 Supporting Information is available from the Wiley Online Library or from the authors.

19

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Figures

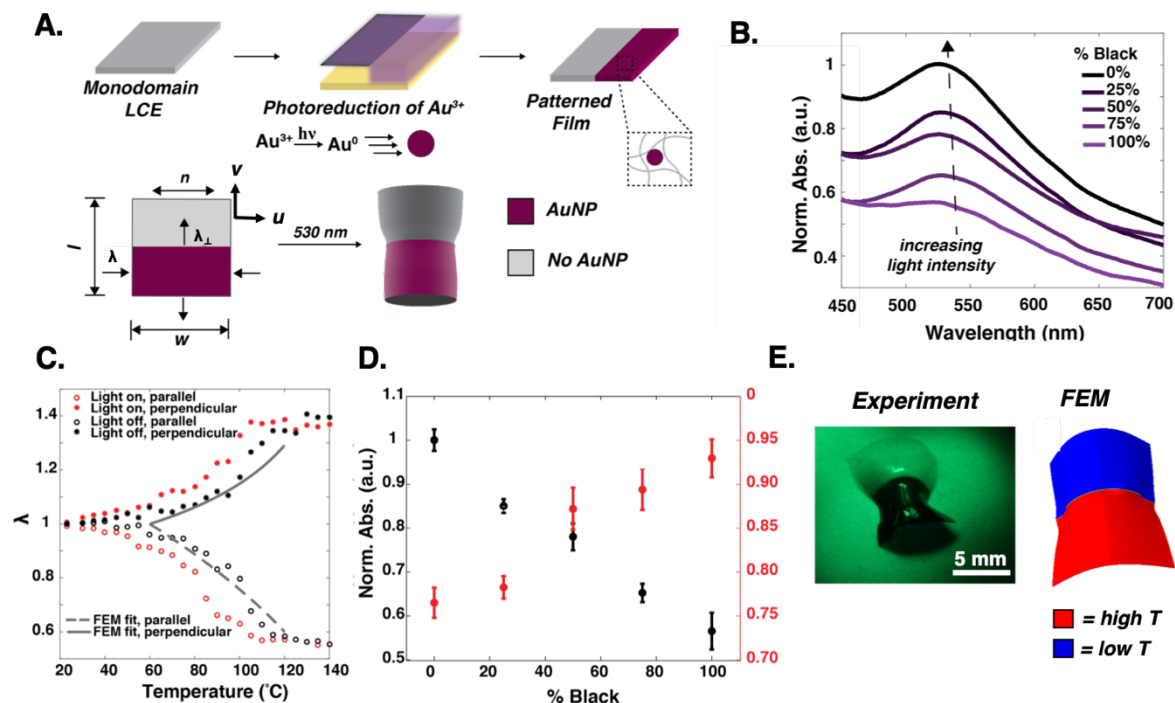


Figure 1. Photopatterning and photothermal properties of LCENCs. (A) AuNPs are spatially incorporated into LCEs via photoreduction of gold salt with UV light. Upon illumination with visible light, local heating induces a contraction along the director and buckling into a prescribed shape. (B) AuNP absorbance is controlled by modulating the light dose via grayscale photomasks that vary from 0% black (transparent) to 100% black (opaque). (C) Stretch vs temperature with (red) and without (black) photothermal heating for the case of highest absorbance. Because of the high T_{NI} of these materials experiments are performed at 85 °C to maximize photo-deformation. (D) Absorbance and stretch as functions of the opacity of the photomasks. Stretch can be spatially programmed over a range of 20%. (E) Example of a sheet programmed with a bi-strip geometry. Contraction along the director parallel to the interface between photothermally-heated and non-heated regions results in rolling about an axis perpendicular to this interface.

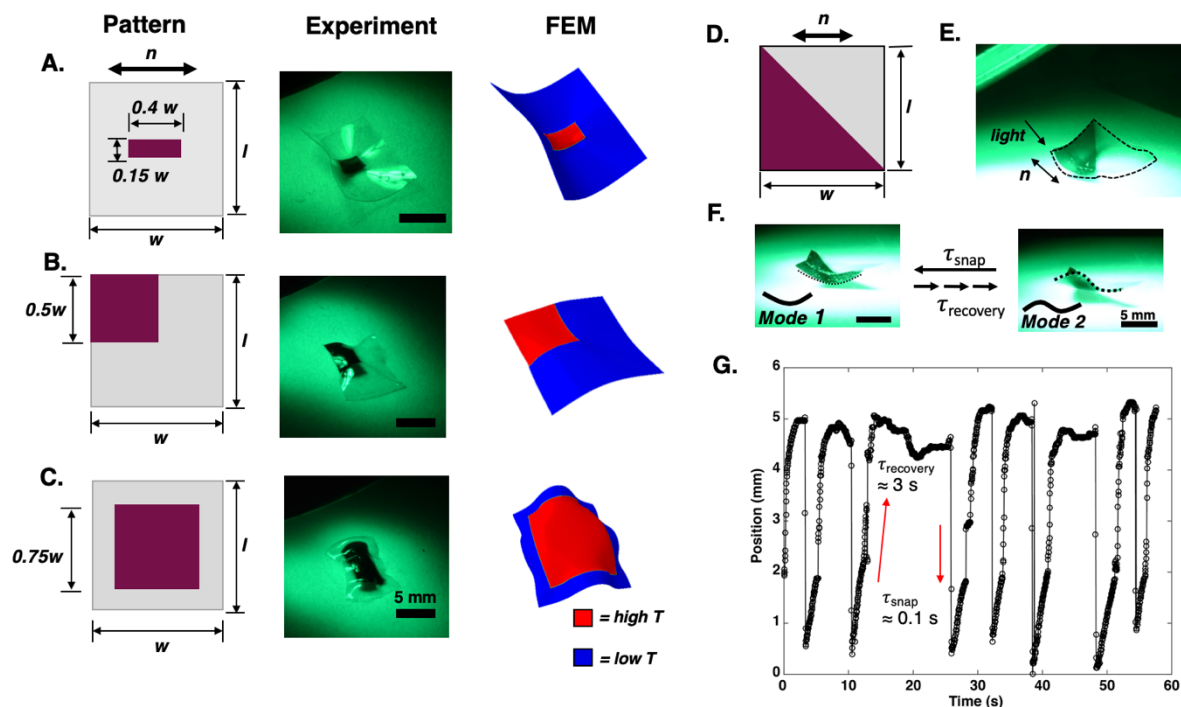
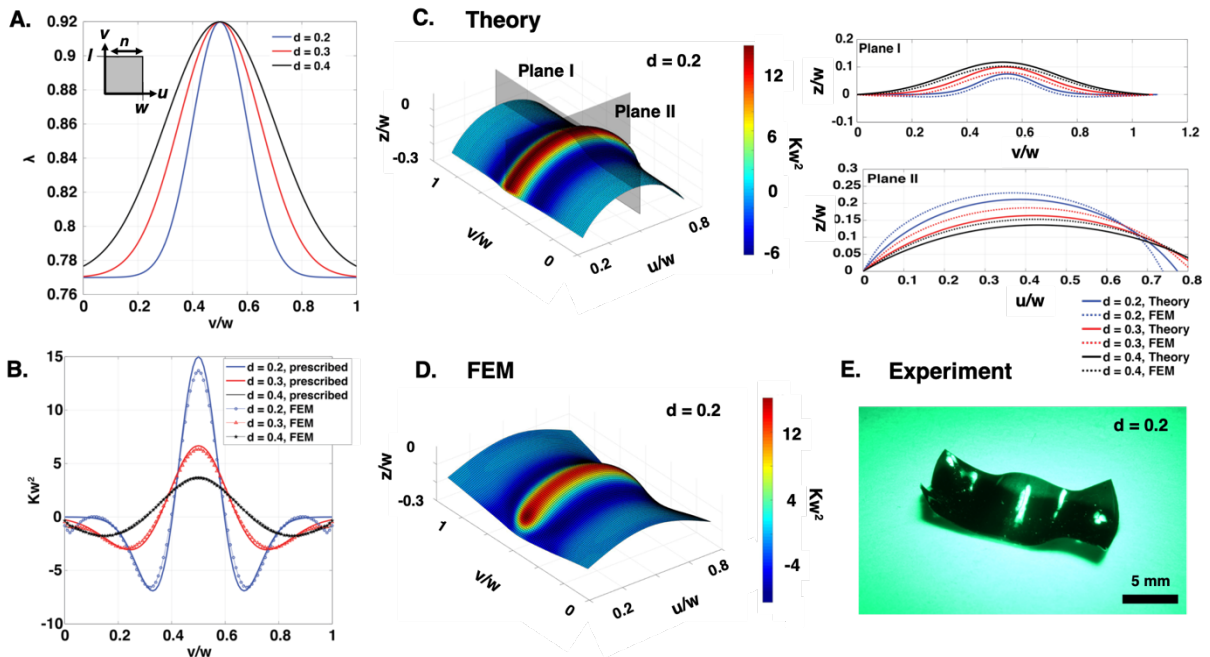


