Surface Patterning of Hydrogels for Programmable and Complex Shape Deformations by Ion Inkjet Printing

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1. Introduction

Smart hydrogels that undergo programmable shape deformations are of great interest owing to their important practical applications in many fields, such as soft machines,[1] microfluidics,[2] optical devices,[3] drug delivery systems,[4] and artificial muscles.[5] Shape deformation processes and the final geometric shapes of the hydrogels are essential for their applications. Rapidly increasing attention has been drawn to the preparation and application of hydrogels that can undergo complex shape deformations.[6]

Shape deformation of hydrogels is generally driven by the nonuniform internal stresses caused by the uneven swelling/deswelling of the different parts of a gel sample. Therefore, macroscopic intrinsic structural inhomogeneity or asymmetry is a prerequisite for the deformation of the gels. In the early stage, the shape deformable hydrogels are typically with different or gradient components across the hydrogel thickness. Bilayer hydrogels[12a,7a,7b] are prepared by combining two gel layers with different responsive rates and/or degrees. Hydrogels with gradient distributive component(s) across the thickness are usually prepared on the assistance of gravity,[8] an applied electric[9] or magnetic field,[10] or using molds with different hydrophilicity/hydrophobicity.[10b,11] Hydrogels with differential distributive component(s) in plane are also prepared and they show in-plane differential responsiveness.[12] The responsive rates and/or degrees of these gels can be adjusted by changing the components[11c,12] and external fields.[9,10b] However, these hydrogels mostly perform very simple bending, folding, and twisting deformations upon external stimuli. Some simple 3D shapes, such as dumbbells, cubes, pyramids, balls, towers, and domes, can also be obtained by designing the location and shape of bilayer hydrogels or by constructing gel parts that can be joined by physical interactions.

To realize flexible programming of complex deformations, it is crucial to diversely and locally change the compositions across the thickness or in plane and hence the responsive properties in different parts of a gel sample. In recent years, several methods[13d,13c,13f] have been developed to pattern as-prepared hydrogels to locally alter their responsive behaviors. By using masks with designed patterns, photolithographic methods enable the selective introduction of chemical cross-links,[13a,b] a second network into as-prepared hydrogels[13c] or the chemical change of the component(s) (e.g., the reduction of graphene oxide nanosheets).[13f] The irradiated and unirradiated regions show different swelling/deswelling properties, causing in-plane stress that can drive shape deformations. The shape deformation of the hydrogels can be programmed by using varying photolithographic patterns, and the deformable degree can be tuned by adjusting the irradiation dose. Ion printing is another method that enables the patterning of hydrogels containing polyelectrolytes. By controllably introducing metal cations into the hydrogels with electrically assisted ionoprinting[13d,13e,g,h] or ion transfer printing[13c] the cross-links between metal cations

Convenient patterning and precisely programmable shape deformations are crucial for the practical applications of shape deformable hydrogels. Here, a facile and versatile computer-assisted ion inkjet printing technique is described that enables the direct printing of batched, very complicated patterns, especially those with well-defined, programmable variation in cross-linking densities, on one or both surfaces of a large-sized hydrogel sample. A mechanically strong hydrogel containing poly(sodium acrylate) is first prepared, and then digital patterns are printed onto the hydrogel surfaces by using a commercial inkjet printer and an aqueous ferric solution. The complication between the polyelectrolyte and ferric ions increases the cross-linking density of the printed regions, and hence the gel sample can undergo shape deformation upon swelling/deswelling. The deformation rates and degrees of the hydrogels can be conveniently adjusted by changing the printing times or the different/gradient grayscale distribution of designed patterns. By printing appropriate patterns on one or both surfaces of the hydrogel sheets, many complex 3D shapes are obtained from shape deformations upon swelling/deswelling, such as cylindrical shell and forsythia flower (patterns on one surface), ding (patterns on both surfaces), blooming flower (different/gradient grayscale distributive patterns on one surface), and non-Euclidean plates (different/gradient grayscale distributive patterns on both surfaces).

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and polyelectrolytes alter the swelling/deswelling properties of the ion printed regions. Patterned hydrogels prepared by these methods can deform into various 3D shapes.

