Programmable Multistable Hydrogel Morphs

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Self-shaping materials have wide applications in soft robotics, biomedical devices, etc. Shape transformations of intelligent materials are usually realized by switching environmental conditions. However, it is challenging to form multistable morphing structures under the same condition. Herein, the programmed deformations of a composite hydrogel into multistable configurations under the same condition are demonstrated. The hydrogel consists of integrated units of through-thickness and/or in-plane gradient structures, where the former leads to bending, folding, or twisting with a predetermined direction and the latter buckles upward or downward with equal possibility. The bistability of buckling affords the integrated hydrogel with multiple possible configurations. The composite hydrogel with multiple in-plane gradient units (number: $n$) and through-thickness gradient ones (number: $m$) theoretically has $2^n \times 2^m$ configurations under the same condition. Although the integration of units with through-thickness gradient does not contribute to the diversity of configurations, it favors forming complex and designable configurations. Both experimental and simulation results show that various stable configurations can be obtained in one composite hydrogel under the same condition by controlling the buckling direction of each unit by a selective preswelling step. This concept and strategy are applicable for other intelligent materials and merit their applications in diverse areas.

Morphing materials have received increasing attention, owing to their promising applications ranging from aircrafts and biomedical devices to soft robotics and intelligent systems.[1–6] To design intelligent morphing materials, nature has provided elegant paradigms and inspiring sources.[7–9]. There are efforts devoted to understanding and mimicking the versatile deformations of natural systems, such as the bending of pinecones and wheat awns,[10–12] the snapping of the Venus flytrap,[13,14] and the twisting of Bauhinia variegata bean pod valves,[15] to name a few. Among the synthetic materials undergoing preprogrammed deformations, hydrogels are particularly interesting because of their open network structures and the drastic volume changes under the actions of external stimuli.[16,17] Heterogeneous expansion or contraction of a responsive gel generates localized internal stresses that govern the transformation of the originally planar gel sheet into a 3D configuration.[9,18–23] A seminal strategy pioneered by Hu et al. relies on the variation in gel composition across the bilayer film.[24] The different responses of the top and bottom layers lead to controllable bending deformation of the bilayer gel. Studart and coworkers applied a magnetic field to locally control the alignment of reinforcing platelets, which were fixed by the subsequent polymerization and gelation process of precursor suspension.[25] By a multistep orientation and gelation procedure, the bilayer composite hydrogel was fabricated in which platelets aligned along a specific direction at each layer. The oriented platelets within the composite hydrogel led to the anisotropic swelling of each layer. Twisting deformation was realized in the bilayer gel with platelets aligned at ±45° from the longitudinal direction of the strip, resulting in a localized saddle-like curvature under external stimulation.

Complex configurations can be obtained by integrating different structures settled with specific deformation modes in the composite hydrogel.[26–29] For example, Yang and coworkers applied photolithography to prepare patterned snowman-shaped bilayer hydrogels, which collapsed into microcapsules through a combination of bending and folding at different parts.[30] The reversible deformation enabled the packaging and releasing of encapsulants on demand. Various soft grippers and actuators have been developed based on similar mechanisms.[24,26,31,32] In addition, shape transformations between different configurations can be realized in one composite hydrogel by incorporating
different types of responsive polymers. Selective actuations of different responsive materials lead to different internal stresses and thus different configurations.[31–33] For instance, Gracias and coworkers patterned various DNA sequences in one composite bilayer hydrogel.\[36\] The localized gels responded to different DNA hairpins, which tuned the cross-linking density locally by molecular recognition. Therefore, structural morphing was realized by sequentially adding different DNA hairpins into the bath solution of the composite gel to activate individual actuation units. However, in the aforementioned mechanisms, the basic units of the composite hydrogels usually consist of dissimilar layers through the thickness of gel sheets (i.e., through-thickness gradient), resulting in bending, folding, and twisting deformations with predetermined directions (Figure 1a). As a consequence, the composite hydrogel has only one configuration under each specific condition, although different configurations may be achieved by tuning environmental conditions. Morphing hydrogels capable of exhibiting multiple stable configurations under the same conditions are less often studied.