Figure 2. Shape transformation via localized photothermal inclusions. Buckling into different shapes in response to (A) rectangular and (B, C) square inclusion are demonstrated experimentally and the resulting shapes are predicted via FEM. (D, E) A square film is patterned with the photothermal region bisecting the film at 45° with respect to the director with incident light on the corner of the photothermal region. (F) The film snaps between a half wavelength to a full wavelength wrinkle reversibly. Upon relaxing to the initial state, the process repeats. (G) Position of the edge of the film with respect to the substrate vs time. The film gradually evolves over a few seconds to Mode 2 before snapping through to Mode 1 in ≈ 0.1 s. The film exhibits mechanical bistability between the two modes and autonomously oscillates between them for the duration of illumination.

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 2 **Figure 3. Patterning smoothly curved sheets with Gaussian stretch profiles.** (A) Stretch
 3 profiles λ for different values of d for $w = l$ (inset). (B) Prescribed and FEM Gaussian curvature
 4 as a function of v at $u/w = 0.5$. (C) Shape prediction of $d = 0.2$ by theory (left) and comparison
 5 of theory to FEM simulations (right) for different values of d . (D) Shape prediction of $d = 0.2$
 6 by FEM. (E) Experimental result for $d = 0.2$ demonstrates buckling into a candy wrapper-like
 7 shape due to regions of highly localized Gaussian curvature that closely matches the predicted
 8 shape by theory and FEM. Results for $d = 0.3$ and 0.4 are provided in the Supporting
 9 Information.

10

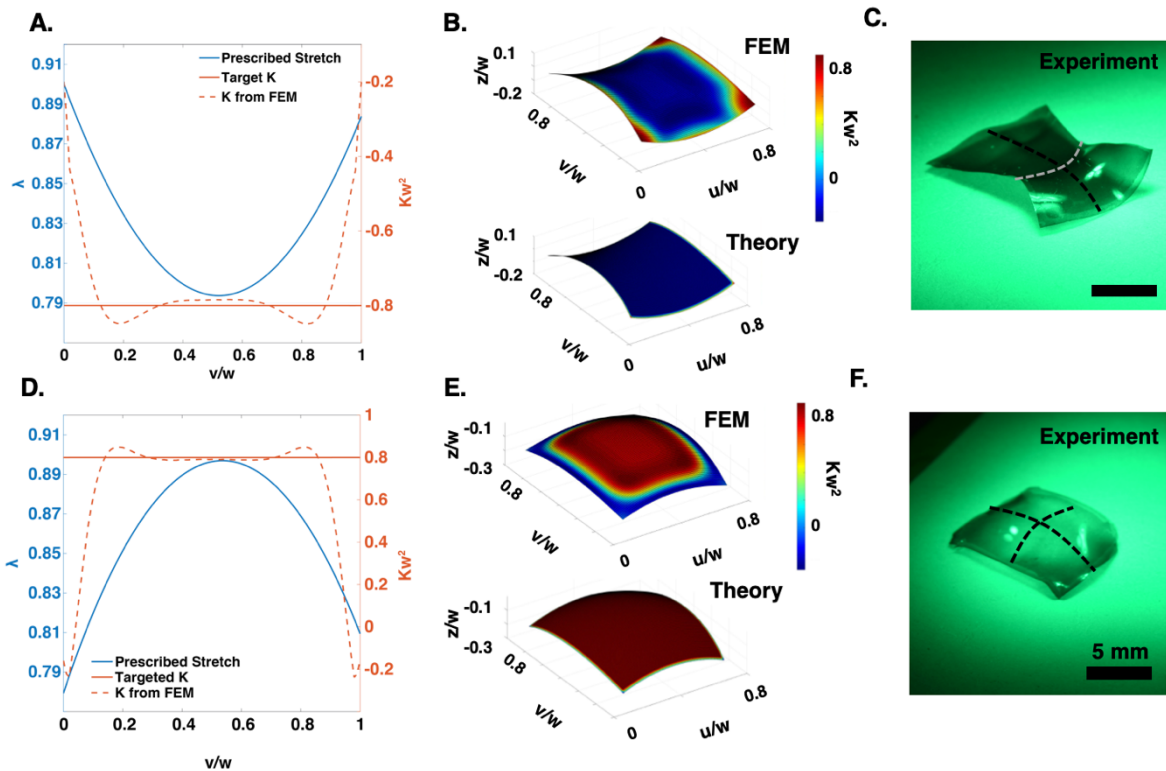


Figure 4. Programmed constant negative and positive Gaussian curvature via ninth-order polynomial stretch profiles. (A) Prescribed and predicted Gaussian curvature, **(B)** FEM simulation (top) and theory (bottom) and **(C)** experiment for negative Gaussian curvature. **(D)** Prescribed and predicted Gaussian curvature, **(E)** FEM simulation and **(F)** experiment for positive Gaussian curvature. White and black lines are drawn as guides to the eyes, with black and white denoting positive and negative curvature, respectively.

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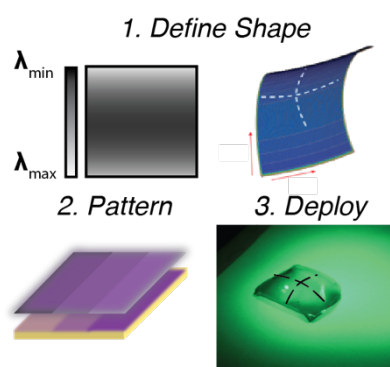
1 Light-driven shape morphing via spatially-patterned photothermal deformation of liquid
2 crystal elastomers is demonstrated. Distinct from shape prescription via modulation of the
3 director orientation, a general method for patterning deformation profiles in monodomain
4 elastomers with a unidirectional director field is presented. A model for prescribing Gaussian
5 curvature via continuous deformation profiles is presented and validated with experiments and
6 finite element analysis.