However, some inherent disadvantages of these patterning methods strongly restrict their practical applications. Patterning with photolithographic methods strongly relies on the masks, and ion printing on the shapes of metal anodes or templates. It is difficult to prepare large-sized masks, anodes, or templates with complex patterns, especially those with well-defined, programmable variation in cross-linking densities. Moreover, the stepwise process of these methods does not allow the continuous, batched production of complicated patterns. Very recently, Huang et al.\cite{14} reported the preparation of shape deformable hydrogels and shape memory polymers by utilizing a projector equipped with a digital micromirror device that allows dynamic spatial control of the light exposure time and hence the formation of pixelated polymer networks with variable degrees of monomer conversion and cross-linking densities. Nevertheless, large-sized samples cannot be obtained due to the size of the projector. Therefore, it remains a great challenge to introduce complex patterns with well-defined, programmable variation in cross-linking densities to large-sized hydrogels through a convenient continuous and batched digital process.

Herein, we report an extremely simple yet novel ion inkjet printing technique to print patterns on hydrogel surfaces. As a well-developed printing technique, computer-assisted inkjet printing has been widely used to print words and images. Recently, it has also been applied as a new technique to pattern materials for preparing microfluidic analytical devices,\cite{15} bioprinted tissues,\cite{16} and chemical sensors.\cite{17} In this work, we printed digital patterns onto hydrogel (containing polyelectrolytes) surfaces by using a commercial inkjet printer and an aqueous solution containing metal cations as the ink. Due to the easy and diverse designing of digital patterns and the facile inkjet printing process controlled by computer, batched and very complicated patterns can be perfectly reproduced on only one or both surfaces of a large-sized hydrogel sample. The patterned hydrogels can deform into many complex 3D shapes.

2. Results and Discussions

2.1. Ion Inkjet Printing Technique

The hydrogel preparation method used in this work is similar to that reported in our previous work.\cite{11c} Differently, homogeneous rather than heterogeneous (Janus) hydrogel sheets were prepared in molds made of two glass plates. The hydrogels were prepared with acrylamide (AAm, 3.0 mol L$^{-1}$) and sodium acrylate (NaAAc, 0.5 mol L$^{-1}$) in the presence of a pre-existing polymer poly(N-vinylpyrrolidone) (PVP, 43 mg mL$^{-1}$) and a very small amount of a chemical cross-linker N,N’-methylene bis(acrylamide) (MBA, 3.5 × 10$^{-3}$ mol L$^{-1}$). Very strong cooperative hydrogen bonding is formed between the pre-existing PVP chains and the in situ polymerized polyacrylamide (PAAm) chains, and hence the PVP-PAAm interpolymer complexes act as cross-linkers for the formation of tough hydrogels.\cite{18} The hydrogels are mechanically strong enough for surface printing and shape deformation (Figure S1, Supporting Information). A flatbed inkjet printer, made up with a common inkjet printer (A3 size: 297 mm × 420 mm) and a movable platform, was used in present work to print patterns on the gel surfaces (Figure 1a and Video S1 (Supporting Information)).

![Figure 1. Ion inkjet printing technique. a) The photograph of the flatbed inkjet printer used in present work, b) the schematic of inkjet printing process and the image of the printed dots on the hydrogel surface as well as the cross-linking between ferric ions and the anionic carboxyl groups of PNaAAc.](image)
An aqueous ferric ion solution (2.0 mol L\(^{-1}\)) was used as the ink. When the ferric ion solution is printed on the gel surface, strong ionic interactions are formed between Fe\(^{3+}\) cations and the anionic carboxyl groups of poly(sodium acrylate) (PNaAac) and the hence more cross-links are introduced into the printed parts (Figure 1b). This method for patterning gel surfaces is termed as ion inkjet printing (IIP). Patterning with IIP introduces metal cations into only a thin layer of hydrogel close to the surface, less than 100 µm even after 5 times printing (Figure S2, Supporting Information). The resolution of printed patterns is determined by the size of ink droplets. As shown in the image of the hydrogel surface printed for 1 time (Figure 1b), the brown round spots are mainly with a diameter around 100 µm. Unfortunately, some bigger and irregular spots were also found, due to the merging of adjacent ink droplets that cannot be quickly absorbed by the hydrogel. Even though, the resolution of the printed patterns can be up to several hundred micrometers. Moreover, the accuracy for repeated printing at the same spot is also high, with only about 0.1 mm increase in the width of a repeatedly printed line (Figure S3, Supporting Information). Considering the macroscopic shape deformation of hydrogels studied in this work, the resolution and the accuracy of the printed patterns are acceptable.