Besides through-thickness gradient-induced deformations, it has been found that in-plane gradient structures (i.e., gel sheets with dissimilar components in planar patterns) can also build up internal stresses and thus induce programmed deformations.[37,38] In a seminal work, Sharon and coworkers fabricated disc gels with nonlinear gradients of poly (N-isopropylacrylamide) content in the radical direction; the localized gels with different polymer contents contracted to different degrees at high temperatures.[18] When the central part contracted more, wrinkles developed at the edge, and when the edge shrank more, the sheet buckled into a dome-like shape. In general, the high-swelling region tends to relieve in-plane compression by out-of-plane deformation.[19] The 2D distribution of one component in a hydrogel film can be well controlled via photolithography by a mask to direct polymerization and/or cross-linking.[40] Such a composite distribution leads to a programmable in-plane internal stress field and may buckle abruptly into 3D configurations. However, just like all mechanical instabilities, the in-plane gradient-induced buckling has no predetermined orientation, and it picks a side almost randomly, owing to through-thickness symmetry. The resulting structure is usually bistable (Figure 1b). The indeterminacy may be overcome by breaking the symmetry kinetically, e.g., by solvent evaporating or preswelling from one side for adequate time, so that the deformation of the gel can be controlled.[41] Integrating multiple (n) bistable buckling units can encode more \((2^n)\) possible configurations into the composite hydrogel. For example, in a previous work,[41] an array of high-swelling disc gels were embedded in a nonswelling gel by photolithography and demonstrated programmed multistable configurations by controlling the buckling direction of each unit via selective preswelling.

In this communication, we aim to extend this concept and strategy to more complex systems with programmed morphing configurations by: 1) redesigning the geometry of high-swelling parts in the buckling unit from uniform circular discs; 2) integrating in-plane-patterned buckling units with other (bending, folding, and/or twisting) units of through-thickness gradients; and 3) controlling the buckling direction of each unit to achieve multistable states. Merging multiple in-plane gradient units (the number: \(n\)) with through-thickness gradient ones (the number: \(m\)) leads to various \((2^n \times 2^m = 2^n)\) possible configurations under the same condition, depending on every individual buckling domain (Figure 1c). The in-plane gradient units with the nature of bistability afford the composite hydrogel multistable configurations, whereas the integration of through-thickness gradient units endows the gel with more complex and desirable configurations. The formation and control of multistable configurations in one integrated hydrogel with in-plane and through-thickness gradient structures were verified by experimental and simulation results. These programmable multistable morphing structures should enrich the design of morphing materials and merit the development of intelligent devices and soft robotics.

The composite hydrogel with multiple in-plane-patterned units was fabricated by multistep photolithography (see details in the Experimental Section). In the composite hydrogel, an array of high-swelling poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) (P(AAm-co-AMPS)) gels were individually embedded in a nonswelling polyacrylamide (PAAm) gel. To have effective buckling deformation with necessary amplitude, the geometry of high-swelling parts was designed as rectangular patches with relatively high aspect ratios (Figure S1, Supporting Information). The PAAm hardly swelled in water, whereas the P(AAm-co-AMPS) gel severely swelled with a high swelling ratio, with a length, \(S\), of 2.6. The buckling of the composite gel containing a rectangular high-swelling region with dimensions of 4.0 mm \(\times\) 1.0 mm caused deformation with \(\approx 90^\circ\) of directional change. A composite gel having six such rectangular patches (Figure S2a, Supporting Information) was used to demonstrate the programmable deformations into multistable configurations with the assistance of a preswelling step to direct the buckling direction of each unit. A pair of silhouetted masks were used

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**Figure 1.** Illustration of the possible configurations of hydrogels with single or multiple units. a) A single unit with through-thickness gradient has a predefined direction and one configuration after bending, folding, or twisting deformations, and the composite with multiple units also has one configuration. b) In contrast, a single unit with in-plane gradient shows out-of-plane buckling with bistable features, and the integration of multiple \((n)\) units leads to \(2^n\) possible configurations. c) The integration of multiple units of through-thickness (number: \(m\)) and in-plane (number: \(n\)) gradient structures leads to multiple \((1^m \times 2^n = 2^n)\) possible configurations.
to control the preswelling of the high-swelling gel from one side, which directed the buckling direction of the separate units in the subsequent free-swelling process to form a stable configuration. Different pairs of the silhouetted masks resulted in different combinations of the series buckled units and thus distinct configurations of the composite hydrogel under the same condition. Several representative configurations are shown in Figure 2a, and the simulation results coincided well with experimental observations.

