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RPPR Final Report
as of 13-Jan-2020

Agency Code:

Proposal Number: 68373CH **Agreement Number: W911NF-16-1-0119**
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STEM Degrees: 2 **STEM Participants:** 7

Major Goals: The overarching goal of this project has been to develop materials chemistry and basic understanding that enable fundamentally new types of hybrid materials, wherein responsive polymer elements are used to couple the chemical or thermal outputs of ‘active’ elements (such as catalysts and photothermal heaters) to shape changes, thereby feeding back to regulate the activity of the elements. Over the course of the project, we made major progress on several topics: (1) hysteretic self-folding in response to enzymatic catalysis, (2) reversible assembly and sustained motion of micro-patterned hydrogel composites, (3) photo-thermal capillary oscillators, and (4) improving shape-control and robustness in self-folding materials.

Accomplishments: See attached pdf file.

Training Opportunities: Valuable training opportunities in materials chemistry, chemo-mechanical systems, polymer physics, chemical catalysis, micro-fabrication approaches, and responsible conduct of research have been provided for seven graduate students and a post-doctoral fellow. Adam Hauser and Tetsu Ouchi both completed their PhD degrees in Polymer Science & Engineering at UMass Amherst during the project, while five other current PhD students (Qi Lu, Minjung Lee, Alexa Kuenstler, Hyunki Kim and David Limberg) and a post-doctoral fellow (Ji-Hwan Kang) have also contributed throughout the course of the project.

RPPR Final Report
as of 13-Jan-2020

Results Dissemination: The results were disseminated through 8 peer reviewed publications, 20 invited talks and seminars by the PI (listed below), and numerous contributed presentations by the students and postdoc involved in the work.

“Driving reconfiguration, assembly, and motion of hydrogel sheets with light”, American Chemical Society Spring Meeting, Orlando, FL, 4/2/19

“Directing shape, assembly, and motion of responsive polymer sheets”, University of Colorado Boulder, Chemical Engineering, 3/8/19

“Fabrication and assembly of shape-programmed polymer sheets”, Tufts University, Department of Physics, 2/8/19

“Fabrication and assembly of shape-programmed polymer sheets”, Rutgers University, Department of Chemistry, 1/29/19

“Origomu: The geometry and mechanics of folding polymer plates and shells”, IMECE, Pittsburgh, PA 11/12/18

“Shaping and reshaping polymer sheets with light” Edwards Symposium: New Horizons in Soft Matter, Cambridge, UK, 9/7/18

“Origomu: The geometry and mechanics of folding polymer plates and shells”, DYFP 2018, Kerkrade, Netherlands, 3/29/18 [Plenary “Snow” talk]

“Geometrically programmed buckling of polymer plates and shells”, CalTech, 3/1/18

“Tailoring structure, properties, and responsiveness of multicomponent polymer materials”, Arkema, King of Prussia, PA 1/25/18

“Geometrically programmed buckling of polymer plates and shells”, University of Illinois, 12/12/17

“Fabrication and (frustrated) assembly of shape programmed polymer sheets”, Workshop on Geometrically Frustrated Self-Assembly, Princeton, NJ, 11/29/17

“Dynamic bio-inspired materials by buckling of polymer films and multilayers”, Harvard University, 11/7/17

“Geometrically programmed buckling of polymer plates and shells”, University of Pittsburgh, 10/19/17

“Photothermally reprogrammable buckling of liquid crystal polymer films”, ILCEC, Rice University, Houston, TX 10/16/17

"Driving shape changes and motion of responsive polymer nanocomposites", American Chemical Society Meeting, Washington, DC, 8/23/17

“Responsive polymer nanocomposites with optically reconfigurable 3D shapes”, Optical Society of America Incubator on Photomechanical Materials, Washington, DC, 6/26/17

“Shape morphing and motion of responsive hydrogel composites”, American Physical Society March Meeting, New Orleans, LA, 3/13/17

“Driving continuous shape reconfiguration and motion of polymer plates and shells”, Keynote presentation, NEW. Mech workshop, Harvard University, 10/22/16

“Dynamic bio-inspired materials by buckling of polymer films and multilayers” ACS Fall 2016 Meeting, Philadelphia, PA, 8/21/16

“Photothermally reprogrammable buckling of hydrogel and liquid crystal polymer films”, International Conference on Liquid Crystals, Kent State University, 8/2/16

RPPR Final Report
as of 13-Jan-2020

Honors and Awards: Ryan Hayward:
2018 Fellow of the American Physical Society
2018 Blavatnik Awards National Finalist
Chair Michelin, visiting professorship at ESPCI, Paris, France (April - May, 2016)

Adam Hauser:
Selected for the 2016 ACS Excellence in Graduate Polymer Research Symposium

