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# Reversible self-bending soft hydrogel microstructures with mechanically optimized designs

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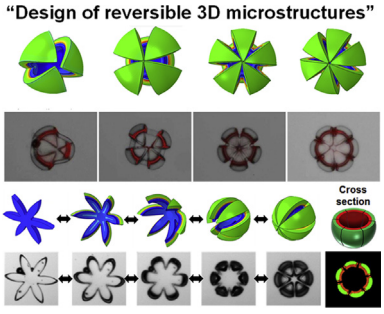
## HIGHLIGHTS

- The capabilities of self-folding reconfigurable microstructure are characterized.
- The finite element method (FEM) provides information in engineering design.
- A rational design methodology for programmable soft materials is provided.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A rational design methodology for materials with optimal mechanical properties is a prerequisite for developing programmable soft matter that undergoes structural changes in response to external stimuli. The goals of this study are to experimentally characterize the capabilities of a self-bending reconfigurable microstructure, provide fundamental information in engineering design, and validate simulations of physics-based models. In this study, the self-bending behavior of hydrogel bilayers, composed of an active layer and a passive layer, is investigated experimentally and theoretically. This self-bending is completely reversible and allows the structure to fold and unfold without permanent deformation. Experimentally, the effects of design parameters on the self-bending behavior of the microstructures of hydrogel bilayers are explored by varying the extrinsic geometric variables. The study of finite element method (FEM) simulations shows that the final shape of the bilayer sheet is governed by intrinsic properties, including the elastic modulus and the swelling ratio, and extrinsic geometrical factors, such as the thickness ratio of the bilayer and the aspect ratio of the structure. Therefore, the self-bending behavior of the planar hydrogel bilayer was confirmed by experiments and simulations in which multiple values were assigned for each of the primary design parameters in origami-based engineering.



## 1. Introduction

The development of advanced functional materials that spontaneously undergo a change in shape or structure, from two-dimensional (2D) to three-dimensional (3D) structures in response

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to external stimuli, is an emerging field in materials science and engineering [1–4]. In particular, stimuli-responsive materials have become increasingly prevalent with their rapid utilization in industry. Additionally, stimuli-responsive materials are able to trigger actions that induce conformational changes in material structures. Therefore, methods are being devised to take advantage of and control these actions.

The easiest way to produce a bending or folding action is to fabricate a hybrid bilayer structure containing one structural layer and another responsive layer. Previously, bilayer thin films made from metallic or semiconducting materials utilized mechanical stress generated from differences in thermal expansion [5–8]. When these bilayers are released from an underlying substrate, the stressed structure either contracts (tensile stress) or expands (compressive stress). The magnitude of stress within the bilayer structure controls the radius of curvature.

Advances in new stimuli-responsive materials have motivated orthogonal experimental and theoretical studies to understand or mimic the basic principles or mechanics of these materials [9–14]. Among these, hydrogels or responsive polymers are promising soft materials for designing structures that undergo shape transformations through a large deformation or displacement, which may occur in response to a wide range of external or internal stimuli, such as solvent composition, temperature, pH, and electric field [15–20]. For example, stimuli-responsive hydrogel bilayers are self-bending materials consisting of two types of materials with different volume expansion properties. Their deformation mechanism has been investigated because of their potential for converting chemical or physical energy into mechanical forces, leading to macroscopic changes in shape or conformation in three-dimensional space [21–23].

The effectiveness of stimuli-responsive polymers or hydrogels critically depends on their capability to undergo desired changes in shape and size so that the mechanical properties may be tuned by controlling the concentration of monomers and the cross-linking density, the thickness ratio of responsive and passive layers, and the dimension of the hydrogel microstructures. In particular, pH-responsive hydrogels are of interest to the drug-delivery community due to their responsiveness within the narrow pH range of the gastrointestinal tract [24,25]. In this case, the key factor that results in shape-change is the modulation of mechanical properties through swelling or shrinking upon exposure to proton ions. Hydrogel microstructures with different polymer layers go through differential deformation upon swelling, allowing the formation of unique 3D structures [26–28].