7
8 **Keyword** photoactive materials

9
10 *Alexa S. Kuenstler***, *Yuzhen Chen***, *Phuong Bui*, *Hyunki Kim*, *Antonio DeSimone**, *Lihua*
11 *Jin**, and *Ryan C. Hayward**

12
13 **Title** Blueprinting Photothermal Shape-Morphing of Liquid Crystal Elastomers

14
15 ToC figure ((Please choose one size: 55 mm broad \times 50 mm high or 110 mm broad \times 20 mm
16 high. Please do not use any other dimensions))



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2

3 Supporting Information

4

5

6 **Title** Blueprinting Photothermal Shape-Morphing of Liquid Crystal Elastomers

7

8 *Alexa S. Kuenstler, Yuzhen Chen, Phuong Bui, Hyunki Kim, Antonio DeSimone*, Lihua Jin*,*
 9 *and Ryan C. Hayward**

10

11 **Constitutive Model of LCEs for FEM Simulations**

12

13 We use the commercial software Abaqus/Standard for our finite element simulations. We

14 implemented the following neo-classical free energy density^[1] for LCEs in Abaqus by writing

15 a user-defined material subroutine (UMAT)

16
$$\psi = \frac{\mu}{2} [\text{Tr}(\tilde{\mathbf{g}}^{-1} \mathbf{F} \tilde{\mathbf{g}}_0 \mathbf{F}^T) - 3] + \frac{K}{2} (J - 1)^2 - \mu \ln J, \quad (\text{S1})$$

17 where μ is the shear modulus, K is the bulk modulus, \mathbf{F} is the deformation gradient and $J =$

18 $\det(\mathbf{F})$, $\tilde{\mathbf{g}}$ is a temperature-dependent three-dimensional metric tensor that describes the

19 anisotropy of LCEs with respect to the isotropic phase in the current configuration,^[2] and $\tilde{\mathbf{g}}_0$

20 denotes $\tilde{\mathbf{g}}$ in the reference configuration which is selected as the nematic phase at temperature

21 $T = 60^\circ\text{C}$. The metric tensor $\tilde{\mathbf{g}}$ can be expressed as

22
$$\tilde{\mathbf{g}} = \tilde{g}_\perp \left[\mathbf{I} + \left(\frac{\tilde{g}_\parallel}{\tilde{g}_\perp} - 1 \right) \mathbf{n} \otimes \mathbf{n} \right], \mathbf{n} = \frac{\mathbf{F} \mathbf{n}_0}{|\mathbf{F} \mathbf{n}_0|}, \quad (\text{S2})$$

23 where \tilde{g}_\parallel and \tilde{g}_\perp are eigenvalues of $\tilde{\mathbf{g}}$ parallel and orthogonal to the director and $\tilde{g}_\parallel \tilde{g}_\perp^2 = 1$, \mathbf{I}

24 is a 3-by-3 identity matrix, \mathbf{n} is a unit vector along the director, and \mathbf{n}_0 denotes \mathbf{n} in the

25 reference configuration. The stretch λ relates to the metric tensors by

26
$$\lambda = \sqrt{\tilde{g}_\parallel / \tilde{g}_{0\parallel}}, \quad (\text{S3})$$

27 where $\tilde{g}_{0\parallel}$ is the eigenvalue of $\tilde{\mathbf{g}}_0$ parallel to the director. To determine the dependence of \tilde{g}_\parallel

28 and \tilde{g}_\perp on temperature, we fit the stretch-temperature relation to the experimental data

29 (**Figure 1C**) and obtain

$$\lambda = 0.6 \sqrt{1 + 1.778 \frac{120-T}{60}}, \quad (\text{S4})$$

where T denotes temperature within the range of 60°C to 120 °C. The stretch λ_{\perp} perpendicular to the director (**Figure 1C**) can be calculated based on incompressibility

$$\lambda_{\perp} = \sqrt{1/\lambda}. \quad (\text{S5})$$

Equations (S4) and (S5) indicate that upon heating, LCEs transition from the nematic phase ($T = 60^{\circ}\text{C}$) to the isotropic phase ($T = 120^{\circ}\text{C}$), yielding a contractive stretch of 0.6 and a tensile stretch of 1.29 parallel and orthogonal to the director, respectively. From the definition of the metric tensor, we know that $\tilde{g}_{\parallel}(T = 120^{\circ}\text{C}) = 1$, and therefore, according to **Equation** (S3), we have $\tilde{g}_{0\parallel} = 1/\lambda^2(T = 120^{\circ}\text{C}) = 2.778$. Based on **Equations** (S3) and (S4), the dependence of \tilde{g}_{\parallel} on temperature can be expressed as

$$\tilde{g}_{\parallel} = 1 + 1.778 \frac{120-T}{60}, \quad (\text{S6})$$

and \tilde{g}_{\perp} can be obtained by $\tilde{g}_{\perp} = \sqrt{1/\tilde{g}_{\parallel}}$.

Self-Shadowing FEM Models

Here we numerically show how self-shadowing effect influences oscillating morphing shown in **Figure 2D-G**. The film with a specific pattern (**Figure 2D**) is illuminated from a 30° angle with respect to the substrate along the edge parallel to the director. Initially, the light intensity is the same everywhere on the film and thus the stretch distributions on photoactive and non-photoactive regions are uniform (**Figure S5A**). The photoactive region curls up, forming Mode 1. Since the angle between the bent photoactive region and the substrate is comparable to 30°, the light can be blocked by the film itself. Therefore, the light intensity in the photoactive region becomes non-uniform: the part around the vertex has a higher light intensity than the part away from the vertex. This non-uniform light intensity leads to non-uniform stretch distributions (**Figure S5B**), yielding a full wavelength wrinkle (Mode 2, **Figure**

1 S5C). Once the Mode 2 is formed, the film itself is unable to block the light. The uniform light
 2 intensity is recovered and thus the mode of the film is switched from Mode 2 back to Mode 1.

3

4 **Stretch Profiles for Given Constant Gaussian Curvature**

5 We obtain the stretch profiles giving constant Gaussian curvature by numerically
 6 solving **Equation (2)**. The target constant (non-dimensional) Gaussian curvature Kw^2 is ± 0.8 .
 7 **Equation (2)** can be solved using Matlab ODE45 solver with a relative error tolerance of
 8 1×10^{-10} . The initial conditions are adjusted such that the stretches are experimentally
 9 accessible in our system. To define a stretch profile yielding the same Gaussian curvature as
 10 the target one, we fit a 9th-order polynomial to the solution such that the relative error of the
 11 obtained Gaussian curvature is less than 1×10^{-6} . As a result, the stretch profile corresponding
 12 to positive Gaussian curvature 0.8 is

13
$$\lambda(v) = 0.0008016v^9 - 0.008048v^8 + 0.02585v^7 - 0.05128v^6 + 0.07006v^5 -$$

 14
$$0.09382v^4 + 0.1015v^3 - 0.4649v^2 + 0.45v + 0.78, \quad (S7)$$

15 and the stretch profile corresponding to negative Gaussian curvature -0.8 is

16
$$\lambda(v) = -0.0003549v^9 - 0.002021v^8 + 0.01206v^7 - 0.01331v^6 - 0.007834v^5 -$$

 17
$$0.00651v^4 + 0.04632v^3 + 0.3555v^2 - 0.4v + 0.9. \quad (S8)$$

18

19 ***Analytical Shape Prediction***

20 We consider a two-dimensional surface ω in \mathbb{R}^2 immersed in a three-dimensional
 21 Euclidean space \mathbf{E}^3 and predict its three-dimensional (3D) shape produced by the metric
 22 tensor shown in **Equation (1)**.

23 The Gaussian curvature K of this surface can be computed by^[3]

24
$$-EK = (\Gamma_{12}^2)_{,u} - (\Gamma_{11}^2)_{,v} + \Gamma_{12}^1 \Gamma_{11}^2 + \Gamma_{12}^2 \Gamma_{12}^2 - \Gamma_{11}^2 \Gamma_{22}^2 - \Gamma_{11}^1 \Gamma_{12}^2, \quad (S9)$$

1 where $E = g_{11} = \lambda^2$, $(\)_{,u}$ and $(\)_{,v}$ are partial derivatives with respect to u and v , $\Gamma_{\beta\gamma}^\alpha$
 2 $(\alpha, \beta, \gamma = 1, 2)$ are the Christoffel symbols, which equal

$$3 \quad \Gamma_{11}^1 = 0, \Gamma_{12}^1 = \Gamma_{21}^1 = \lambda'/\lambda, \Gamma_{22}^1 = 0, \Gamma_{11}^2 = -\lambda^2\lambda', \Gamma_{12}^2 = \Gamma_{21}^2 = 0, \Gamma_{22}^2 = -\frac{1}{2}\lambda'/\lambda. \quad (\text{S10})$$

4 Here $(\)'$ denotes differentiation with respect to v . With Equations (S9) and (S10), we can
 5 obtain the dependence of Gaussian curvature K on stretch profile $\lambda(v)$, as shown in Equation
 6 (2).

