Northumbria Research Link

Citation: Liu, Yingzhi, Sun, Ansu, Sridhar, Sreepathy, Li, Zhenghong, Qin, Zhuofan, Liu, Ji, Chen, Sherry, Lu, Haibao, Zhong Tang, Ben and Xu, Bin (2021) Spatially and Reversibly Actuating Soft Gel Structure by Harnessing Multimode Elastic Instabilities. ACS Applied Materials & Interfaces, 13 (30). pp. 36361-36369. ISSN 1944-8244

Published by: American Chemical Society

URL: <https://doi.org/10.1021/acsami.1c10431> <<https://doi.org/10.1021/acsami.1c10431>>

This version was downloaded from Northumbria Research Link:
<http://nrl.northumbria.ac.uk/id/eprint/46650/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)

**Northumbria
University**
NEWCASTLE

UniversityLibrary

Spatially and Reversibly Actuating Soft Gel Structure by Harnessing Multimode Elastic Instabilities

Yingzhi Liu,[†] Ansu Sun,[†] Sreepathy Sridhar, Zhenghong Li, Zhuofan Qin, Ji Liu, Xue Chen, Haibao Lu,* Ben Zhong Tang,* and Ben Bin Xu*

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 36361–36369

Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Autonomous shape transformation is key in developing high-performance soft robotics technology; the search for pronounced actuation mechanisms is an ongoing mission. Here, we present the programmable shape morphing of a three-dimensional (3D) curved gel structure by harnessing multimode mechanical instabilities during free swelling. First of all, the coupling of buckling and creasing occurs at the dedicated region of the gel structure, which is attributed to the edge and surface instabilities resulted from structure-defined spatial nonuniformity of swelling. The subsequent developments of post-buckling morphologies and crease patterns collaboratively drive the structural transformation of the gel part from the “open” state to the “closed” state, thus realizing the function of gripping. By utilizing the multi-stimuli-responsive nature of the hydrogel, we recover the swollen gel structure to its initial state, enabling reproducible and cyclic shape evolution. The described soft gel structure capable of shape transformation brings a variety of advantages, such as easy to fabricate, large strain transformation, efficient actuation, and high strength-to-weight ratio, and is anticipated to provide guidance for future applications in soft robotics, flexible electronics, offshore engineering, and healthcare products.

KEYWORDS: hydrogel, swelling, creasing, buckling, shape transformation

1. INTRODUCTION

Soft matter-based biosystems widely exist in nature to support lives such as octopus, starfish, caterpillars, etc., by fulfilling adaptive shape changes and responsive motions to allow them to survive in complex environments.^{1–5} Inspired by these features, a number of soft actuator concepts^{6–11} have been developed to mimic dedicated actuations/motions, e.g., soft grippers actuated by inflation of a pneumatic network to manipulate fragile and irregular objects,¹² a humidity- and light-driven liquid crystal network actuator¹³ to mimic self-shape morphing of flowers, and bellow-like actuators¹⁴ with origami structures enabled various motions. The discovery of superior bio-inspired robotic structure/mechanisms with desired working capacity, efficient actuation, high strength-to-weight ratio, on-demand shape programmability, and low cost is highly desired for frontier engineering applications.

Responsive hydrogel-based configurable structures can undergo shape transformation and perform complicated pattern generation spontaneously and reversibly in the presence of external stimuli, such as temperature, ionic strength, pH, light, solvent, and electric field.^{15–19} Together with its soft, biodegradable, and biocompatible properties, a hydrogel has been seen as an ideal candidate to build soft robotics,²⁰ soft actuators,^{21,22} and soft electronics.^{23,24} Notably,

Palleau et al.²⁵ created soft hydrogel tweezers through electrically assisted ionoprinting and demonstrated the gripping/releasing of small objects. Using a 3D printing technique, Xu and co-workers²⁶ fabricated an airplane-like swimming gel robot that could remotely control different motions under near-infrared light. Yuk et al.²⁰ exploited the hydraulic actuation of hydrogels to develop soft robotics, which is capable of optical and sonic camouflage in water. While the above attempts provide advancements in exploring the novel actuating mechanism, the overall fabrication, assembly, and actuation of these devices heavily rely on the support from instruments and infrastructure, which will considerably limit the application/commercialization of hydrogel actuators at the scale-up level.

Mechanical instabilities including wrinkling,^{27–33} creasing,^{34–37} folding,^{38–40} ridging,^{41–44} buckling,^{45,46} and bending⁴⁷ have brought a unique approach to realize programmable

Received: June 4, 2021

Accepted: July 12, 2021

Published: July 22, 2021

Figure 1. Swelling-induced multimode elastic instabilities. (a) Illustration of the isotropic swelling of a homogeneous gel unit and the swelling-induced instabilities in a multilayer gel structure. (b) The schematic of buckling on the edge of a gel cylinder shell. (c) Schematic illustration of the fabricating gel structure by injecting the presolution into a 3D printed “semi-cylindrical shell” mold, the molecular structure of the hydrogel, and the definitions of geometrical factors. The observations of morphologies at various time intervals on the axial edges of the gel structure under (d) an optical microscope and (e) a laser scanning confocal fluorescence microscope (LSCM), and on the circumferential outer surface with (f) the optical microscope and (g) the LSCM on the selective zone in the optical image (scale bar = 1 mm). (h) The illustration of stress states for the edge and back areas at the designated time. Images (d–f) are formatted with the same scale bar of 5 mm.

shape transformations of soft tissues. When the hydrogel is under isotropic swelling, it cannot cause instability to induce structural deformation, only a uniform increase in volume is induced (Figure 1a). Therefore, substantial efforts have been devoted to developing a planar structure with a multilayer,^{48,49} different responsiveness,⁵⁰ or density gradient^{51,52} to improve the controllability and efficiency of instability-induced 3D shape transformations or preparing homogeneous hydrogel structures upon constrained swelling⁵³ (Figure 1a,b). Especially, Gong et al. studied the formation of surface creasing and bulk bending of a piece of the hydrogel with a cuboid shape or disc shape induced by free swelling.^{54,55} Recently, researchers have been exploring the generation of instabilities on curved structures,^{53,56} where the structural anisotropy-guided formation of nonuniform stresses could create instabilities in a designable and efficient fashion to induce the shape transformations, as being discussed by non-Euclidean shell theory.^{57,58} However, the actuation of shape transformation by modulating and coordinating multimode instabilities induced by free swelling in a 3D curved gel structure has been rarely exploited.