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Ryan Hayward
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: David Limberg
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Hyunki Kim
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Tetsu Ouchi
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Ji-Hwan Kang
Person Months Worked: 7.00 **Funding Support:**
Project Contribution:
International Collaboration:

International Travel:
National Academy Member: N
Other Collaborators:

ARO Interim Report—**Scientific Progress and Accomplishments**

W911NF-16-1-0119: Chemo-mechanical polymer constructs
for feedback, homeostasis, and oscillation

Ryan C. Hayward, University of Massachusetts Amherst

The overarching goal of this project has been to develop materials chemistry and basic understanding that enable fundamentally new types of hybrid materials, wherein responsive polymer elements are used to couple the chemical or thermal outputs of 'active' elements (such as catalysts and photothermal heaters) to shape changes, thereby feeding back to regulate the activity of the elements. Over the course of the project, we made major progress on several topics: (1) hysteretic self-folding in response to enzymatic catalysis, (2) reversible assembly and sustained motion of micro-patterned hydrogel composites, (3) photo-thermal capillary oscillators, and (4) improving shape-control and robustness in self-folding materials.

1. Hysteretic self-folding driven by enzymatic catalysis

A potentially powerful element in the design of self-regulating and oscillatory responsive materials is a system that exhibits hysteretic switching between distinct states. Of specific interest for the current project is a construct with bistability between an "off" state showing low catalytic activity and an "on" state showing high catalytic activity, where the state of the system responds to the product of the catalytic reaction. While a system that varies smoothly and non-hysteretically between these states will typically settle into a "partially on" steady state, sharp and hysteretic switching is anticipated to provide oscillatory behavior between these two widely-separated states.

To this end, we have explored self-folding materials based on the origami "square twist" motif that is well known to show mechanical bistability between open (unfolded) and closed (flat folded) states. Partial folding of the structure requires significant deformation (bending and stretching) of the panels, providing a large energy barrier between the two states. This causes the origami to undergo a discontinuous snapping transition from one state to the other (Fig. 1A). As shown in Fig. 1B, the system consists of a pH-sensitive

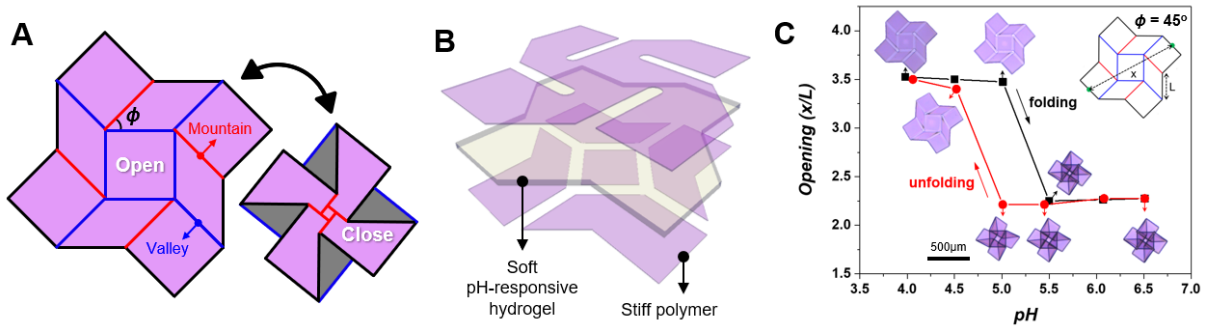

Fig. 1. Illustrations of (A) bistable folding of a square twist origami, and (B) the micropatterned trilayer structure used to make pH-responsive self-folding origami, consisting of thin layers of glassy polymer patterned with openings in the bottom layer to define valley folds and the top layer to define mountain folds sandwiching a soft pH-responsive hydrogel layer. (C) Titration curve showing hysteretic folding as a function of pH.

gel (PDEAM-co-AA; copolymer of *N, N*-diethyl acrylamide and acrylic acid) sandwiched between two thin films of stiff polymer (P*p*MS; poly(*p*-methyl styrene)), where benzophenone (BP) photo-crosslinkers in the polymer chains allow patterning of the three layers, and thereby definition of the folding angles and directions for each crease. Here, the folding angles of all the hinges are designed to be 0 ° (flat, unfolded) at pH 4 and 180 ° (fully folded) at or above neutral pH. As shown in Fig. 1C, a square twist with plane angle $\phi = 45^{o}$ shows hysteretic folding as the pH is varied. The normalized edge-to-edge distance (x/L) decreases sharply upon folding as the pH is increased from 5 to 5.5, while it shows a similarly sharp unfolding when the pH is reduced from 5 to 4.5, corresponding to a hysteresis of roughly 0.5 pH units.