Besides linear integration, buckling units with in-plane gradient structures can be arranged in a branched model. As shown in Figure 2b and Figure S2b, Supporting Information, four buckling units were integrated into a four-arm composite hydrogel. By separately controlling the buckling direction of each unit, different configurations were obtained from the same composite hydrogel.

The unit with in-plane gradient structures can also be integrated with other units with through-thickness gradient structures to form multistable configurations. As shown in Figure 3a and Figure S3a, Supporting Information, a bending unit with the bilayer structure (a typical structure with through-thickness gradient) was integrated with the buckling unit with an in-plane gradient, which formed two distinct configurations because of the bistability of the in-plane gradient-induced buckling deformation. A spiral configuration was formed when buckling and bending were in the same direction, whereas a hook-like configuration was formed when the buckling direction was opposite the bending one. Moreover, in-plane gradient-induced buckling can also be combined with the through-thickness gradient-induced bending for multistable configurations. As shown in Figure 3b and Figure S3b, Supporting Information, two buckling units were stacked with the folding unit from the two ends of the gel strip containing a narrow bilayer structure. The central part folded with a predetermined angle, which depended on the width of the narrow bilayer structure, whereas the units at two ends buckled toward the inside or outside that can be controlled by the preswelling step. Therefore, this composite hydrogel deformed into different configurations. In these distinct configurations of the composite gels, the bending or the folding unit had a well-defined direction, and the buckling unit with bistable states afforded diversity of the final configurations.

Different modes of deformations can be combined into one composite hydrogel by integrating structures with in-plane and through-thickness gradients. As shown in Figure 4a and Figure S4, Supporting Information, the in-plane gradient-mediated buckling to form the cylinder helix (region I) and the folded shape (region II) was combined with the through-thickness gradient-mediated twisting (region III) and folding (region IV) in one composite hydrogel. The in-plane gradient-mediated deformations had a feature of bistability, resulting in the formation of a left- or right-handed cylinder helix in region I and folded shapes in opposite directions in region II. Owing to the through-thickness gradient, the chirality of twisting deformation and the direction of folding deformation were predetermined in regions III and IV. Consequently, the composite hydrogel showed four distinct complex yet programmable configurations (Figure 4b).

The multistable deformations in the composite hydrogels are fully reversible, because the deformations, despite being of

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Figure 2. Various configurations of the composite hydrogel with a) linear or b) branched integrations of multiple units of in-plane gradient structures. The buckling direction of each unit was programmed by a site-specific preswelling process that built a transient through-thickness gradient in the high-swelling regions. Geometries of the composite gels are shown in the left, and the experimental observations (the upper) and simulated configurations (the bottom) after the programmed deformations are shown in the right. The pairs of silhouetted masks for site-specific preswelling are shown as the insets of the photographs. Color scale: swelling ratio. Scale bar: 5 mm.
different modes, are driven by the swelling mismatch that can be generated or diminished by external stimuli. In this work, the highly swollen polyelectrolyte hydrogel contracted its volume in the saline solution due to the electrostatic shielding effect and became reswollen in pure water. When the NaCl concentration of the saline solution was raised to 0.5 m, the swelling mismatch can be almost diminished (Figure S5, Supporting Information). The flattened composite hydrogel can be reshaped to other 3D configurations using different pairs of silhouetted masks to guide the site-specific preswelling in water. The deformation degree can also be controlled by the magnitude of the swelling mismatch. Therefore, the configurations of composite hydrogels can be elaborately controlled by both combining the preswelling step to control the morphing structures and tuning the ionic strength to control the deformation degree (Figure 5). We should note that the relatively large deformation magnitude of separate units in pure water, when compared with that in Figure 1a, was because of the different lengths of rectangular high-swelling gels (Figure S2 and S6, Supporting Information). Furthermore, a single unit with an in-plane gradient was repeatedly incubated in pure water, 0.01, and 0.5 m of NaCl solutions in sequence. The swelling behavior of the high-swelling hydrogel, as well as the deformation of the unit with in-plane gradient, showed good reproducibility after four cycles (Figure S7, Supporting Information).