In this work, we propose a novel actuation technology by introducing locally confined development of mechanical

instabilities on a 3D curved gel structure with the shape of a “semi-cylindrical shell”. Under freestanding swelling, instabilities are first initialized at dedicated areas with buckling occurring on the axial edges and creasing on the circumferential outer surface. Subsequently, the developments of post-buckling geometries and crease patterns enable the directional releasing of strain energy, thus drive the shape transformation of the gel structure from the “open” state to the “closed” state, and realize the function of gripping. By optimizing the inputs from the gel composition and geometrical design, we achieve swelling-driven programmable shape morphing and demonstrate the potential application as an autonomous gripper.

2. RESULTS AND DISCUSSION

A 3D curved gel structure with the shape of a “semi-cylindrical shell” is designed and fabricated by synthesizing the poly-(acrylamide-co-sodium acrylate) hydrogel (PAAm-co-NaAc) in a 3D printed mold, as shown in Figure 1c (more details are given in the Experimental Section). The preliminary reason to choose the curved shell design is to utilize the strain growth in the circumferential direction to achieve a “closed” state (see Figure S1). The obtained hydrogel structure is subsequently

Figure 2. Geometrical analysis on multimode instabilities and their collaborative effect on the transformation of the gel structure. The observations of swelling-induced morphological developments at 8 min for the axial edges with (a) an optical microscope, a fluorescence microscope, and a reconstructed 3D image from the LSCM based on the selected area in the optical image, and for the circumferential outer surface with (b) the optical microscope, LSCM, and cross sections along the axial and circumferential directions from the LSCM based on the selected area in the optical image. The analytical plots of time-dependent evolutions of structure deformation during swelling: (c) wavelength (λ) and amplitude (A) of buckling and (d) surface crease depths (μ_H and μ_V) and crease spacings (χ_H and χ_V). (e) The experimental observation and the finite element simulation of the post-buckling development. (f) G/L versus H/H_0 . Green area: I-closing regime; pink area: II-holding regime; and purple area: III-reopening regime.

immersed in deionized (DI) water to introduce freestanding swelling. An exemplified design is selected to show the swelling-induced morphological developments, with an outer diameter of $D_{\text{out}} = 10$ mm, an inner diameter of $D_{\text{in}} = 5$ mm, an initial thickness of $H_0 = (D_{\text{out}} - D_{\text{in}})/2 = 2.5$ mm, an initial axial length of $L_0 = 10$ mm, and an open angle of $\theta = 180^\circ$. After swelling, morphological developments are observed on the specific locations: buckling (Figure 1d,e) occurs at the axial edges and reticulated creases (Figure 1f,g) appear on the circumferential outer surface. The geometrical characteristic of this designed structure enabled the coexistence of buckling and creasing with clear preferences on the location, unveiling an interesting energy distribution throughout the designed gel structure, which has not been reported elsewhere.

The buckling at the axial edges shows an early onset (<30 s, Figure 1d), and then post-buckling development is observed with a reduction in buckling numbers but an increase in wavelength (λ , Figure 1e). Another interesting event taking place at the circumferential outer surface is the initiation of axial creasing lines, whose length aligns with the axial direction

at around 30 s (Figure 1g), which means that the region undergoes circumferential compression. The overall stress evolutions as per location are illustrated in Figure 1h with uniaxial stress localizing (σ_{xx}) on the edge section. However, a translational biaxial stress state (σ_{xx} and σ_{yy} , σ_{yy} represents the stress in the circumferential direction) is presented for the back area where an equibiaxial stress state ($\sigma_{xx} = \sigma_{yy}$) appears to occur soon as the hydrogel swells, by generating a biaxial “grid”-type creasing at around 1 min and such biaxial creasing explicitly grows till 12 min with the aspect ratio of a single unit of the “grid” (see the red dash box in Figure 1g) being reasonably maintained. When the gel structure swells from 12 to 30 min, the neighboring axial creasing separates from each other faster than the circumferential creases, leading to the vanish of axial creasing lines at 30 min (see the red and yellow arrows in Figure 1g). The circumferential creases rule the place thereafter, till reaching the global isotropic swelling state (see Figure S2) after 4 h. The transdirectional development of the creasing pattern from axial creasing lines to the biaxial “grid” and then to circumferential creases represents the self-

Figure 3. Time-dependent shape morphing analysis by varying geometrical factors. (a) Different initial thicknesses (H_0), $D_{\text{out}} = L_0 = 10$ mm, and $\theta = 180^\circ$. (b) Different initial lengths (L_0), $D_{\text{out}} = 10$ mm, $H_0 = 2.5$ mm, and $\theta = 180^\circ$. (c) Different initial angles (θ), $D_{\text{out}} = L_0 = 10$ mm, and $H_0 = 2.5$ mm. (d) The effects of geometry factors on shape transformation times. (e) The normalized thickness follows an apparently diffusive scaling at short times (slope of the dashed line). (f) Phase diagram by plotting the bending angle difference $\Delta\alpha$ and normalized length $\bar{L}$. The shaded area represents the fully closed region (i.e., $G/L = 0$) and the unshaded part is the partial closed region (i.e., $G/L > 0$).

regulation of strain energy and then the release of the strain energy in the circumferential direction.