To demonstrate the catalytically-driven hysteretic folding of this structure, we pattern a urease-loaded hydrogel on the central panel of the origami (Fig 2A). We work with a 1-10 mM strength buffer at pH 4; when the enzyme-loaded gel is immersed in this solution along with 0.1 M urea, the generation of ammonia locally increases the pH up to values as high as 10. Fig. 2B shows the transient response of a square twist origami based on buffer strength-dependent local pH change due to the enzymatic reaction within the central urease-loaded gel. As the pH increases to 8-10 over time, a front of color change from yellow to blue is observed due to the presence of bromothymol blue. This increase in pH due to diffusion of ammonia causes the origami to fold over a time-scale of 30 – 200 s, depending on surrounding buffer capacity. In the case of 10 mM buffer strength, one full cycle of closing and opening of the square twist is observed, suggesting the system is close to an oscillatory regime. In addition, we introduce a flow of 2 mM pH 4 buffer solution containing 0.1 M urea from a micro-capillary tip (around 200 μm in diameter) near the origami as an alternative means to 'consume' the ammonia generated

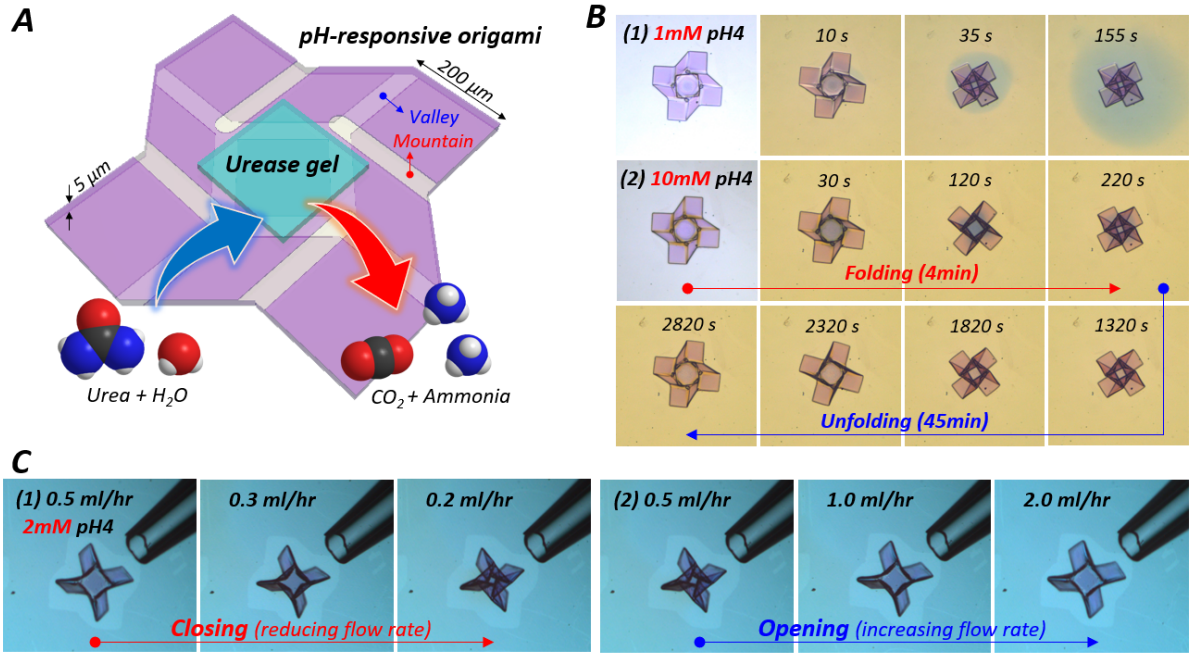

Fig. 2. (A) Schematic illustration of mechanically bistable folding of a square twist origami with urease gel for enzymatic reaction. (B) Buffer strength-dependent transient folding. (C) Hysteretic enzymatically-driven opening/closing with flow.

by the the urease-urea reaction (Fig 2C). Interestingly, we find a hysteretic transition of enzymatically-driven opening/closing. While closing takes place upon decreasing flow rate in the range of 0.5 – 0.2 mL/hr, re-opening does not proceed until a range of 1.0 – 2.0 mL/hr. Although these results are promising, to date, sustained chemo-mechanical oscillations have not been identified. We suspect that the snap-through transition may not be sufficiently sharp, such that the system can settle into both high- and low-activity steady states. Further study to expand the parameter range and also to vary the sharpness of the snap-through instability is likely to be quite interesting.