### 2.2. Patterning Hydrogel Surfaces with IIP

IIP technique possesses some distinct features, due to the easy and diverse designing of complicated patterns and the inkjet printing process controlled by computer. (1) It allows facile and versatile surface printing of batched patterns on a large-sized hydrogel sample in one printing process. For example, batched small hexagons can be printed on a large-sized hexagonal hydrogel sample (~30 cm in length) (Figure 2a). The size of printed pattern(s) is only limited by the size of hydrogel samples and the printer. (2) Very complicated patterns generated with computer can be perfectly reproduced on the hydrogel surfaces. Figure 2b shows the patterns based on or modified from rose curves. The curves or modified patterns are perfectly printed on the hydrogel surfaces. (3) Symmetrical and/or asymmetrical patterns can be printed on both sides of the hydrogels. Figure 2c shows the schematics of the printing patterns, in which the parts with darker and lighter colors indicate the patterns that will be printed on the front and back surfaces of the hydrogel sheets, respectively, and the appearance of the hydrogel sheets with both surfaces printed with the patterns. The patterns on the two surfaces are mutually reciprocal or perpendicular. The patterning on both surfaces of hydrogel sheets makes them undergo complex 3D shape deformations upon swelling, and this will be demonstrated in the following part. (4) Moreover, patterns with different or gradient grayscale distribution (heterogeneous patterns) can be easily obtained by changing the printing times or by printing patterns with grayscale difference or gradient distribution. Figure 2d shows the hydrogel samples with only one surface printed with heterogeneous patterns, such as flowers with different printing times, and rectangles with different or gradient grayscale distributions.

Similarly, both surfaces of the hydrogel sheets can also be printed with patterns with different or gradient grayscale distributions (Figure 2e).

### 2.3. Controllable Introduction of Ferric Ions

The patterning of hydrogel surfaces with different or gradient grayscale distributions should lead to the different distribution of ferric ions. To quantitatively determine the amount of ferric ions introduced on the hydrogel surfaces, hydrogel squares (1 cm × 1 cm) printed for 1, 3, or 5 times (Figure 3a) and a hydrogel strip (1.5 cm × 7.5 cm) printed with a pattern with a gradient grayscale distribution (Figure 3b) were prepared, and then the contents of ferric ions on them were measured. With the increase of printing times, the color of the patterns become darker (Figure 3a1), more ink spots appear (Figure 3a2), and the measured content of the ferric ions increases linearly with increasing printing times (Figure 3a3). When a pattern with a gradient grayscale distribution is printed, the color, the number of ink spots, and the content of ferric ions change gradually along the distribution direction (Figure 3b). Therefore, it is reasonable to conclude that the IIP technique is capable of controllable introduction of ferric ions and hence cross-linking density on the hydrogel surfaces, which is very helpful for programing the shape deformation of hydrogels.

### 2.4. Swelling/Deswelling Induced Shape Deformations of Patterned Hydrogels

The swelling/deswelling behavior of the hydrogels patterned with ferric ions is altered, due to the increase of cross-links in the printed parts induced by the formation of metal-coordination complex between ferric ions and carboxyl groups.\(^{[19]}\)

To determine the effect of IIP on the swelling/deswelling properties of the hydrogels, all surfaces of hydrogel cubes with a side length of 1.5 cm were printed for 1, 3, or 5 times, and then their volume changes were measured after being immersed in water for 5 min (or in ethanol for 40 min). The volume change ratios, defined as the increased (positive value) or decreased (negative value) volume to the original volume, of the patterned hydrogels gradually decrease with the increase of printing times, from 128% (or ~24%) for the pristine hydrogel to 64% (or ~10%) for the hydrogel sample printed for 5 times (Figure 4a). Therefore, the swelling/deswelling behavior of the hydrogels can be easily adjusted with IIP technique.