Macroscopically, we observe the global transformation of the gel structure from “open” to “closed” and then returning to the “open” state (Figure 1d,e). The post-buckling development and evolution of the creasing pattern collaboratively drive the gel structure to close from 4 to 15 min. The geometrical developments at the axial edges make a direct effort to allow the edges to physically contact each other; on the other hand, the release of energy in the circumferential direction regulated by the creasing pattern supports these buckling developments to accelerate structure closing. Beyond that, adaptive structural harmonization starts from 30 min, by developing a single buckling pattern at each axial edge toward $\lambda > L$ (L refers to the axial length after the gel structure swells). The gel structure stays at the “closed” configuration until 60 min and then gradually reopens. Once reaching the end of the morphing process, all surfaces of the gel structure resume to the smooth state with the instability patterns completely disappeared (Figure S2). An isotropically swollen “semi-cylindrical shell”-shaped gel structure is presented ($D_{\text{out}} = 29.2$ mm, $H = 7.2$ mm, and $L = 28$ mm).

Once the gel structure swells, water molecules diffuse into the surface to create a thin gradient layer with swelling-induced strain, therefore leading to a multilayer configuration in a finite depth with generating spatially nonuniform stress in the thin gradient layer. Wavy buckling patterns are found on both the axial (Figure 2a) and circumferential edges (Figure S3). However, the post-buckling phenomenon on the axial edges with strong out-of-plane morphological development directly contributes to the “closing” of the gel structure. The crease

patterns are observed both on the circumferential inner (Figure S3) and outer (Figure 2b) surfaces initially, but the full sequence transition (from axial creasing lines to the biaxial creasing “grid” and then to circumferential creasing lines) only occurs at the circumferential outer surface, where the transdirectional regulation on strain energy leads to the releasing of strain energy along the circumferential direction and effectively drives the shape morphing. It is worth noting that hydrogel parts in the “hemispherical shell” shape are also fabricated, and the observations of morphologies at various time intervals of the hydrogel part are summarized in Figure S4, where a similar shape transformation from “open” to “closed” is found by swelling the part. However, the underlying mechanics seems much more complicated as the strain development on the hemispherical shell is arbitrary. Therefore, we defer the research of this structure in the future work.

To trace the morphological evolutions, we plot the wavelength (λ) and amplitude (A) of buckling in Figure 2c and the crease spacing and depth (χ , μ) in Figure 2d as a function of swelling time (t). When swelling progresses, the coalescence of adjacent buckling is observed. When the gel structure transforms from the “open” state (green area) into the “closed” state (pink area), the wavelength keeps growing, while the amplitude increases to the peak value at the closure and then decreases to 0 (Figure 2c). In Figure 2d, the crease depths (μ_H and μ_V) first achieve maximum values and then start to fade. The evolution trend of the average crease spacing (χ_H and χ_V) follows a linear relationship with the square root of swelling time, which agrees well with the theory.^{59,60}

We next investigate how buckling contributes to the global “closure” of the soft structure. The degree of swelling is defined

Figure 4. Reproducibility and demonstration of the hydrogel structure. (a) Schematic illustration of a loop of open–close–recovery cycle and (b) cyclic testing with open–close for the gel structure. Time-lapsed gripping motion captures for the hydrogel gripper with (c) sharp finger design and (d) flat finger design. (e) A demonstration of gripping strength using the designed hydrogel gripper (four fingers, $D_{\text{out}} = 10$ mm, $D_{\text{in}} = 5$ mm, $L_0 = 3$ mm, $\theta = 180^\circ$) to pick up a magnetic stirrer from water. The scale bar is 5 mm.

as H/H_0 , where H is the thickness of the swollen structure at a certain swelling time. The development of the wavy buckling profile on the axial edges can be evidenced by merging neighboring waves into a big one (see the yellow and red arrows in Figure 2e and Movies S1). A diagram (Figure 2f) is created by plotting the normalized closing factor of G/L , where G refers to the gap distance between edges (see Figure 2e). Figure 2f presents three regimes for the morphing of the gel structure: I-closing regime with G/L decreasing from 1 to 0 and close at $G/L = 0$ (green area), the swelling time when $G/L = 0$ is defined as the closing time; II-holding regime with G/L remaining at 0 (pink area); III-reopening regime with G/L gradually increasing from 0 to ~ 1 (purple area), the opening time is the time when G/L starts increasing from 0, and the recovery time is the time when G/L returns to ~ 1 . The results of finite element analysis (full simulation in Movies S2 and Figure 2e,f) show a good agreement with the experiment results.

We then explore the efficiency of shape transformation by tuning the geometrical variables with different initial thicknesses (H_0) in Figure 3a, initial axial lengths (L_0) in Figure 3b, and open angles (θ) in Figure 3c. In Figure 3a, we fix the values of the outer diameter ($D_{\text{out}} = 10$ mm), angle ($\theta = 180^\circ$), and length ($L_0 = 10$ mm); thus, the area of the circumferential outer surface ($S_{\text{cy}} = \pi D_{\text{out}} L_0 \theta / 360^\circ$) remains unchanged, while the annulus surface area ($S_{\text{an}} = 0.25 \pi (D_{\text{out}}^2 - D_{\text{in}}^2) \theta / 360^\circ$) increases with the increase of thickness. It is found that the gel structure with smaller H_0 reaches the full closure earlier. The gel structure with $H_0 = 5$ mm ($D_{\text{in}} = 0$) cannot close completely because the bending stiffness resists the closing. In Figure 3b, S_{an} remains unchanged, while S_{cy} decreases as L_0 decreases when the values of the outer diameter ($D_{\text{out}} = 10$ mm), angle ($\theta = 180^\circ$), and thickness ($H_0 = 2.5$ mm) are constant. We discover that the gel structure with a longer axial length is likely to hold the “closing” stage for

an extended period. The gel structure with an L_0 of 3 mm does not close completely, and the reason could be the insufficient axial length, which does not allow the buckling profile to evolve. In Figure 3c, without changing D_{out} , L_0 , and H_0 ($D_{\text{out}} = L_0 = 10$ mm, $H_0 = 2.5$ mm), both S_{an} and S_{cy} increase as θ increases. The gel structure with bigger θ needs less time to close, and those with smaller θ (e.g., 120 and 150°) are unable to reach a full closure. With the decrease of θ , extra circumferential distance is needed for the gel structure to reach the “closed” state, which brings more challenges to fulfill this configuration change.