2. Reversible assembly and sustained motion of composite hydrogels

A key component of our approach is to spatially pattern functional nanoparticles within stimuli-responsive hydrogels. In one example, we have developed a simple method for in situ photo-patterning of AuNPs within crosslinked stimuli-responsive polymer films. Briefly, the benzophenone pendent group, which serves as a photo-crosslinker, has been further used as a photo-catalyst to reduce Au^{3+} ions to Au NPs. This approach enables us to photo-pattern both the overall shape of the responsive hydrogel shape, as well as the local concentration of Au NPs, as shown in Fig. 3.

This method opens unique opportunities in the design of light-responsive materials, thanks to the ability of Au NPs to efficiently convert visible light into heat through their surface plasmon resonance absorption (Fig. 3C), coupled with the approach we developed for interfacial assembly of shape-programmed particles [1]. We have taken advantage of the photothermal actuation of Au NP-patterned hydrogels to drive dynamic assembly, dis-assembly, and rotational motion of objects at an air-water interface. Fig.

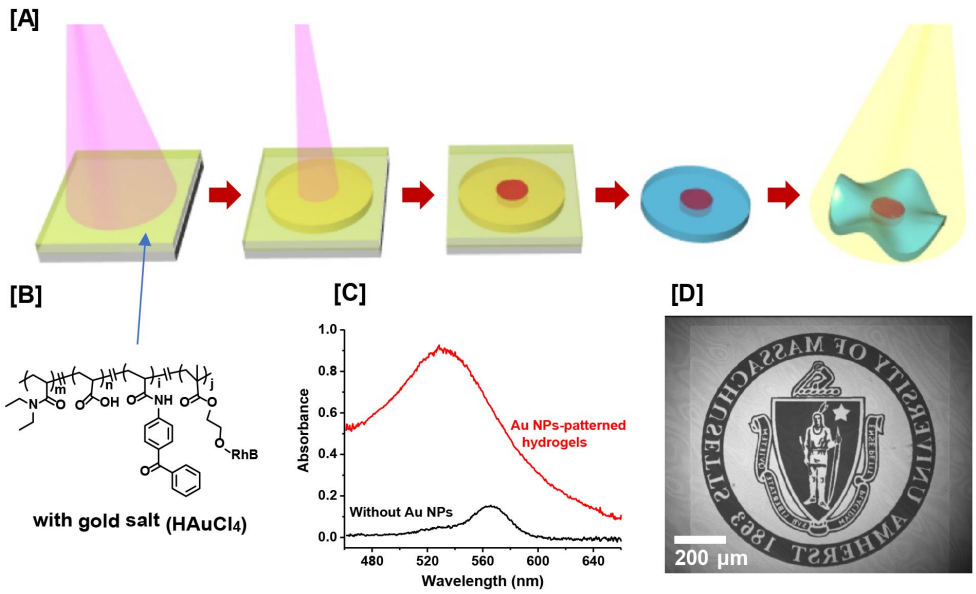

Fig. 3. (A) Schematic illustration of the fabrication of hydrogel films with patterned incorporation of Au NPs. (B) Chemical structure of the photo-crosslinkable polymer and the gold salt. (C) UV-Vis spectrum of the hydrogel and the Au NP-loaded hydrogels. (D) UMASS seal patterned (mirror image) with Au NPs.