As demonstrated earlier, the programmability of multistable configurations is conceptually different from the different configurations of a composite hydrogel incorporated with multiple responsive polymers, which require different conditions to form different transformations. In our case, different configurations are obtainable under the same condition, and the configurations of the integrated gel essentially possess multistability. The differences rely on the presence and control of the buckling unit with in-plane gradients and bistability. However, multiple

![Figure 3. Multistable configurations of the composite gels with integrated units of through-thickness and in-plane gradient structures. a) Integration of one buckling unit and one bending unit. b) Integration of one folding unit and two buckling units. Buckling upward or downward led to distinct configurations of the composite hydrogel. Silhouetted masks are shown as the insets of the photographs. Scale bar: 5 mm.](image)

![Figure 4. Multistable configurations of integrated hydrogels with different gradient structures and deformation modes. a) A schematic for the geometry of the integrated hydrogel. Region I and region II have in-plane gradients and deform in cylinder helices with different handedness and folded shapes into different directions, respectively. Region III has a layered fibrous structure and shows twisting deformation with predefined handedness, whereas region IV has a narrow bilayer structure and shows folding deformation with a predetermined direction. b) Distinct configurations of the integrated hydrogel. Silhouetted masks are shown as the insets of the photographs. Scale bar: 5 mm.](image)
responsive polymers can also be incorporated in the integrated hydrogel with in-plane and through-thickness gradient structures, which should further enrich the programmability of deformation and the diversity of final configurations.

In conclusion, we have demonstrated a new strategy to impart the composite hydrogel with multistable configurations. The composite hydrogels consisted of multiple units with in-plane and through-thickness gradient structures. The former structure led to out-of-plane buckling with a feature of bistability, whereas the latter structure led to bending, folding, or twisting deformations with well-defined directions. Therefore, the units with in-plane gradient structures afforded the composite hydrogel multistability of the final configurations, and the integration of units with through-thickness gradient structures favored the formation of complex and designable configurations. Both experimental and simulation results showed that various stable configurations can be obtained in one composite hydrogel under the same condition by controlling the buckling direction of the unit with in-plane gradient structures. The programmed deformation of the hydrogel into different configurations was fully reversible due to the tunable swelling mismatch, providing an avenue for configuration transformations on demand. The integration of different units can be extended from linear to branched and networked, and different responsive polymers can be incorporated into one composite hydrogel, enriching the obtainable configurations from different dimensions. This conceptually new strategy should be applicable for other intelligent materials including shape memory polymers, liquid crystalline elastomers, and shape memory alloys and merit their applications as biomedical devices, flexible electronics, etc.

### Experimental Section

**Fabrication of Composite Hydrogels:** The patterned hydrogel was synthesized by multistep photolithographic polymerization. A precursor aqueous solution containing acrylamide (AAm), N,N'-methylenebisacrylamide (MBAA, chemical cross-linker), and 2,2'-azo-bis-(2-methylpropionamide) (V-50, photoinitiator) was injected into a reaction cell consisting of a glass substrate and a polyethylene terephthalate (PET) film (thickness: ≈0.1 mm), which were separated by a frame of 0.2 mm-thick silicon rubber. A photo-mask prepared by ink-jet printing was placed atop the glass substrate. After irradiation under UV light (UVHAND 100, Hönle; 365 nm, 5 mW cm⁻²) for 45 s, the exposed regions formed a patterned PAAm hydrogel. The reaction cell was opened to remove the unreacted solution, and the patterned gels were selectively left on the glass substrate due to the relatively high hydrophilicity. Another patterned PAAm gel with the same or different feature was prepared by the same process. Two glass substrates with patterned PAAm gels were assembled face to face with a frame of 0.4 mm-thick silicon spacer. Another precursor solution containing AAm, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), MBAA, and V-50 was injected into the interspace between the preformed PAAm gels, and the reaction cell was immediately exposed to UV light for 3 min without the photo-mask. The patterned composite PAAm/P(AAm-co-AMPS) hydrogel was thus obtained. By tuning the pattern and location of PAAm gels on each substrate before the face-to-face assembly, different gradient structures, as well as the uniform structure, were constructed in one composite hydrogel. The recipes of precursor solutions for the fabrication of composite hydrogels are shown in Table S1, Supporting Information. The detailed dimensions of the as-prepared composite hydrogels are shown in Figure S2–S4, Supporting Information.