Apparently, the “closed” state is easier to be achieved for the gel structure with larger S_{cy} and smaller S_{an} , where the geometrical landscape is energetically favored by the post-buckling development. Longer opening time and recovery time are needed once the volume of gel structure increases, i.e., thickness/length/angle increases (see Figure 3d), providing better control to morph the structure. In Figure 3e, we map the swelling kinetics by plotting the change in the thickness of the gel structure normalized by its initial thickness, $(H - H_0)/H_0$, as a function of $\sqrt{t}/H_0$. After transforming from the “open” state into the “closed” state (regime I, green area) and then the “holding” stage (regime II, pink area), the gel structure recovers (regime III, purple area) to the “semi-cylindrical shell” shape and regain the homogeneity. Even at this time, the gel structure is not fully swollen, and it continues to swell isotropically (regime IV, orange area) to the final state (regime V, yellow area) in which the hydrogel could no longer absorb water. By the linear fitting of the initial slope of data in Figure 3e, a diffusion coefficient constant of $D = 6.93 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ is estimated from the “open” state to the end of the “holding” stage, which is in the similar magnitude to that for the polyacrylamide hydrogel in previous reports.^{16,61,62}

We next numerically scale the “closed” state by utilizing Euler–Bernoulli curved beam theory and considering the

swelling competition between the circumferential outer surface and annulus surfaces (see the [Experimental Section](#) for the details). We define $\Delta\alpha > 0$ and $\bar{L} > \bar{L}_c$ with the bending angle difference $\Delta\alpha = ac(H/H_0 - 1)\theta' - (2\pi - \theta')$ and the normalized length $\bar{L} = L_0/H_0$, where a is the parameter associated with the geometric parameters of the sample and $a = D_{\text{out}} \ln(D_{\text{out}}/D_{\text{in}})/(D_{\text{out}} \ln(D_{\text{out}}/D_{\text{in}}) - 2H_0)$, $\theta' = \pi\theta/360^\circ$, and H/H_0 is the swelling ratio after regime III, at which the gel structure starts to swell isotropically. The two parameters c and $\bar{L}_c$ generally depend on the diffusion kinetics and the mechanical behavior of the hydrogel. Currently, there is no explicit mathematical expression to calculate their exact values. Here, we estimate the values of the two parameter by our experiments, i.e., choosing the values that can satisfy the most experimental data. Therefore, $c = 0.19$ and $\bar{L}_c = 1.5$ are taken for the best fit of the current experiments. A phase diagram (in terms of $\Delta\alpha$ and $\bar{L}$, [Figure 3f](#)) can be therefore created to show the threshold of closure by applying the above definitions and experimental inputs. Overall, a good quantitative agreement has been reached between theoretical predictions and experimental results, with one exceptional data (pointed out by the red arrow in [Figure 3f](#)) from a gel structure with a bigger thickness ($H_0 = 4$ mm). Since Euler–Bernoulli theory is only applicable to thin beams, its estimation on the shift of the bending angle for a thick gel structure might be less accurate; therefore, we decide to extend the research on modeling the shape morphing in the thick structure in the future work.

The swelling behavior of the gel structure ($D_{\text{out}} = L_0 = 10$ mm, $D_{\text{in}} = 5$ mm, and $\theta = 180^\circ$) is assessed with different BisAA contents in [Figure S5a](#). For the gel structures with higher BisAA concentrations (e.g., 37.4 and 44.2 mM in [Figure S5a](#)), they are hard to reach a full closure. For those gel structures with lower BisAA concentrations (e.g., between 3.4 and 13.6 mM in [Figure S5c](#)), their closing times are almost identical, while the automatic opening time and the full recovery time decrease as BisAA content increases. The swelling behavior of the gel structure is also studied for swelling at various concentrations of the phosphate-buffered saline solution (PBS). Our hydrogel has an ionic strength of 168 mM, which is similar to the ionic strength in 0.01 M PBS (156.6 mM); thus, the gel structure achieves limited swelling when immersed into 0.01 M PBS ([Figure S5d](#)). As shown in [Figure S5b](#), with the lower concentration of PBS, the gel structure closes more rapidly. While these results show some interesting phenomena, we unfortunately have not obtained a systematic clue from these results. We will keep exploring this part of research in our future work plan to create complicated swelling gradients in the soft gel structure.

We perform the cyclic actuation ([Figure 4a](#)) by deswelling the “reopened” gel structure through a conventional air-drying process and then saturating in 0.01 M PBS for 10 min till reaching the original shape, from which a new swelling cycle starts ([Figure S6](#)). Afterward, we assess the reproducibility of the shape morphing of the gel structure with $D_{\text{out}} = L_0 = 10$ mm, $D_{\text{in}} = 5$ mm, and $\theta = 180^\circ$. The gel structure presents good reproducibility for 30 cycles ([Figure 4b](#)). After 30 cycles, the sample cannot recover completely, which could be attributed to trivial structure degeneration (fatigue) during the experiments. We further design gel grippers with four fingers to demonstrate their efficiencies of autonomous gripping. Both hydrogel grippers can be actuated in DI water within 3 min to reach full closure and 20 min to fully reopen in DI water, as shown in [Figure 4c,d](#). These four-finger designs

optimize the shape morphing by dramatically reducing the closing time. There are no significant differences in actuation performance for the devices between the designs of the sharp finger and the flat finger. A demonstration of weight lifting is performed for the gripper (with about 0.14 g weight), using it to pick up a small magnetic stirrer (weight is about 2 g) from water ([Figure 4e](#) and [Movie S3](#)), which is 15 times the weight of the gripper. This gripping strength could be potentially applied in soft robotics for offshore/marine engineering.