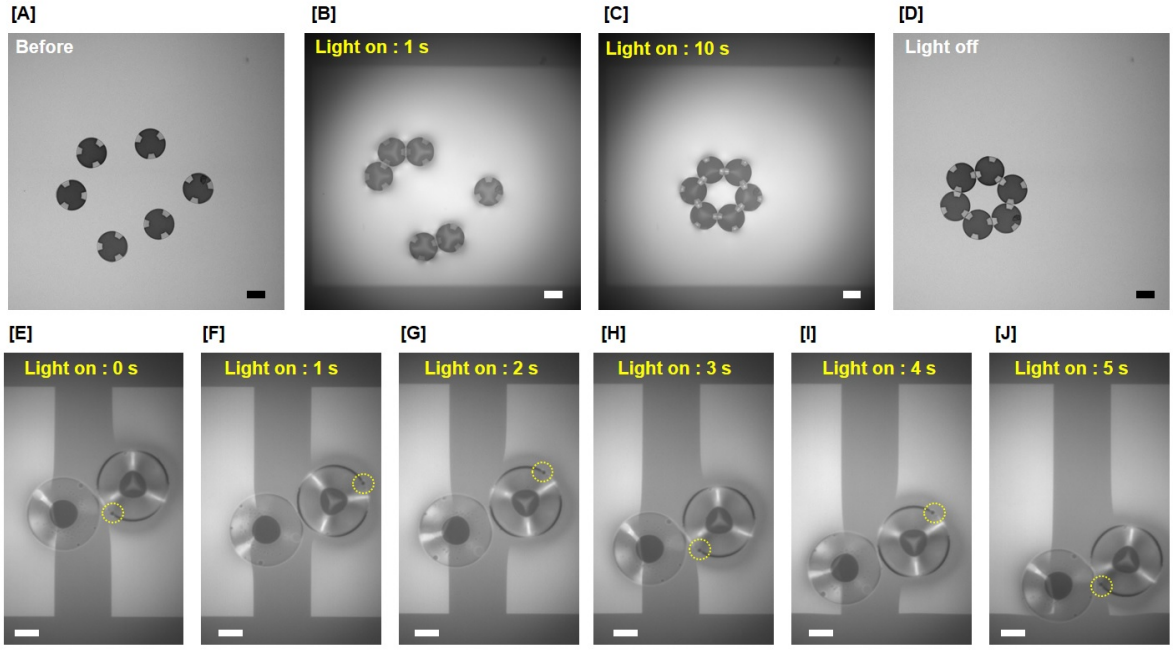

Fig. 4. (A) Au NP-patterned hydrogel disks before illumination and (B-C) under flood light. (D) The assembled structure remained after the light was off. (E-J) Au NPs-patterned hydrogel disks under gap-patterned light. The scale bar is 200 μm.

4A shows a collection of such disks patterned with Au NPs everywhere except in three patches located at equal spacings around the disk edge. Illumination (Fig. 4B-C) causes the disks to buckled into a programmed shape with three wrinkles due to the local increase in temperature (and therefore volumetric shrinkage) of the regions containing Au NPs. The resulting distortion of the air/water interface (thanks to pinning of the three-phase contact line at the disk edge) provides strong capillary interactions between particles, causing them to assemble into structures with 'bond' valences and angles specified by the Au NP pattern. Wrinkling is reversible when the light is turned off, with relatively fast (a few seconds) kinetics in both directions. Interestingly, we also found that selectively illuminated one disk gave rise to disassembly, due to repulsive capillary interactions between the wrinkled illuminated disk and flat, non-illuminated disks. Remarkably, we also found that the combination of patterned illumination and patterned disks could drive a previously unknown mode of sustained interfacial rotation. When two disks are illuminated with a pattern containing a dark stripe covering the region of inter-particle contact (Fig. 4), wrinkling of the regions outside of the dark stripe gives rise to a capillary torque that causes the particles to rotate. However, as the wrinkled regions enter the dark, they relax, weakening the capillary attraction and thus giving rise to a sustained torque. Thanks to the continuous counter rotation of the two disks, they also propel themselves along the direction of the dark stripe. These findings have recently been published in *Advanced Materials* [2].

3. Photothemocapillary oscillators

As an unexpected outgrowth of our work on polymer sheets with photo-thermally reprogrammable shapes, we discovered a new type of oscillator that relies on the balance between surface energy and photothermally induced Marangoni forces. The system (Fig. 5A) consists of a thin polyacrylamide hydrogel disk, ~ 1 mm in radius, loaded with gold nanoparticles as photo-thermal heat generators, adsorbed at the air/water interface on top of a small water droplet (volume: 100 – 300 μL). Interestingly, although the disk is more dense than water, surface tension holds it at the apex of the drop, where the interface is the least curved (due to the influence of gravity on the drop shape). When the apex of the drop is illuminated with light of sufficient intensity, the resulting photo-thermal heat generation yields a temperature gradient that pulls the disk away from the apex due to Marangoni forces. After leaving the illuminated region, however, heat generation ceases, and the disk returns towards the apex due to capillary forces. This yields an oscillatory motion of the disk with well-defined amplitude and frequency, although in some cases the direction of motion is highly irregular.

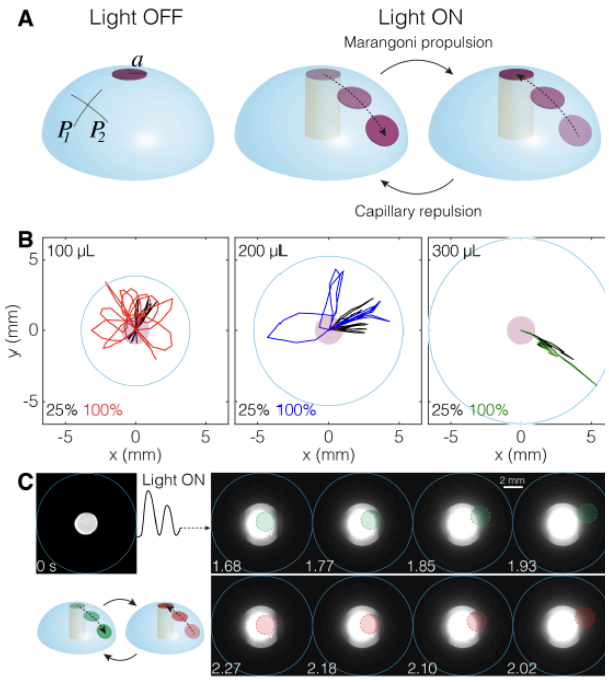

Fig. 5 (A) Schematic illustration of the photothermocapillary oscillator, along with (B) recorded traces for several different droplet volumes and light intensities (where 100% = 40 W/cm^2), and (C) a series of images showing the disk position throughout one cycle.