The different swelling/deswelling behavior of the unprinted and printed parts leads to the deformation of the hydrogels. Two kinds of deformations, i.e., bending/unbending and expansion/contraction, can be achieved by printing only one or both surfaces of the hydrogels (Figure S4, Supporting Information). Expansive/contractive deformable hydrogels are prepared by printing symmetrically on both surfaces of the as-prepared hydrogels. As demonstrated with a circular hydrogel sheet, it expands upon swelling in water, while contracts upon deswelling in ethanol (Figure S5, Supporting Information).
Meanwhile, hydrogel strips with only one surface printed or two surfaces asymmetrically printed bend toward the printed or the more printed side upon swelling in water, while unbend when they are deswelled in ethanol. The bending/unbending deformation is reversible when the swelling/deswelling process is repeated (Figure S6, Supporting Information).

Because of the controllable swelling/deswelling behavior of the hydrogels with IIP technique, the deformation rate and degree of the hydrogels can be easily adjusted. As shown in Figure 4b, the hydrogel strip with only one surface printed bends faster and the bending degree is higher with the increase of printing times. Notice that the hydrogel strips bend to the unprinted side after the printing (negative bending degrees),
due to the swelling induced by the aqueous ferric solution. Once
they are immersed in water, the faster swelling of the unprinted
side leads to the inversion of their bending direction. Similarly,
the expansion/contraction ratios of the hydrogels with two sur-
faces printed symmetrically can also be adjusted by changing
the printing times (Figure S7, Supporting Information).

Figure 3. a) Macroscopic photographs (a1), images (a2) and the contents of introduced ferric ions (a3) of the hydrogel squares (1 cm × 1 cm)
printed for 1, 3, or 5 times. b) Macroscopic photograph (b1), images (b2) and the contents of introduced ferric ions (b3) on the hydrogel sample
(1.5 cm × 7.5 cm) printed with a pattern with a gradient grayscale distribution. For hydrogel with a gradient grayscale distribution, the photographs
were recorded with a space of 1.5 cm along the deep color side to light color side, and the ferric ions were measured in the squares (1.5 cm × 1.5 cm)
cut along the distribution direction. The photographs in (b1) and (b2) were recorded with the hydrogels printed for 1 time, and ferric ion concentrations
in (b3) were measured with the hydrogels printed for 5 times.

2.5. Programming the Shape Deformations of the Patterned Hydrogels

Due to the complicated patterning of one or both surfaces of
hydrogel samples, diverse complex 3D shape deformations can
be achieved.

Figure 4. Swelling/deswelling behavior and shape deformation of patterned hydrogels. a) The volume change ratios of the pristine hydrogel and the
patterned cube hydrogels (side length = 1.5 cm) with all surfaces printed for different times after being swelled in deionized water for 5 min or being
deswelled in ethanol for 40 min. b) The bending angles of the hydrogel strips (length: 25 mm, width: 2 mm, and thickness: 1 mm) printed for different
times in water. The initial states of the patterned hydrogels were observed in n-hexane that is immiscible with water. The inset shows the bending/
unbending of the hydrogel strip printed for 5 times.
2.5.1. Shape Deformation of Hydrogels with Patterns Printed on Only One Surface

See Figure S8 (Supporting Information) for the designed patterns and the hydrogel samples after printing. Upon swelling, the rectangular hydrogel sample printed with hexagon frameworks similar to carbon nanotube (Figure S8a, Supporting Information) bends into a cylindrical shell, mimicking the transformation from graphene to carbon nanotube (Figure 5a1); the hydrogel strip printed with lines 45° to the long edge direction (Figure S8b, Supporting Information) deforms into a right-handed helix (Figure 5a2); a flat annular ring (Figure S8c, Supporting Information) deforms into a donut shaped ring (Figure 5a3); a hexagon printed with densely or loosely packed small hexagons (Figure S8d,e, Supporting Information) deforms into a triangle (Figure 5a4) or a protuberant hexagon similar to tortoise shell (Figure 5a5). The hydrogels printed with patterns based on rose curves (Figure 2b) deform into a forsythia flower (Figure 5a6), protuberant hexagons with sexfoil patterns (Figure 5a7,a8), and domes with many other refined patterns on them (Figure 5a9–a11), respectively.