3. CONCLUSIONS

We describe an autonomous shape transformation of a 3D curved gel structure by harnessing swelling-induced multimode mechanical instabilities. The initiation and programmable developments of multimode instabilities including buckling at axial edges and creasing at the circumferential outer surface have been realized in the dedicated regions. The coexistence and the regional developments of buckling and creases collaboratively drive the global shape morphing of the gel structure from the “open” state to the “closed” state. Numerical analysis creates a phase diagram to understand the effects of the geometries and swelling ratio on the “gripping” efficiency. We successfully demonstrate the actuations of several conceptual designs with good reproducibility by tailoring the structure and tuning the swelling. This mechanics-enabled shape transformation of the 3D curved gel structure brings a valuable approach to design and develop soft robotics with desired efficiency and integrability, which can be applied in future healthcare devices, human–machine interfaces, wearable electronics, etc.

4. EXPERIMENTAL SECTION

4.1. 3D Printing Mold. To fabricate the 3D curved gel structure with the shape of a “semi-cylindrical shell”, molds were created via Stratasys Objet 24 3D printing system (Z Resolution: 28 μm). The molds were designed by Solidworks software before printing. The printed parts were cleaned and rinsed with isopropanol (IPA), before being annealed on a hot plate at 100 $^\circ\text{C}$ for 15 min to allow the printed parts to be fully matured. The assembly of a gelation chamber was constructed by the printed male and female parts and wax-based sealants to prevent any possible leaking.

4.2. Synthesis of Hydrogels. The polyacrylamide hydrogel was synthesized by free-radical polymerization using ammonium persulfate as an initiator. One milliliter of an aqueous pre-gel solution containing 1173.3 mM acrylamide (monomer), 168.6 mM sodium acrylate (NaAc, charged monomer), and 6.8 mM *N,N'*-methylenebisacrylamide (BisAA, cross-linker) was prepared and degassed under 1 mTorr for 10 min after mixing and dissolving sufficiently. After that, this pre-gel solution mixed with 1.5 μL of *N,N,N',N'*-tetramethylethylenediamine (TEMED, accelerator) and 5 μL of a 10 wt % aqueous ammonium persulfate solution (APS) was rapidly loaded into a 3D printing mold. The mold was treated with 1H,1H,2H,2H-perfluorooctyltrichlorosilane from the vapor phase at room temperature (23 $^\circ\text{C}$) for 2 h to facilitate the release of the hydrogel structure after 30 min gelation process. All chemicals were used as received from Sigma-Aldrich.

4.3. Characterization. To monitor the formation and evolution of surface/structure morphologies, a trace amount of the rhodamine-B monomer was added into the pre-gel solution to enhance the visual contrast and allow the high-resolution imaging with a camera. The as-fabricated hydrogel was submerged into DI water to swell. During the swelling process, the hydrogel was gently taken out from DI water to observe under an optical microscope (Nikon LV100) at regular time intervals. A small amount of fluorescein isothiocyanate-dextran (~ 1 mg) was added into the pre-gel mixture to label the gel structure and facilitate imaging under an LSCM (Nikon A1R).

4.4. Finite Element Simulations. Finite element simulations were conducted using a commercial software (Abaqus). The gel was modeled as an incompressible Neo-Hookean material. Based on the analogy between heat transfer and solvent diffusion, thermal expansion was used here to simulate swelling, and the corresponding coupled temperature–displacement analysis was conducted. It is noted that the simulations focused on the global structure deformations, while the local surface creases caused by surface instability were neglected considering the numerical convergence. The explicit dynamic solver was used in the simulations, and the static results were obtained after the kinetic energy was dissipated.

4.5. Numerical Approach for the Fully Closed State. The “semi-cylindrical shell”-shaped gel structure could be regarded as an initially curved beam with the cross section of $L_0 \times H_0$. $\theta' = \pi\theta/360^\circ$ was introduced for convenience. By Euler–Bernoulli beam theory and scaling analysis, the bending angle of the beam due to the tension at the outer surface could be roughly estimated as

$$\alpha = a\varepsilon_0\theta' \quad (1)$$

where $a = D_{\text{out}} \ln(D_{\text{out}}/D_{\text{in}})/(D_{\text{out}} \ln(D_{\text{out}}/D_{\text{in}}) - 2H_0)$, ε_0 is the tensile strain on the outer surface, and ε_0 is related to the swelling strain $(H/H_0 - 1)$, with H/H_0 being the swelling ratio for the gel structure swelling after regime III, at which the gel structure started to swell homogeneously. The explicit expression of ε_0 as a function of $(H/H_0 - 1)$ depends on the diffusion kinetics and the mechanical behavior of the hydrogel. Here, for simplicity, we take $\varepsilon_0 = c(H/H_0 - 1)$, with c being a constant parameter. Then, eq 1 could be rewritten as

$$\alpha = ac(H/H_0 - 1)\theta' \quad (2)$$

To reach the fully closed state, the gel structure must bend/rotate at a minimum angle of $(2\pi - \theta')$. Then, from eq 2, we obtain the following requirement of the bending angle

$$\Delta\alpha > 0 \quad (3)$$

with $\Delta\alpha = ac(H/H_0 - 1)\theta' - (2\pi - \theta')$.

We also need to consider the swelling competition between the circumferential outer surface and annulus surfaces. If the fabricated gel structure was too short (i.e., small length), the water molecules would quickly enter through the annulus surfaces and mainly diffuse along the gel length. In this case, the inner core beneath the circumferential outer surface would be in the partially swollen state, and the tension induced by the swelling mismatch between the circumferential outer surface and the inner core would not be large enough to induce bending. To assess this effect, the following requirement of the structure length is proposed

$$\bar{L} > \bar{L}_c \quad (4)$$

with normalized length $\bar{L} = L_0/H_0$. $\bar{L}_c$ is the critical normalized length for full closure. By combining eqs 3 and 4, we establish the criterion for the appearance of the full closure state, based on the geometries and swelling of the gel structure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c10431>.