7 We assume that the 3D shape is axisymmetric about the v axis and thus the map χ :

8 $\omega \subset \mathbb{R}^2 \rightarrow \hat{\omega} \subset E^3$ is given by

$$9 \quad \chi(u, v) = \left[r(v) \cos\left(\frac{u}{R_0} + \psi(v)\right) \quad r(v) \sin\left(\frac{u}{R_0} + \psi(v)\right) \quad z(v) \right], u \in [0, l], v \in [0, w],$$

10 (S11)

11 where functions r , ψ and z depend only on v , and R_0 is a positive constant that will be
 12 determined later. The metric tensor of the surface $\hat{\omega}$ is given by

$$13 \quad \mathbf{g}_{\hat{\omega}} = \nabla\chi^T \nabla\chi = \begin{bmatrix} \left(\frac{r}{R_0}\right)^2 & \frac{r^2\psi'}{R_0} \\ \frac{r^2\psi'}{R_0} & r'^2 + z'^2 + r^2\psi'^2 \end{bmatrix}. \quad (\text{S12})$$

14 Since the LCE sheets are very thin, it is reasonable to assume that their final configurations
 15 are essentially stress-free and their metric tensors given by **Equation** (S12) match the target
 16 metric tensor shown in **Equation** (1), i.e.

$$17 \quad \begin{bmatrix} \left(\frac{r}{R_0}\right)^2 & \frac{r^2\psi'}{R_0} \\ \frac{r^2\psi'}{R_0} & r'^2 + z'^2 + r^2\psi'^2 \end{bmatrix} = \begin{bmatrix} \lambda(v)^2 & 0 \\ 0 & \frac{1}{\lambda(v)} \end{bmatrix}. \quad (\text{S13})$$

18 From **Equation** (S13), we obtain

$$19 \quad r(v) = \lambda(v)R_0, \quad (\text{S14})$$

$$20 \quad \psi'(v) = 0, \quad (\text{S15})$$

$$21 \quad z'(v) = \pm \frac{1}{\sqrt{\lambda(v)}} \sqrt{1 - \left(R_0\sqrt{\lambda(v)}\lambda'(v)\right)^2}, R_0 \leq \frac{1}{\sqrt{\lambda(v)|\lambda'(v)|}}. \quad (\text{S16})$$

1 Given a stretch profile $\lambda(v)$, we can obtain $r(v)$ from **Equation** (S14) and $z(v)$ by evaluating
2 numerically the integral on the right-hand side of **Equation** (S16). In addition, we set $\psi = 0$.
3 The 3D shape for this stretch profile can then be determined by **Equation** (S11) with an
4 appropriate R_0 , which is selected such that the following bending energy is minimized

$$5 \quad E_b = \int_0^l \int_0^w (4H^2 - K) dudv, \quad (\text{S17})$$

6 where H and K denote mean and Gaussian curvatures of the surface $\hat{\omega}$, respectively.

7 The prediction of the geometric theory outlined above match closely the results of the
8 FEM simulations, as shown in **Figures** 3, 4, S6, S8. The fact that isometric embeddings of the
9 target metric with the lowest possible bending energy agree very well with those obtained by
10 numerical simulations indicates that the configurations obtained numerically with FEM (and,
11 by extension, the configurations observed experimentally) obey the target metric almost fully
12 and thus are nearly stretch-free.

13 Moreover, the good match between the predictions of the geometric theory (which does
14 not rely on the choice of a constitutive model and of material parameters for the material
15 response) and the results of the FEM numerical simulations (which use a specific constitutive
16 model based on the neo-classical free energy density) suggest that the morphing concept we
17 demonstrate is robust, with the potential to be used for other materials beyond those considered
18 in this paper.

19

20 ***Prescription of Photomasks***

21 The workflow of determining the appropriate photomask to generate a desired shape is shown
22 in Figure S7. A calibration curve for stretch as a function of % black was generated by
23 performing a linear fit of experimentally-measured stretch. Next, the computed stretch profile
24 is decomposed into 256 slices as a function of v and the calibration curve is used to define a
25 numerical value between 0 (0% black) and 1 (100% black). Finally, the `image()` and

1 colormap(gray) functions in Matlab are used to convert the 256 slices into a square image
2 where each slice has a constant gray value along u. Following generation of the grayscale
3 images, masks are re-sized in Illustrator to the appropriate dimensions.

4

5 *Thermal and Mechanical Properties*

6 Thermal gravimetric analysis (TGA) was performed using a TA instruments TGA 2950.
7 Samples were heated from room temperature at $20\text{ }^{\circ}\text{C min}^{-1}$ to $600\text{ }^{\circ}\text{C}$ and the weight percent
8 of gold nanoparticles was calculated from the difference in maximum weight loss between
9 neat and nanocomposite samples. Differential scanning calorimetry (DSC) was performed on
10 a TA instruments DSC Q200. Samples of $\approx 3\text{ mg}$ mass were heated to 150°C , cooled to -50
11 $^{\circ}\text{C}$, and heated again to 150°C at 10°C . All values were calculated from the second heating
12 cycle. Mechanical properties were determined from tensile tests performed on $10\text{ mm} \times 1\text{ mm}$
13 $\times 0.05\text{ mm}$ strips using a TA instruments Q800 Dynamic Mechanical Analyzer. Samples were
14 loaded along the director at 0.2 N min^{-1} and the elastic moduli were calculated from linear fits
15 to the initial linear regime of the deformation curve.

16

17 *Heat Transfer Calculations*

18 FEM

19 The temperature profile within a thin illuminated sheet is simulated using PDE Toolbox in
20 Matlab. The simulated geometry is an axisymmetric disk of material with thermal
21 conductivity $k = 0.2\text{ W m}^{-1}\text{ K}^{-1}$, radius $a_d = 5\text{ mm}$ and thickness $t = 50\text{ }\mu\text{m}$, possessing a
22 centered circular photothermal inclusion of radius $a_p = 2.5\text{ mm}$ (**Figure S2**). In reality, the
23 heat generation will decrease through the thickness following an exponential, rather than step-
24 wise, function, with a penetration depth that depends on nanoparticle concentration. As a
25 simplified approach to understand the potential effects of this non-uniformity in heat

1 generation through the thickness, we therefore take the photothermal inclusion to occupy only
 2 the top half of the disk thickness. The photothermal heat generation in this region is estimated
 3 as $Q = 3.2 \cdot 10^7 \text{ W m}^{-3}$, chosen to match the total heat generated based on the maximum
 4 experimental value of absorbance ($A \approx 0.7$) and a light intensity of 200 mW cm^{-2} . We treat
 5 heat loss from the disk as dominated by convection, with a heat transfer coefficient of $h = 33$
 6 $\text{W m}^{-2} \text{ K}^{-1}$ as estimated from heat transfer correlations for a horizontal plate.^[4] We consider
 7 two limits: (i) free convection from both the top and bottom surfaces of the disk and (ii) free
 8 convection from only the top surface and insulation at the bottom surface. The experiments
 9 are expected to fall between these limits, since convection from the bottom surface is likely to
 10 be less efficient than from the top, due to the presence of the underlying hot plate. The results
 11 shown in **Figure S2B-C** reveal two key points. First, thermal diffusivity leads to in-plane
 12 broadening (**Figure S2B**) by only a modest amount, with the lateral variation in temperature
 13 restricted to a region of only $\sim 1 \text{ mm}$ across the edge of the heated feature. To better
 14 understand the extent of lateral broadening, we turn to the approximate 1D analytical solution
 15 in the following section. Second, for both cases, the temperature is nearly constant through the
 16 thickness of the film (**Figure S2C**), despite the generation of heat only in the top half of the
 17 film, due to the small thickness of the heated features in comparison to their lateral
 18 dimensions, and the rapid transport of heat by thermal conduction across the film thickness.