To validate and better understand the proposed mechanism, we developed a simple model that incorporates time-dependent heating of the disk, capillary forces, viscous drag, and inertia. Using best estimates for all physical quantities except for two treated as adjustable parameters—the effective mass, reflecting that motion of the disk also requires motion of surrounding water, and the effective drag coefficient—we obtain excellent qualitative reproduction of the observed behavior, as summarized in Fig. 6. Critically, we observe an increase in the oscillation frequency with the intensity of light (Fig. 6A and D), which would not generally be expected for a simple harmonic oscillator. As illuminated by our model, this effect results from the highly non-linear 'spring constant' provided by the capillary restoring force as the disk moves further from the apex (Fig. 6C). This work was published in *Physical Review Letters* [2].

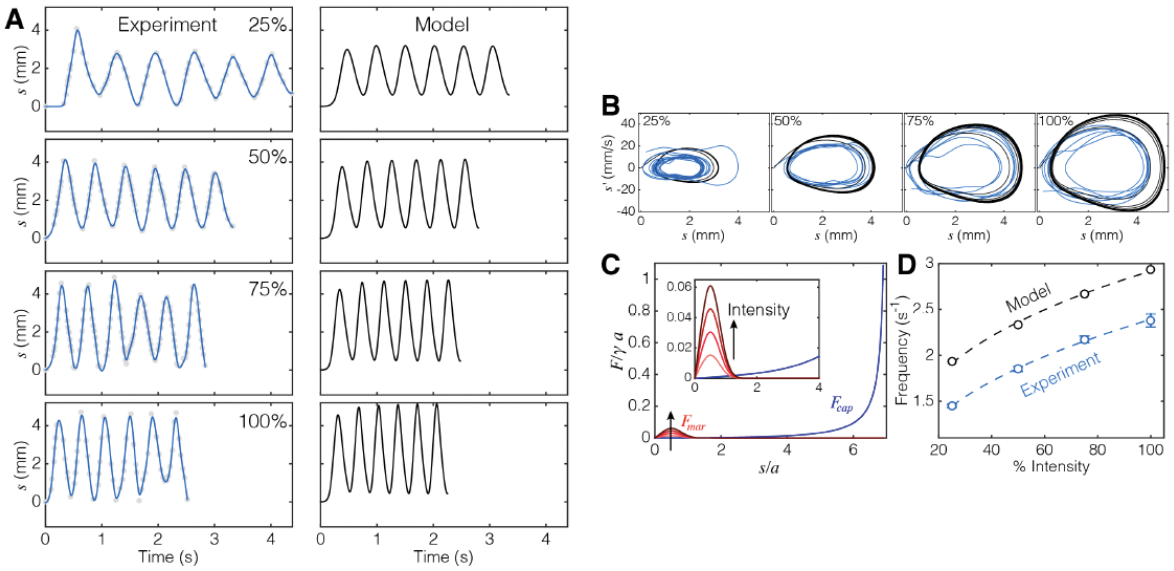

Fig. 6 (A) Time-dependent position *s* and (B) position-velocity phase portraits showing excellent qualitative agreement between experiment and model. (C) The highly nonlinear capillary restoring force leads to (D) an increase in oscillator frequency with light intensity.

4. Improving shape control and robustness of self-folding materials

Underlying all of the work described here is the ability to pattern the 3D shape of stimuli-responsive polymer films. While the platforms we had in place at the beginning of the current grant were already quite powerful in this regard (e.g., as described in [4-5]), we identified at least two key limitations that remained. First, while most platforms developed to date have allowed for the prescription of patterns of *either* mean curvature due to through-thickness variations in deformation *or* Gaussian curvature due to in-plane variations in deformation, few have enabled programming of both simultaneously. Second, few if any studies to date have focused