Schematic of the reversible morphing of the “semi-cylindrical shell”-shaped gel part under swelling/deswelling; final equilibrium state of the gel structure at an immersion time of 240 min; buckling on the circumferential edge and the inner zone; swelling-induced mechanical instabilities of the hemispherical shell hydrogel; spontaneous shape transformation of the gel structure controlled by the swelling ratio; and reproducibility of the actuating gel structure (PDF)

Development of the wavy buckling profile on the axial edges by an optical microscope (Movie S1) (MP4)

Finite element analysis results (Movie S2) (MP4)

Demonstration of gripping strength using a designed hydrogel gripper to pick up a magnetic stirrer from water (Movie S3) (MP4)

■ AUTHOR INFORMATION

Corresponding Authors

Haibao Lu — Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China; orcid.org/0000-0003-2744-8828; Email: luhb@hit.edu.cn

Ben Zhong Tang — Department of Chemistry, The Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction and Institute for Advanced Study, The Hong Kong University of Science and Technology, Kowloon, Hong Kong 999077, China; orcid.org/0000-0002-0293-964X; Email: tangbenz@ust.hk

Ben Bin Xu — Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.; orcid.org/0000-0002-6747-2016; Email: ben.xu@northumbria.ac.uk

Authors

Yingzhi Liu — Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China; Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Ansu Sun — Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Sreepathy Sridhar — Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Zhenghong Li — Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China; Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Zhuofan Qin — Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Ji Liu — Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China

Xue Chen — Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, U.K.

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsami.1c10431>

Author Contributions

[†]Y.L. and A.S. contributed equally to this work. The idea was initiated by B.B.X. and H.L. who piloted the research program

and designed the experiments with Y.L. and A.S. Y.L. and A.S. carried out the experiments with the assistance of S.S. and Z.L. on gel fabrication, 3D printing, and pattern transformation. B.B.X., X.C., and Z.Q. developed the analytical simulations. B.B.X., Y.L., H.L., J.L., and B.Z.T. analyzed and interpreted the data. B.B.X., Y.L., H.L., J.L., and B.Z.T. defined the scope together and wrote the paper with contributions from all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the National Natural Science Foundation of China (NSFC) under Grant Nos. 11672342 and 11725208 and the Engineering and Physical Sciences Research Council (EPSRC) grant-EP/N007921 and Royal Society Kan Tong Po International Fellowship 2019-KTP\RI\191012.