19
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21 **Analytical Model**

22 As the FEM model results confirm the uniformity of temperature along the z-direction of the
 23 plate, we can further reduce the heat transfer problem to 1D, where we balance the divergence
 24 in radial flux of heat outward from the heated region against the heat lost by convection, i.e.

$$25 \quad kt \left[\frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) \right] = hT \quad (\text{S18})$$

1 with the following boundary conditions: (1) $T=T_0$ at $r = a_p$, and (2) $T \rightarrow 0$ at $r \rightarrow \infty$. Here, T
2 represents the temperature increase above ambient. The appropriate solution to this
3 (Helmholtz) equation, which satisfies the boundary conditions is

$$4 \quad T = T_0 K_0(qr)/K_0(qa_p) \quad (\text{S19})$$

5 where K_0 represents the modified Bessel function of the second kind, and $q^{-1} = (kt/h)^{1/2}$
6 describes the characteristic length-scale for spatial broadening of the temperature profile.
7 Using the parameters $t = 0.05$ mm, $k = 0.2$ W m⁻¹ K⁻¹, and $h = 33$ W m⁻² K⁻¹ as above, this
8 length is $q^{-1} = 0.55$ mm, consistent with the limited extent of lateral broadening found via
9 FEM.

10

11 **Measurement**

12 Photothermal heat generation was measured using a FLIR E4 thermal imaging camera
13 (**Figure S3E**). In good agreement with the FEM results, the temperature increase above
14 ambient in the center of the photothermal region was ≈ 20 K, and lateral broadening of the
15 temperature profile, relative to the illuminated region, occurred over a characteristic length
16 scale of ≈ 0.5 mm.

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18 *List of Movies*

- 19 1. Top-view of snapping film
- 20 2. Side-view of snapping film

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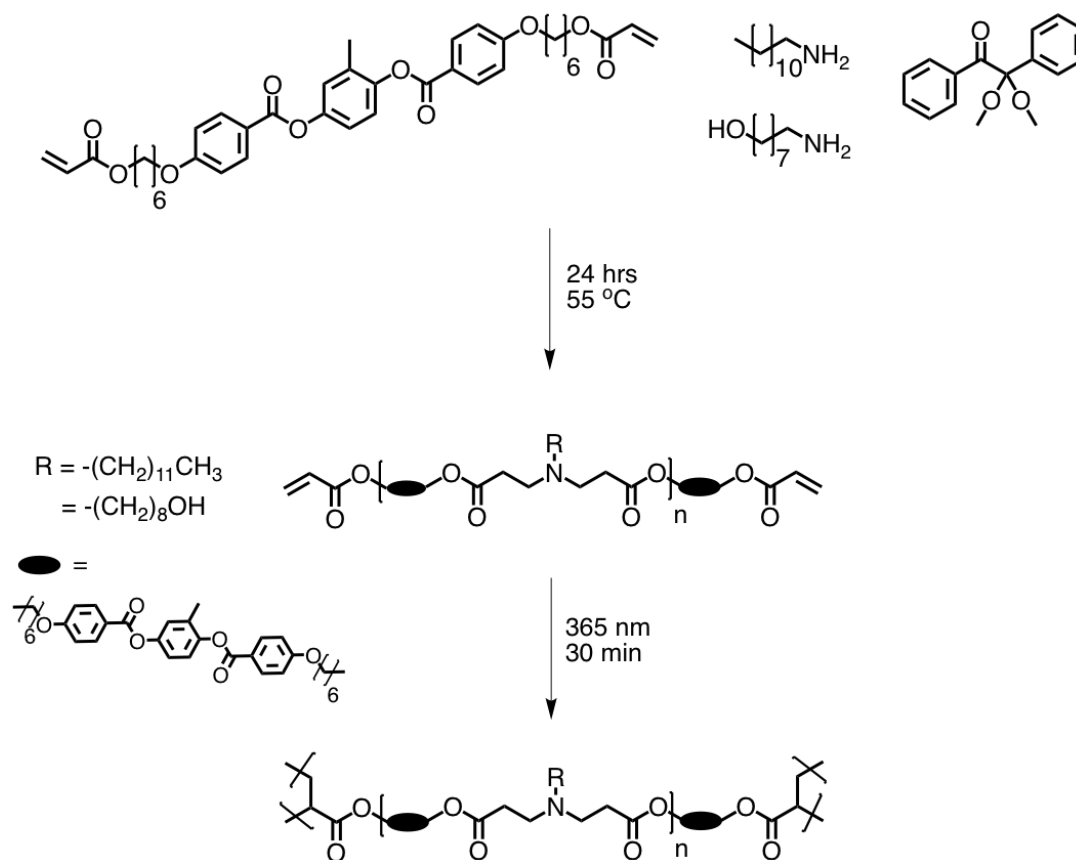
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1 Supplementary Figures

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Scheme S1. Synthesis of liquid crystal elastomers. Telechelic oligomers are first synthesized via the reaction of a slight excess of diacrylate mesogens to amine chain extenders and the cross-link density is dictated by this stoichiometry. Subsequently, the preserved diacrylate end-groups are used to photo-crosslink the oligomers to lock-in a monodomain alignment.