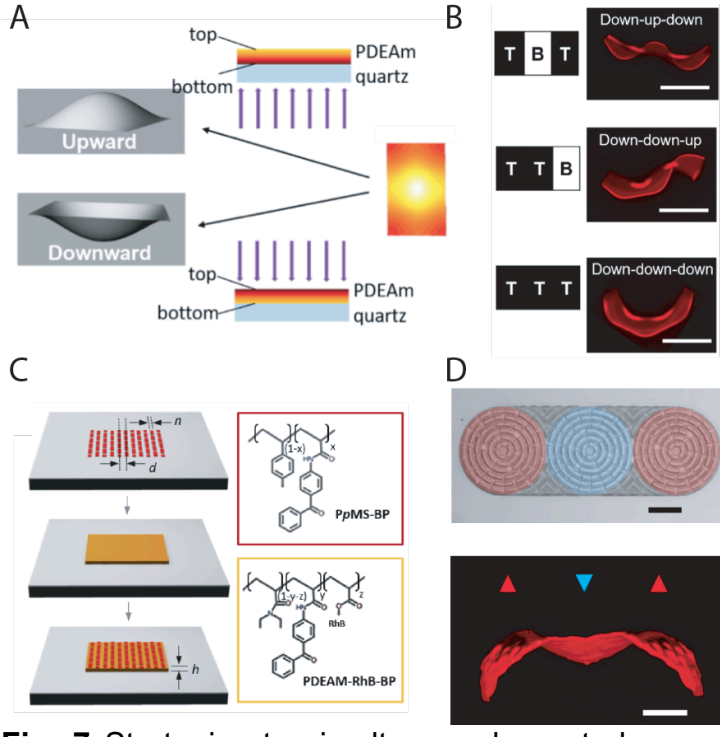

Fig. 7 Strategies to simultaneously control mean and Gaussian curvature in shape morphing sheets. (A-B) Through thickness gradients coupled with two sided exposure. (C-D) Asymmetric trilayers of rigid plastic films sandwiching a soft hydrogel film.

on the robustness of self-folding materials, while anecdotal evidence from our work suggested that such systems were often prone to misfolding, especially as the complexity of the design increased.

To address the first limitation, we devised two new strategies, as summarized in Fig. 7. In one case, we introduced a controlled amount of UV absorber within a thin film of photo-crosslinkable polymer, such that irradiation led to a gradient of crosslink density, and therefore swelling, through the film thickness (Fig. 7A). Using a transparent quartz substrate and a dual-sided exposure technique, it was therefore possible to bias the direction of mean curvature in any region of a pattern of swelling, enabling, e.g., the strings of positive Gaussian curvature 'bumps' in Fig. 7B to be programmed with the desired sequence of buckling directions. This work has recently been submitted for publication [6]. In the other case, we rely on a trilayer of two patterned rigid plastic films sandwiching a soft swellable hydrogel layer (Fig. 7C). In particular, we focused on striped geometries, with parallel orientation of the stripes on opposing faces, which leads to a composite-like response of anisotropic swelling. By controlling the in-plane orientation of the stripes, it is possible to control the Gaussian curvature, while variation in the widths of the stripes between the top and bottom surfaces gives rise to a preferred direction of curvature. For example, the concentric circles in Fig. 7D were patterned with wider stripes on the bottom surface in the outer two features (shaded red), or with wider stripes on the top surface in the inner feature (shaded blue). This led to controlled buckling of the resulting conical features upward or downward, respectively. A manuscript describing these results is being prepared for submission in the near future [7].

To address the second limitation, we developed a new approach for robust self-folding of origami structures as shown in Fig. 8. In our system (as previously described in Fig. 1B), self-folding origami consists of the trilayer films with a stimuli-responsive hydrogel sandwiched by photo-patterned thin stiff polymers on top and bottom to define mountain and valley creases, respectively. Here, a simple mechanism is introduced by separating the actuation into two discrete steps using different thermo-responsive hydrogels. First, the vertices are pre-biased to move into the desired direction from the flat state by selectively swelling one of the two hydrogels after releasing the structure from its supporting substrate at high temperature. Subsequently, the creases are folded toward their target angles by activating swelling of the second hydrogel upon cooling to room temperature.

We first consider the example of a 3-fold symmetric degree-6 vertex with alternating mountain and valley folds as a simple origami prone to misfolding. In the configuration space (Fig. 8B), there are two distinct branches (i.e., 'pop-up' and 'pop-down' states) that bifurcate from the flat state, and both branches are initially downhill in energy. Due to uncontrolled manufacturing imperfections or kinetic factors in the swelling process, the origami can thus readily adopt the frustrated state if it begins to fold along the undesired branch. To induce pre-biasing toward the desired branch prior to folding the creases, we replace the middle gel layer in a circular region around the vertex with a more hydrophilic copolymer that swells more at elevated temperature. The bucking direction can be controlled by patterning a smaller concentric circle of PpMS-BP on either the top or bottom side of the vertex, which allows to overcome even a severe 'mistake' in the prescribing of target angles of the creases as described in Fig 8C. Since biasing of the buckling direction of each vertex can be individually programmed to move upward or downward, furthermore,

it is possible to robustly select the desired branch even in multi-vertex structures with reasonably high complexity. For a Randlett bird design with 11 vertices (Fig. 8D), our strategy provides a significant improvement of self-folding robustness. Out of 20 samples, none were found to misfolding, placing a lower bound on the frequency of proper folding of 0.85 (at 95% confidence), compared to samples without biased vertices which fold properly with a frequency of only 0.45 ± 0.15. This work has recently been accepted for publication in *Advanced Materials* [8].