REFERENCES

- (1) Wehner, M.; Truby, R. L.; Fitzgerald, D. J.; Mosadegh, B.; Whitesides, G. M.; Lewis, J. A.; Wood, R. J. An Integrated Design and Fabrication Strategy for Entirely Soft, Autonomous Robots. *Nature* **2016**, *536*, 451–455.
- (2) Woodward, M. A.; Sitti, M. Morphological Intelligence Counters Foot Slipping in the Desert Locust and Dynamic Robots. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, E8358–E8367.
- (3) Elphick, M. R.; Melarange, R. Neural Control of Muscle Relaxation in Echinoderms. *J. Exp. Biol.* **2001**, *204*, 875–885.
- (4) Lin, H. T.; Leisk, G. G.; Trimmer, B. Goqbot: A Caterpillar-Inspired Soft-Bodied Rolling Robot. *Bioinspiration Biomimetics* **2011**, *6*, No. 026007.
- (5) Ren, Z.; Hu, W.; Dong, X.; Sitti, M. Multi-Functional Soft-Bodied Jellyfish-Like Swimming. *Nat. Commun.* **2019**, *10*, No. 2703.
- (6) Liu, J.; Gao, Y.; Wang, H.; Poling-Skutvik, R.; Osuji, C. O.; Yang, S. Shaping and Locomotion of Soft Robots Using Filament Actuators Made from Liquid Crystal Elastomer–Carbon Nanotube Composites. *Adv. Intell. Syst.* **2020**, *2*, No. 1900163.
- (7) Pena-Francesch, A.; Jung, H.; Demirel, M. C.; Sitti, M. Biosynthetic Self-Healing Materials for Soft Machines. *Nat. Mater.* **2020**, *19*, 1230–1235.
- (8) Dong, X.; Lum, G. Z.; Hu, W.; Zhang, R.; Ren, Z.; Onck, P. R.; Sitti, M. Bioinspired Cilia Arrays with Programmable Nonreciprocal Motion and Metachronal Coordination. *Sci. Adv.* **2020**, *6*, No. eabc9323.
- (9) Liu, L.; Broer, D. J.; Onck, P. R. Travelling Waves on Photo-Switchable Patterned Liquid Crystal Polymer Films Directed by Rotating Polarized Light. *Soft Matter* **2019**, *15*, 8040–8050.
- (10) Matsuda, T.; Kawakami, R.; Namba, R.; Nakajima, T.; Gong, J. P. Mechanoresponsive Self-Growing Hydrogels Inspired by Muscle Training. *Science* **2019**, *363*, 504–508.
- (11) Ni, C. J.; Chen, D.; Zhang, Y.; Xie, T.; Zhao, Q. Autonomous Shapeshifting Hydrogels via Temporal Programming of Photo-switchable Dynamic Network. *Chem. Mater.* **2021**, *33*, 2046–2053.
- (12) Yang, D.; Mosadegh, B.; Ainla, A.; Lee, B.; Khashai, F.; Suo, Z.; Bertoldi, K.; Whitesides, G. M. Buckling of Elastomeric Beams Enables Actuation of Soft Machines. *Adv. Mater.* **2015**, *27*, 6323–6327.
- (13) Wani, O. M.; Verpaalen, R.; Zeng, H.; Priimagi, A.; Schenning, A. An Artificial Nocturnal Flower via Humidity-Gated Photoactuation in Liquid Crystal Networks. *Adv. Mater.* **2019**, *31*, No. 1805985.
- (14) Martinez, R. V.; Fish, C. R.; Chen, X.; Whitesides, G. M. Elastomeric Origami: Programmable Paper-Elastomer Composites as Pneumatic Actuators. *Adv. Funct. Mater.* **2012**, *22*, 1376–1384.
- (15) Guvendiren, M.; Burdick, J. A.; Yang, S. Solvent Induced Transition from Wrinkles to Creases in Thin Film Gels with Depth-Wise Crosslinking Gradients. *Soft Matter* **2010**, *6*, 5795–5801.
- (16) Xu, B.; Hayward, R. C. Low-Voltage Switching of Crease Patterns on Hydrogel Surfaces. *Adv. Mater.* **2013**, *25*, 5555–5559.
- (17) Xu, B. B.; Liu, Q.; Suo, Z.; Hayward, R. C. Reversible Electrochemically Triggered Delamination Blistering of Hydrogel Films on Micropatterned Electrodes. *Adv. Funct. Mater.* **2016**, *26*, 3218–3225.
- (18) Yang, C.; Suo, Z. Hydrogel Ionotronics. *Nat. Rev. Mater.* **2018**, *3*, 125–142.
- (19) Liu, K.; Zhang, Y.; Cao, H.; Liu, H.; Geng, Y.; Yuan, W.; Zhou, J.; Wu, Z. L.; Shan, G.; Bao, Y.; Zhao, Q.; Xie, T.; Pan, P. Programmable Reversible Shape Transformation of Hydrogels Based on Transient Structural Anisotropy. *Adv. Mater.* **2020**, *32*, No. 2001693.
- (20) Yuk, H.; Lin, S.; Ma, C.; Takaffoli, M.; Fang, N. X.; Zhao, X. Hydraulic Hydrogel Actuators and Robots Optically and Sonically Camouflaged in Water. *Nat. Commun.* **2017**, *8*, No. 14230.
- (21) Li, M.; Wang, X.; Dong, B.; Sitti, M. In-Air Fast Response and High Speed Jumping and Rolling of a Light-Driven Hydrogel Actuator. *Nat. Commun.* **2020**, *11*, No. 3988.
- (22) Ionov, L. Hydrogel-Based Actuators: Possibilities and Limitations. *Mater. Today* **2014**, *17*, 494–503.
- (23) Kim, C.-C.; Lee, H.-H.; Oh, K. H.; Sun, J.-Y. Highly Stretchable, Transparent Ionic Touch Panel. *Science* **2016**, *353*, 682–687.
- (24) Liu, X.; Liu, J.; Lin, S.; Zhao, X. Hydrogel Machines. *Mater. Today* **2020**, *36*, 102–124.
- (25) Palleau, E.; Morales, D.; Dickey, M. D.; Velez, O. D. Reversible Patterning and Actuation of Hydrogels by Electrically Assisted Ionoprinting. *Nat. Commun.* **2013**, *4*, No. 2257.
- (26) Xu, B.; Han, X.; Hu, Y.; Luo, Y.; Chen, C. H.; Chen, Z.; Shi, P. A Remotely Controlled Transformable Soft Robot Based on Engineered Cardiac Tissue Construct. *Small* **2019**, *15*, No. 1900006.
- (27) Li, F.; Hou, H.; Yin, J.; Jiang, X. Near-Infrared Light-Responsive Dynamic Wrinkle Patterns. *Sci. Adv.* **2018**, *4*, No. eaar5762.
- (28) Wang, T.; Yang, Y.; Fu, C.; Liu, F.; Wang, K.; Xu, F. Wrinkling and Smoothing of a Soft Shell. *J. Mech. Phys. Solids* **2020**, *134*, No. 103738.
- (29) Ma, T.; Li, T.; Zhou, L.; Ma, X.; Yin, J.; Jiang, X. Dynamic Wrinkling Pattern Exhibiting Tunable Fluorescence for Anticounterfeiting Applications. *Nat. Commun.* **2020**, *11*, No. 1811.
- (30) Yang, S.; Khare, K.; Lin, P.-C. Harnessing Surface Wrinkle Patterns in Soft Matter. *Adv. Funct. Mater.* **2010**, *20*, 2550–2564.
- (31) Stoop, N.; Lagrange, R.; Terwagne, D.; Reis, P. M.; Dunkel, J. Curvature-Induced Symmetry Breaking Determines Elastic Surface Patterns. *Nat. Mater.* **2015**, *14*, 337–342.
- (32) Li, T.; Hu, K.; Ma, X.; Zhang, W.; Yin, J.; Jiang, X. Hierarchical 3D Patterns with Dynamic Wrinkles Produced by a Photocontrolled Diels-Alder Reaction on the Surface. *Adv. Mater.* **2020**, *32*, No. 1906712.
- (33) Liu, L.; Onck, P. R. Topographical Changes in Photo-Responsive Liquid Crystal Films: A Computational Analysis. *Soft Matter* **2018**, *14*, 2411–2428.
- (34) Liu, Q.; Ouchi, T.; Jin, L.; Hayward, R.; Suo, Z. Elastocapillary Crease. *Phys. Rev. Lett.* **2019**, *122*, No. 098003.
- (35) Trujillo, V.; Kim, J.; Hayward, R. C. Creasing Instability of Surface-Attached Hydrogels. *Soft Matter* **2008**, *4*, 564–569.
- (36) Jin, L.; Cai, S.; Suo, Z. Creases in Soft Tissues Generated by Growth. *Europhys. Lett.* **2011**, *95*, No. 64002.
- (37) Kim, J.; Yoon, J.; Hayward, R. C. Dynamic Display of Biomolecular Patterns through an Elastic Creasing Instability of Stimuli-Responsive Hydrogels. *Nat. Mater.* **2010**, *9*, 159–164.
- (38) Kim, P.; Abkarian, M.; Stone, H. A. Hierarchical Folding of Elastic Membranes under Biaxial Compressive Stress. *Nat. Mater.* **2011**, *10*, 952–957.
- (39) Al-Rashed, R.; Jimenez, F. L.; Marthelot, J.; Reis, P. M. Buckling Patterns in Biaxially Pre-Stretched Bilayer Shells: Wrinkles, Creases, Folds and Fracture-Like Ridges. *Soft Matter* **2017**, *13*, 7969–7978.