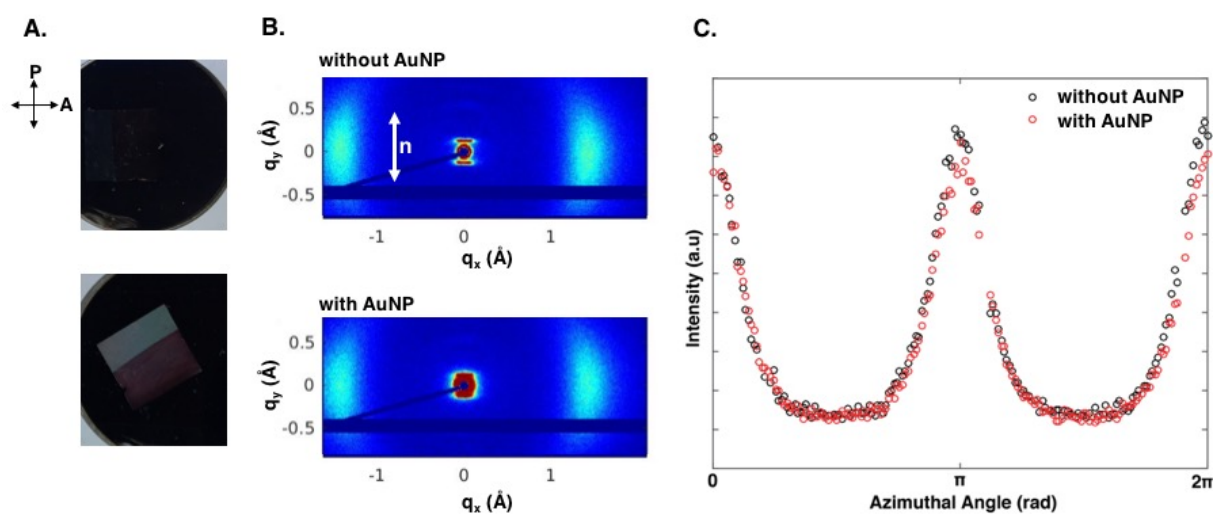
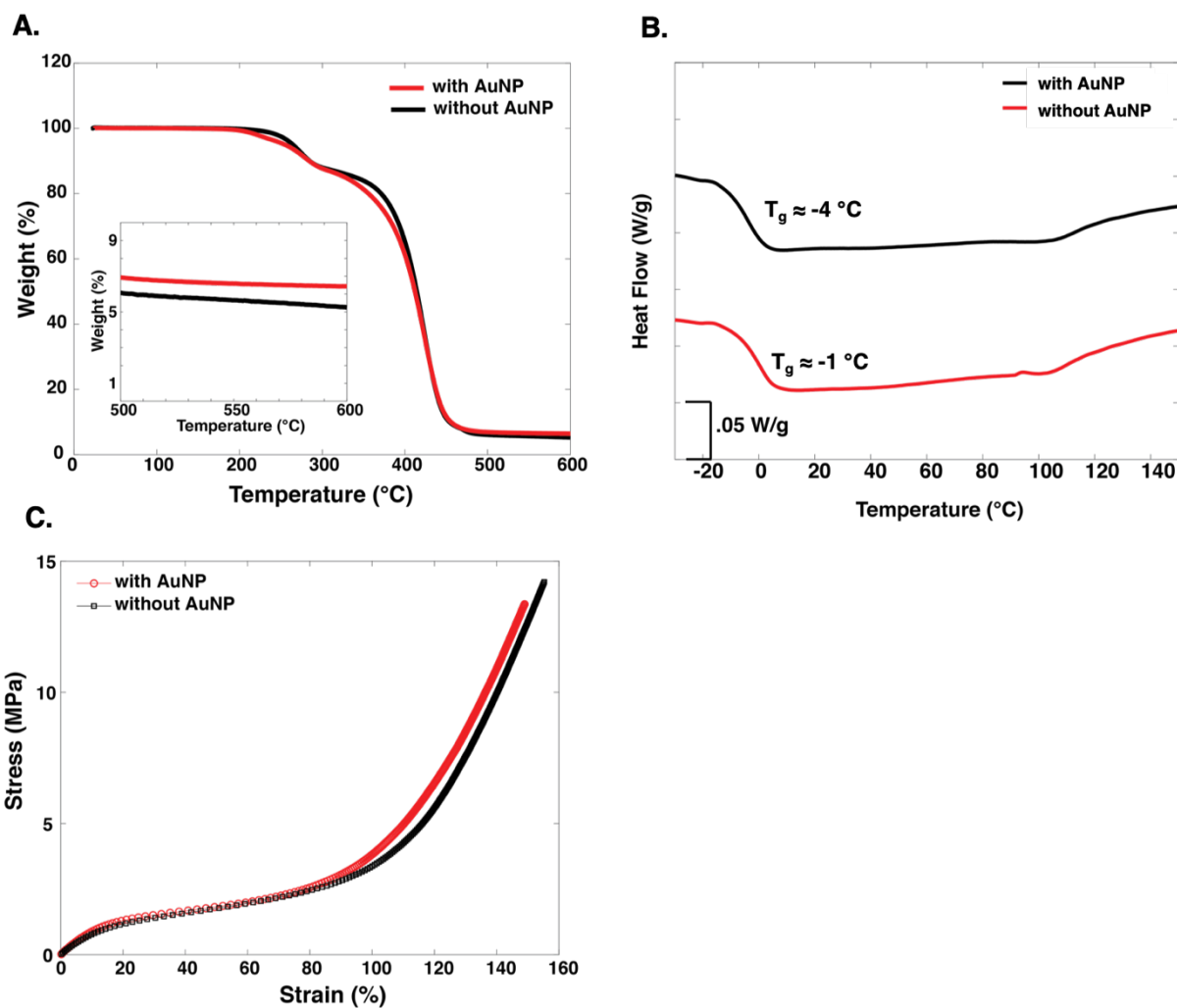
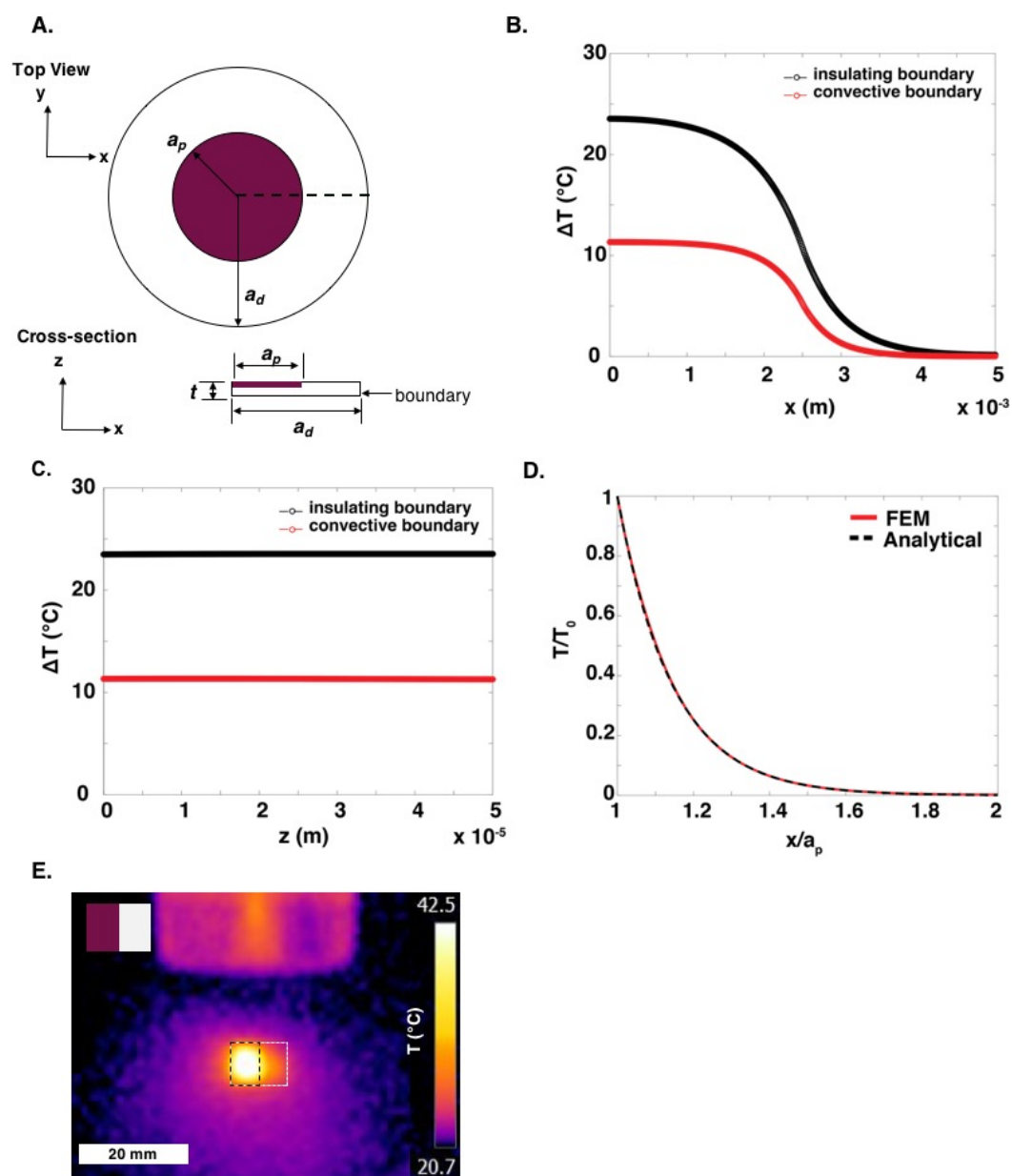
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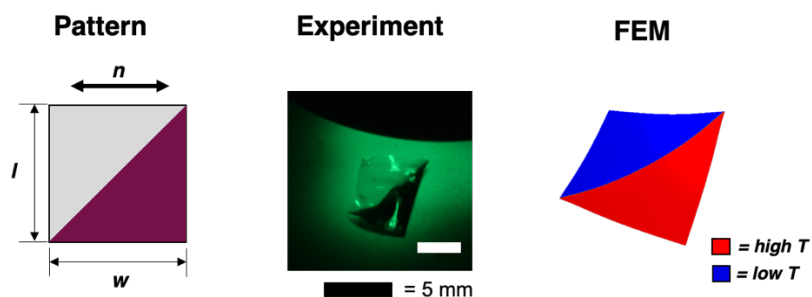
Figure S1. (A) A patterned LCE viewed through cross-polarizers. The sample is uniformly dark when the director is parallel to the polarizer and bright when the director is at a 45° to the polarizer, indicating a planar nematic sample with a unidirectional director field. (B) Wide-angle x-ray scattering of regions of the sample without (top) and with (bottom) AuNPs shows good alignment of mesogens in both cases. (C) Average intensity vs azimuth for regions of the same film with and without AuNPs. The order parameter in both regions is $S \approx 0.6$.