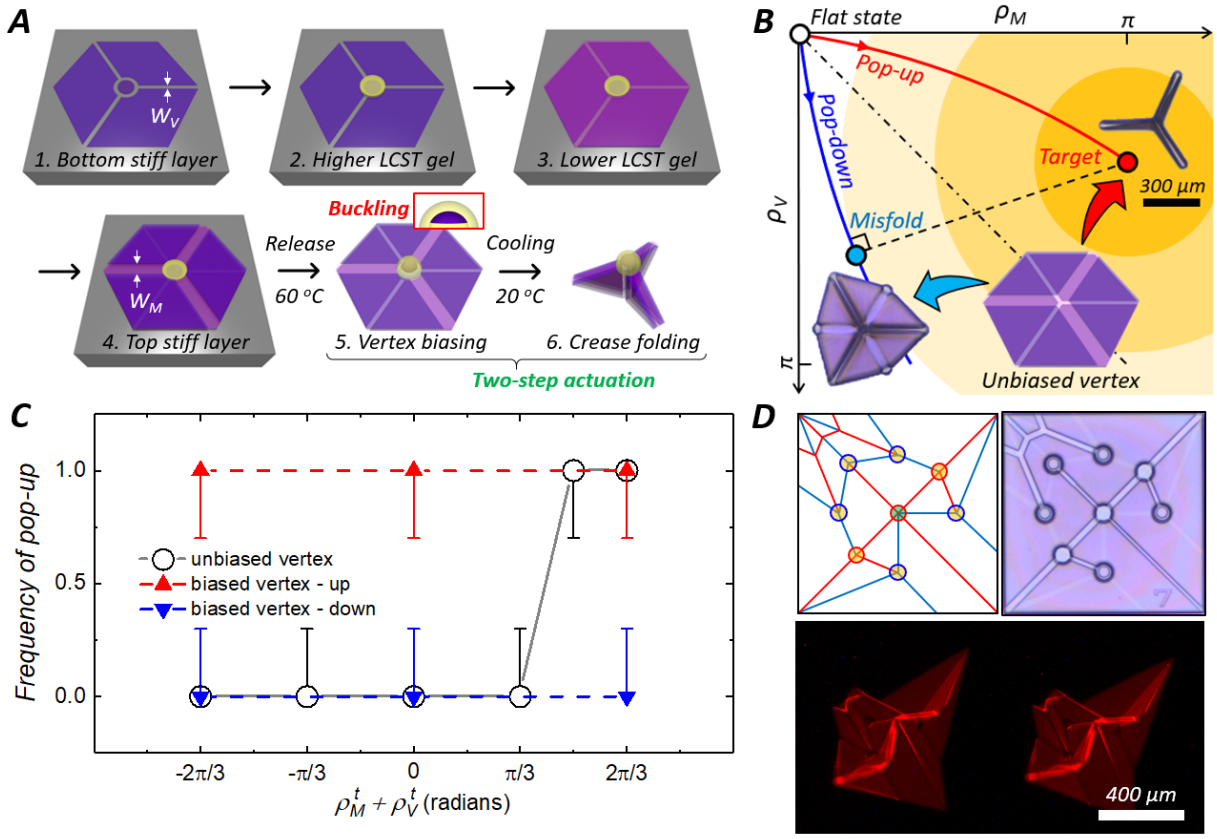

Fig. 8 (A) Fabrication schematic of robust self-folding origami based on trilayer films with vertex biasing. (B) Configuration space for the symmetric degree-6 vertex; a bifurcation without vertex biasing between the target shape along the 'pop-up' branch and the metastable frustrated shape along the 'pop-down' branch. (C) Frequency of folding along the pop-up branch for symmetric degree-6 origami both with and without vertex biasing, for different target angles of mountain/valley creases. (D) Randlett bird crease pattern with vertex biasing; fluorescence micrograph of two birds that have properly self-folded after biasing.

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3. A.W. Hauser, S. Sundaram, R.C. Hayward, "Photothermocapillary oscillators", Physical Review Letters 121, 158001 (2018). DOI: 10.1103/PhysRevLett.121.158001

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8. J.-H. Kang, H. Kim, C.D. Santangelo, R.C. Hayward*, “Enabling Robust Self-folding Origami by Pre-Biasing Vertex Buckling Direction”, Advanced Materials, accepted (2019).