- (40) Ebata, Y.; Croll, A. B.; Crosby, A. J. Wrinkling and Strain Localizations in Polymer Thin Films. *Soft Matter* **2012**, *8*, 9086–9091.
- (41) Yang, Y.; Dai, H. H.; Xu, F.; Potier-Ferry, M. Pattern Transitions in a Soft Cylindrical Shell. *Phys. Rev. Lett.* **2018**, *120*, No. 215503.
- (42) Ouchi, T.; Yang, J.; Suo, Z.; Hayward, R. C. Effects of Stiff Film Pattern Geometry on Surface Buckling Instabilities of Elastic Bilayers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23406–23413.
- (43) Jin, L. Mechanical Instabilities of Soft Materials: Creases, Wrinkles, Folds, and Ridges. Doctoral Dissertation, Harvard University, 2014.
- (44) Edmondson, S.; Frieda, K.; Comrie, J. E.; Onck, P. R.; Huck, W. T. S. Buckling in Quasi-2D Polymers. *Adv. Mater.* **2006**, *18*, 724–728.
- (45) Nojoomi, A.; Arslan, H.; Lee, K.; Yum, K. Bioinspired 3D Structures with Programmable Morphologies and Motions. *Nat. Commun.* **2018**, *9*, No. 3705.
- (46) Zhao, Q.; Yang, X. X.; Ma, C. X.; Chen, D.; Bai, H.; Li, T. F.; Yang, W.; Xie, T. A Bioinspired Reversible Snapping Hydrogel Assembly. *Mater. Horiz.* **2016**, *3*, 422–428.
- (47) Holmes, D. P.; Roché, M.; Sinha, T.; Stone, H. A. Bending and Twisting of Soft Materials by Non-Homogenous Swelling. *Soft Matter* **2011**, *7*, 5188–5193.
- (48) Na, J. H.; Evans, A. A.; Bae, J.; Chiappelli, M. C.; Santangelo, C. D.; Lang, R. J.; Hull, T. C.; Hayward, R. C. Programming Reversibly Self-Folding Origami with Micropatterned Photo-Crosslinkable Polymer Trilayers. *Adv. Mater.* **2015**, *27*, 79–85.
- (49) Cangialosi, A.; Yoon, C.; Liu, J.; Huang, Q.; Guo, J.; Nguyen, T. D.; Gracias, D. H.; Schulman, R. DNA Sequence-Directed Shape Change of Photopatterned Hydrogels via High-Degree Swelling. *Science* **2017**, *357*, 1126–1130.
- (50) Wang, Z. J.; Hong, W.; Wu, Z. L.; Zheng, Q. Site-Specific Pre-Swelling-Directed Morphing Structures of Patterned Hydrogels. *Angew. Chem., Int. Ed.* **2017**, *56*, 15974–15978.
- (51) Fan, W.; Shan, C.; Guo, H.; Sang, J.; Wang, R.; Zheng, R.; Sui, K.; Nie, Z. Dual-Gradient Enabled Ultrafast Biomimetic Snapping Hydrogel Materials of Hydrogel Materials. *Sci. Adv.* **2019**, *5*, No. eaav7174.
- (52) Zhou, Y.; Duque, C. M.; Santangelo, C. D.; Hayward, R. C. Biasing Buckling Direction in Shape-Programmable Hydrogel Sheets with through-Thickness Gradients. *Adv. Funct. Mater.* **2019**, *29*, No. 1905273.
- (53) Lee, H.; Zhang, J.; Jiang, H.; Fang, N. X. Prescribed Pattern Transformation in Swelling Gel Tubes by Elastic Instability. *Phys. Rev. Lett.* **2012**, *108*, No. 214304.
- (54) Arifuzzaman, M.; Wu, Z. L.; Takahashi, R.; Kurokawa, T.; Nakajima, T.; Gong, J. P. Geometric and Edge Effects on Swelling-Induced Ordered Structure Formation in Polyelectrolyte Hydrogels. *Macromolecules* **2013**, *46*, 9083–9090.
- (55) Takahashi, R.; Ikura, Y.; King, D. R.; Nonoyama, T.; Nakajima, T.; Kurokawa, T.; Kuroda, H.; Tonegawa, Y.; Gong, J. P. Coupled Instabilities of Surface Crease and Bulk Bending during Fast Free Swelling of Hydrogels. *Soft Matter* **2016**, *12*, 5081–5088.
- (56) Pezzulla, M.; Stoop, N.; Steranka, M. P.; Bade, A. J.; Holmes, D. P. Curvature-Induced Instabilities of Shells. *Phys. Rev. Lett.* **2018**, *120*, No. 048002.
- (57) Pezzulla, M.; Stoop, N.; Jiang, X.; Holmes, D. P. Curvature-Driven Morphing of Non-Euclidean Shells. *Proc. R. Soc. A* **2017**, *473*, No. 20170087.
- (58) Stein-Montalvo, L.; Costa, P.; Pezzulla, M.; Holmes, D. P. Buckling of Geometrically Confined Shells. *Soft Matter* **2019**, *15*, 1215–1222.
- (59) Tanaka, T.; Sun, S.; Hirokawa, Y.; Katayama, S.; Kucera, J.; Hirose, Y.; Amiya, T. Mechanical Instability of Gels at the Phase Transition. *Nature* **1987**, *325*, 796–798.
- (60) Tanaka, T.; Sun, S. T.; Hirokawa, Y.; Katayama, S.; Kucera, J.; Hirose, Y.; Amiya, T. Mechanical Instability of Swelling Gels. In *Studies in Polymer Science*; Elsevier Science Publishers B.V.: Amsterdam, 1988.
- (61) Takahashi, K.; Takigawa, T.; Masuda, T. Swelling and Deswelling Kinetics of Poly(N-Isopropylacrylamide) Gels. *J. Chem. Phys.* **2004**, *120*, 2972–2979.
- (62) Li, Y.; Tanaka, T. Kinetics of Swelling and Shrinking of Gels. *J. Chem. Phys.* **1990**, *92*, 1365–1371.