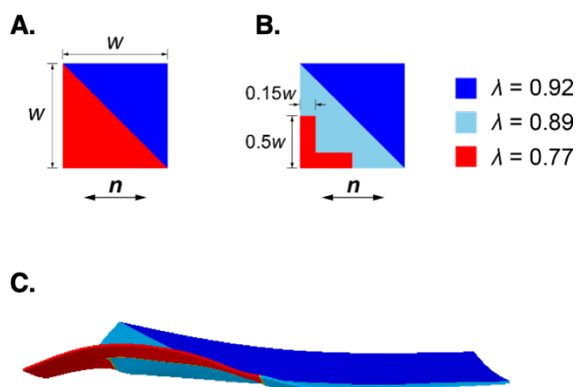
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3 **Figure S2.** (A) Nanocomposites contain ≈ 1 wt% nanoparticles as evaluated by
4 thermogravimetric analysis (TGA). (B) DSC thermograms of a LCE with and without AuNPs.
5 Glass transition temperatures are within instrumental error indicating that introduction of
6 nanoparticles does not cause significant mechanical changes. An upturn at $\approx 100^\circ\text{C}$ is
7 indicative of T_{NI} , consistent with reports for similar systems where no nematic-isotropic
8 endotherm is observed due to the small magnitude ($\Delta H < 10$ J/g) and the breadth of the
9 transition over a large temperature range. (C) Stress versus strain curves show that the
10 modulus remains unchanged after introduction of nanoparticles.
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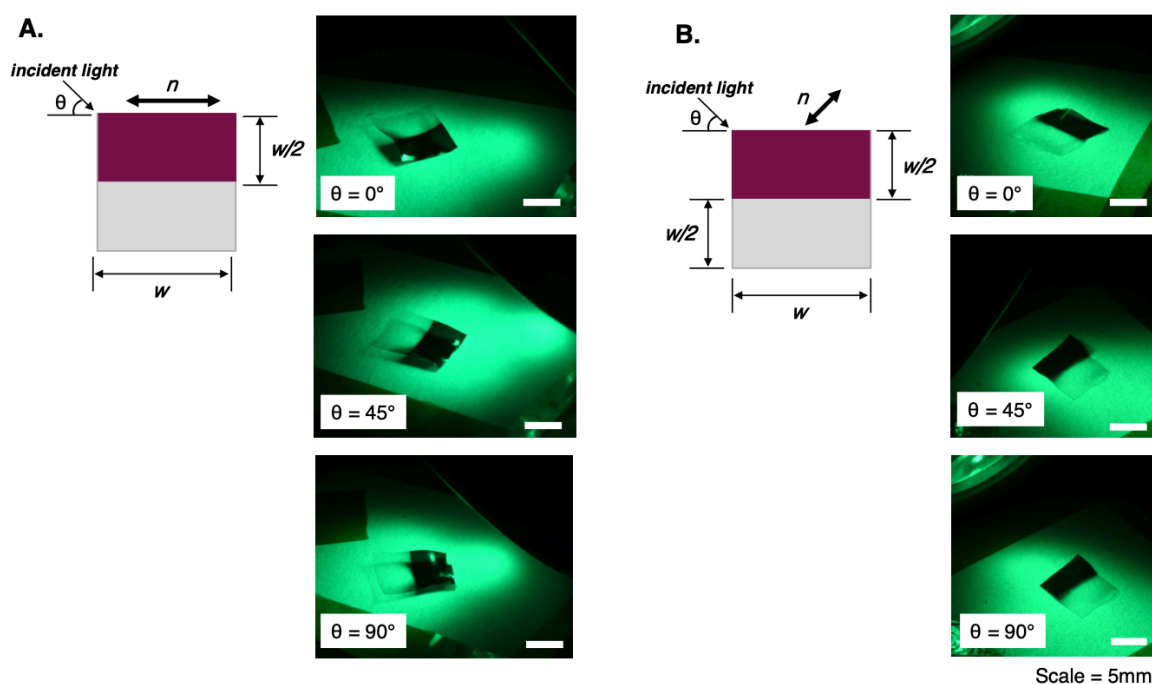
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3 **Figure S3.** (A) Geometry of a photoactive disk in FEM simulations (top) and its cross-section
4 (bottom) for a cut made as indicated by the dashed line. The bottom boundary is subjected to
5 an insulating or a convective boundary condition in separate trials. (B) Radial temperature
6 distribution shows limited thermal broadening (< 1 mm) for both boundary conditions. (C)
7 Through-thickness temperature variation is minimal (< 0.2 °C) for both boundary conditions.
8 (D) Comparison of FEM and analytical solution shows excellent agreement. (E) Thermal
9 image of a film (outlined with a white dotted line) containing a photothermal stripe (outlined
10 in a black dashed line) shows heat generation is localized to the nanoparticle-containing
11 region of the film.