**Programmed Deformations of the Composite Hydrogel:** A hole-containing mask used for site-specific preswelling was prepared by laser cutting the PET film. The as-prepared composite hydrogel was sandwiched by two silhouetted masks, which was immersed in water to selectively swell the P(AAm-co-AMPS) regions under the holes to direct the buckling direction of the composite gel. The deformed hydrogel was then exposed to the 0.5 M NaCl solution for 5 min without the photo-mask. The patterned composite hydrogel can also be programmed into other configurations by similar selective preswelling and subsequent free-swelling procedures.

**Measurements of the Swelling Ratio and Young’s Modulus of Gels:** PAAm and P(AAm-co-AMPS) hydrogel sheets were prepared. The as-prepared gels were cut into disc shapes and swelled in water or saline solution with different concentrations of NaCl. The swelling ratio in length, S, was calculated by \( S = l/l_0 \), in which \( l_0 \) and \( l \) refer to the diameter of the gel in equilibrated and as-prepared states, respectively. The tensile measurements were conducted by a tensile tester (Instron 3343) at room temperature at a deformation rate of 100 mm min⁻¹. The samples were cut from the gel sheet into dumbbell shapes with an initial gauge length of 12 mm and width of 2 mm. Young’s modulus was obtained from the slope of the stress–strain curve below a strain of 10%.

**Numerical Modeling of the Swelling Gel Structures:** The solvent transportation and deformation processes of the gels were simulated by solving the differential equations for mechanical equilibrium

\[
\frac{\partial \sigma}{\partial x} = 0 \tag{1}
\]

and mass diffusion

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( m \frac{\partial \mu}{\partial x} \right) \tag{2}
\]

where \( s \) is the field of nominal stress, \( C \) is the nominal concentration of solvent molecules, and \( \mu \) is the chemical potential of solvent. Molecular...
incompressibility is assumed such that the nominal concentration is related to the deformation gradient tensor \( F \) by

\[
\Omega C = J - 1
\]

(3)

with \( \Omega \) being the volume of a solvent molecule and \( J = \det F \) the volumetric swelling ratio. Assuming the migration of solvent molecules to be similar to the self-diffusion of the solvent, we have mobility

\[
m = \frac{D}{\kappa T} \left( 1 - \frac{1}{J} \right)
\]

(4)

with \( D \) being the diffusion coefficient and \( \kappa T \) the absolute temperature in the unit of energy.

Following the common practice of modeling polymeric gels, the constitutive behavior of the gel was prescribed in terms of the free-energy density \( W \), and more specifically we adopted the Flory–Huggins–Rehner model and let \(^{[42–46]}\)

\[
W = \frac{1}{2} N \kappa T (F_{ik} F_{ik} - 3 - 2 \ln \det F) + \frac{k T}{\Omega} \left( J - 1 \right) \ln \left( 1 - \frac{1}{J} \right) - \frac{R T}{\Omega} J
\]

(5)

The nominal stress is then given by

\[
s_i = \frac{\partial W}{\partial F_{ik}} (W - \mu C)
\]

(6)

Substituting Equation (3) in Equation (6) and then in Equations (1) and (2), together with proper boundary conditions, yielded a closed set of partial differential equations for the fields of deformation \( \mathbf{x}(\mathbf{x}, t) \) and chemical potential \( \mu(\mathbf{x}, t) \). This initial boundary-value problem was solved numerically through the commercial finite element package COMSOL Multiphysics 5.3a. Very small artificial viscosity was added to stabilize time integration.\(^{[47]}\) The nonswelling parts of the gels were modeled as incompressible neo-Hookean solids. A normalized dimensionless form of the equations was solved, and a typical dimensionless parameter, \( N \Omega = 0.001 \), was taken for all calculations. Depending on the spatial symmetry of the deformed geometry, part of or the entire structure was modeled for each problem. The mask-enabled selective preswelling was modeled by applying a chemical-potential boundary condition in specific regions on the surface of a gel, earlier than other regions.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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