Therefore, understanding the principle behind conversion of stimuli into mechanical action capable of changing shape or dimensions is a critical scientific and engineering issue that must be addressed in order to state the design rules for soft actuators [29–31]. The driving force for initiating the transformation of 2D objects to 3D microstructures is mainly attributed to the residual internal stress programmed in responsive 2D objects with separate swelling properties. By harnessing this responsive internal stress, desired transformational shapes can be designed. In several cases, modulation of the 2D object could have a large impact on its final 3D shape. However, only a few studies are available that demonstrate the relationship between the physical/chemical properties of the responsive object and its self-responsive behavior at the micron scale. Moreover, the lack of understanding of the mechanics of shape transformations occurring through self-responsive behavior seriously limits further advancement in guided transformation of self-responsive soft matter. Therefore, it is important to understand the role of the magnitude of the strength difference between the passive and responsive parts of 2D soft matter. Such an understanding is an important step in developing the basic design rules for more elegant matter and paves the way for producing programmable soft matter on demand.

Here, we have explored this basic concept in order to investigate the relationship between mechanical properties and self-bending behavior. This was accomplished through simple control of the microstructural dimension in order to extract basic design rules. Interestingly, it was found that these microstructures can reproducibly fold into pre-determined configurations. A simple and thorough understanding of the relationships involved in fabricating actuating microstructures is not yet available. Such an understanding would be highly useful for the chemical engineering and mechanical engineering fields. This is the main purpose of the present study.

First, we investigate soft microstructures of a hydrogel bilayer, which is used as a model system to represent a reversible stimuli-responsive actuator. Uniform bilayer microstructures are prepared using a simple micromolding technique without the need for complex facilities. Highly flexible polymeric hydrogels are selected as both responsive and passive layers, in order to maintain tight binding between the two layers without delamination. The bilayer microstructure enables a reversible transformation from two-dimensional sheets to bent three-dimensional structures with pre-determined curvatures. The resultant 3D microstructures with different curvatures provide useful information for uncovering the basic relationship between their chemical and mechanical properties simply by inducing folding or unfolding of the hydrogel bilayer. The actuating behavior predicted from finite element method (FEM) simulations is consistent with the experimental results obtained from the self-bending microstructures and more complicated flower-like microstructures. In particular, a specific design is capable of folding into a target shape by using one or more responsive materials. While several modeling methods have been utilized previously to simulate these designs, none has the capacity to quickly simulate an entire self-folding model. Furthermore, the microstructures can be easily functionalized by simple incorporation of magnetic nanoparticles. We demonstrate the feasibility of remotely controlling the movements of these microstructures.

## 2. Materials and methods

### 2.1. Materials

2-hydroxyethyl methacrylate (HEMA, 97%), poly(ethylene glycol) diacrylate (PEG-DA, Mn = 700), acrylic acid (AA, 99%), ethanol (EtOH, ≥99.5%), isopropyl alcohol (IPA, ≥99.5%) and 2-hydroxy-2-methylpropiophenone (Darocur 1173, 97%), Iron(III) oxide (nanopowder, <50 nm particle size) were purchased from Sigma-Aldrich Chemicals (St. Louis, MO) and used without further purification except when mentioned specifically. Deionized water (>18 MΩ·cm) was obtained from the Milli-Q water (Milford, MA, USA) and pH of the water was adjusted by using 1N HCl and 1N NaOH without any addition of salts.

### 2.2. Measurement of elastic modulus

The elastic moduli of the responsive and passive layers were measured using a dynamic mechanical analyzer (DMA8000, PerkinElmer, USA). The moduli of the responsive and passive layers were measured at pH 11 because the responsive layer is sensitive to pH. Cylindrical specimens were prepared with a diameter of 2.5 mm and a height of 3 mm. For the modulus measurements, the specimens were fully swollen at pH 11. The DMA results show both the storage modulus (representing the elastic portion) and the loss modulus (representing the viscous portion). In a previous study, the measured storage modulus is considered to be the