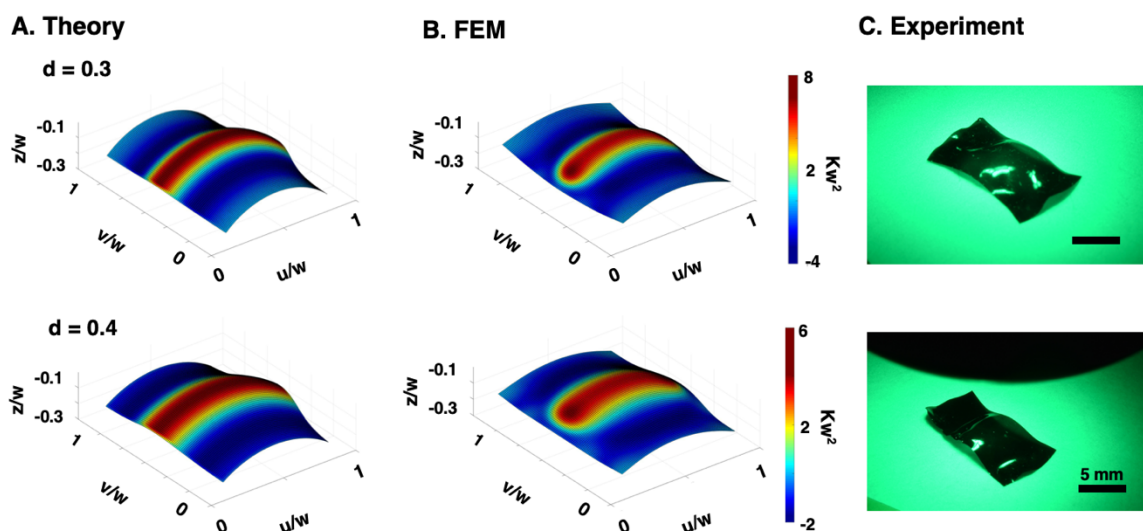
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2 **Figure S4.** Patterned nanocomposite that oscillates under oblique illumination is observed to
3 adopt a stationary morphology under overhead illumination.
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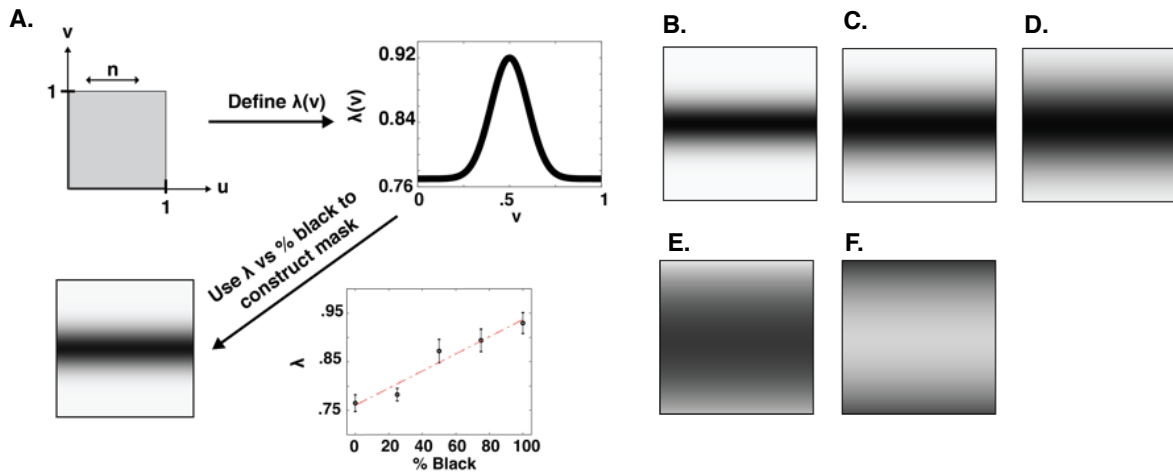
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8 **Figure S5.** (A) The patterned film that leads to oscillation. (B) A simplified model of self-
9 shadowing in FEM simulations is realized by imposing a maximum contraction (red) along
10 the edge closest to the light source and a smaller contraction in regions that would be blocked
11 by the light (light blue). (C) This model produces Mode 2 buckling, suggesting that self-
12 shadowing can shift the preferred configuration, thereby driving oscillatory snapping.
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2 **Figure S6.** Oblique illumination at different angles for a photothermal stripe patterned (A)
3 parallel to the director and (B) at a 45° to the director. No oscillation is observed for either
4 case regardless of illumination angle.
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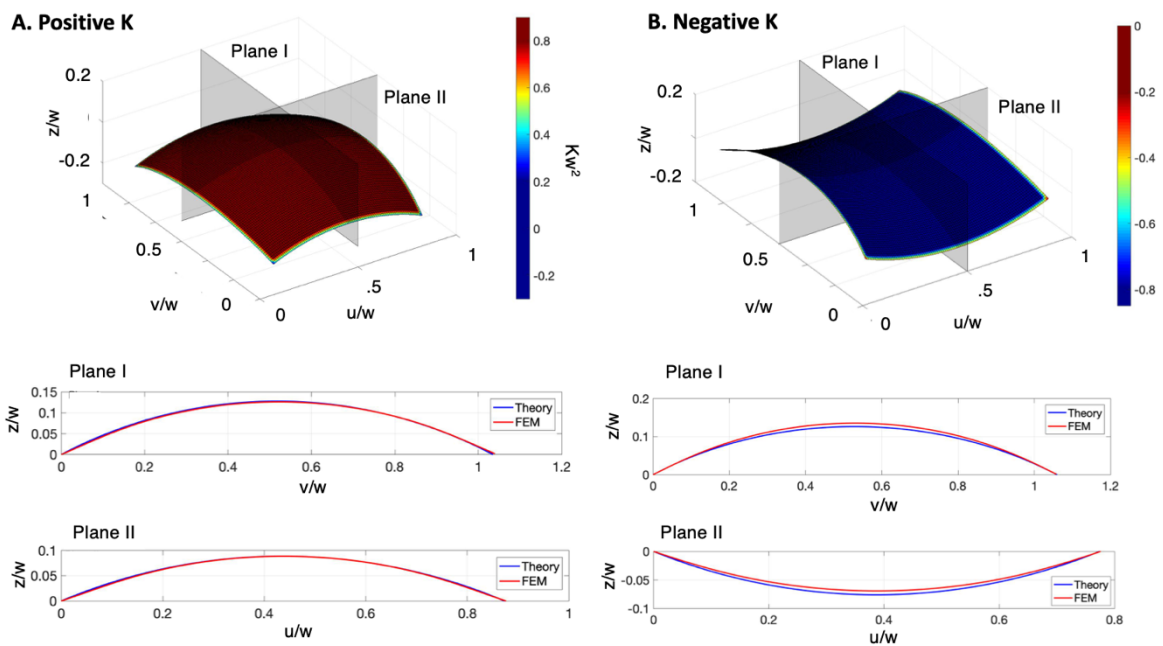


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11 **Figure S7.** Shape predicted by (A) Theory and (B) FEM for Gaussian stretch profiles with d
12 = 0.3 (top row) and $d = 0.4$ (bottom row). (C) Experiments match the predicted shape.
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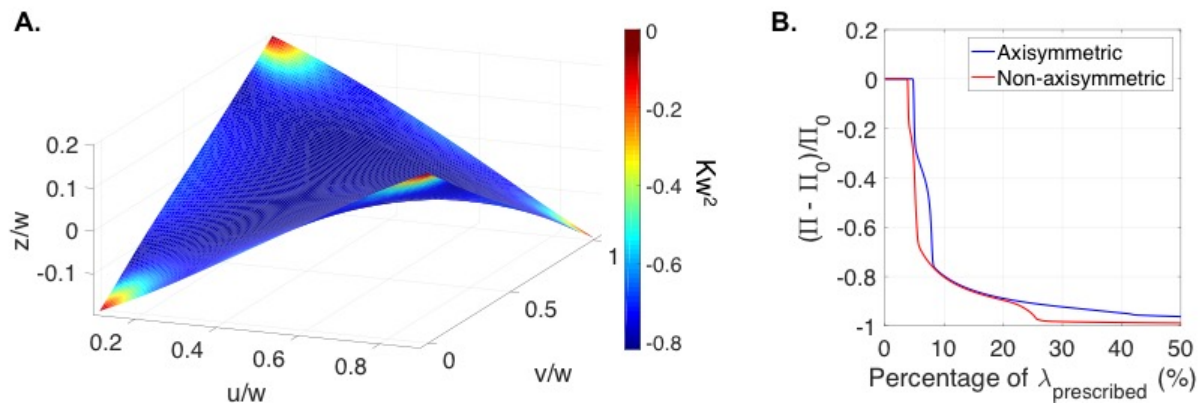
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Figure S8. (A) Workflow of photomask generation. Photomasks used to pattern Gaussian profiles with (B) $d = 0.2$, (C) $d = 0.3$, and (D) $d = 0.4$ and constant (E) positive and (F) negative Gaussian curvature.



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Figure S9. Comparison of curvature predicted by theory and FEM for (A) positive Gaussian curvature and (B) negative Gaussian curvature.



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3 **Figure S10. (A)** Non-axisymmetric mode predicted by the FEM for the prescribed constant
4 negative Gaussian curvature via the stretch profile shown in Figure 4A. **(B)** Normalized free
5 energy difference between the curved states Π and the flat state Π_0 as a function of percentage
6 of prescribed stretches $\lambda_{prescribed}$. The non-axisymmetric mode bifurcates from the flat state
7 at a lower stretch and is energetically preferred. To achieve the axisymmetric mode in the
8 FEM simulations, a symmetric boundary condition about $u/w = 0.5$ is applied. The non-
9 axisymmetric mode, however, has free boundary conditions in the FEM simulations.

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13 **References**

- 14
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