2.5.2. Shape Deformation of Hydrogels with Patterns Printed on Both Surfaces

The different swelling and deformation behavior of the hydrogel sheets with two surfaces patterned makes them undergo complex 3D shape deformations upon swelling. The flat annular ring printed with patterns on the two surfaces that are alternating and mutually reciprocal (Figure 2c1) deforms into a waved annulus (Figure 5b1), the hydrogel sample with four-leaved clover patterns, which are perpendicular to each other on two surfaces (Figure 2c2), deforms into a ding (a type of cooking vessel in ancient China) (Figure 5b2 and Video S2 (Supporting Information)), the circular hydrogel sheet printed with lines that are perpendicular to each other (Figure 2c3) deforms into a saddle shaped structure (Figure 5b3). Interestingly, the rectangular hydrogel strip printed with lines that are at ±45° to the long edge direction on the two surfaces (Figure 2c4) deforms to a twist shape (Figure 5b4), as the sheet intends to bend in two opposite and perpendicular directions.[10b,21] The structure of the hydrogel strip is very similar to the seed pods of Bauhinia variegate with outer and inner layers reinforced by cellulose microfibrils that are oriented roughly at ±45° with respect to the pod’s longitudinal axis in the two layers, and the shape deformation of the hydrogel strip is also very similar to the seed pod opening process of Bauhinia variegate that turns an initially flat pod valve into a twist shape.[22]

2.5.3. Shape Deformation of Hydrogels with Different or Gradient Patterns on One or Both Surface(s)

A blooming flower shaped structure is obtained by swelling the assembled five-petaled flower shaped hydrogel sheets with only one surface printed for different times (Figure 5c1). The rectangular hydrogel samples with different or gradient grayscale distributions (Figure 2d–d4) deform into anomalous tubes with a big opening in the middle (Figure 5c2), two big
openings in the two ends (Figure 5c3), or one big opening at one end (Figure 5c4), due to the higher swelling ratio of the less cross-linked parts. Similarly, when gradient or different grayscale distributive patterns are printed symmetrically on both surfaces of the hydrogels, the uneven swelling/deswelling of the hydrogel samples also leads to their deformations. The circular hydrogel sample with a gradient grayscale decrease from the center to edge (Figure 2e1) deforms into a plate with waved edge upon swelling (left photograph in Figure 5d1) and a dome upon deswelling (right photograph in Figure 5d1). On the contrary, the circular hydrogel sample with a gradient grayscale decrease from the edge to center (Figure 2e2) deforms into a dome upon swelling (left photograph in Figure 5d2) and a saddle (right photograph in Figure 5d2) upon deswelling, similar to the deformation of non-Euclidean plates reported by Sharon and co-workers.\(^\text{[12]}\) The hydrogel strips with a grayscale decrease along the short edge (Figure 2e3) deform into a bent strip with one rippled side (Figure 5d3) similar to crochets.\(^\text{[23]}\) Furthermore, to simulate the shape deformation of the lily leaf that undergoes more growth strain in the edge than that in the midvein,\(^\text{[24]}\) hydrogel “leaf” is prepared by printing both sides with more printing times in the middle part (Figure 2e4), and the hydrogel “leaf” deforms into a structure with rippled edges very similar to lily leaf upon swelling (Figure 5d4).

The flexible and precise control of the local swelling/deswelling behaviors of hydrogels enables the programmable shape deformations, which will be helpful for the understanding of transformation of non-Euclidean plate deformations\(^\text{[25]}\) and the events during the lifetime of plants, such as the blooming of flowers,\(^\text{[26]}\) the shape change of leaves, and the opening of seed pods.\(^\text{[27]}\)

3. Conclusion

In present work, we employed ion inkjet printing as a facile and versatile technique to pattern hydrogel surfaces. This computer-assisted design and printing process allows the direct printing of batched and very complicated patterns, especially those with different or gradient grayscale distributions, on only one or both surfaces of a large-sized hydrogel sample. The introduction of metal ions into the hydrogels alters the cross-linking densities of the printed regions, leading to their different swelling/deswelling behaviors with comparison to the unprinted regions, which drive the shape deformations of the hydrogels. Moreover, by printing patterns on one and/or both surface(s), hydrogels showing bending/unbending and/or expansive/contractive deformations can be obtained. The deformation rates and degrees of the hydrogels can be conveniently adjusted by changing the cross-linking densities of the printed regions. A variety of complex 3D shapes, such as cylindrical shell, right-handed helix, forsythia flower, saddle, blooming flower, and lily leaf-like shapes, are obtained by printing appropriate patterns on the hydrogels. As one can expect, more complex 3D shapes can also be obtained.

This technique is superior to most existing methods in its convenience and diversity in the designing and printing very complicated patterns. In addition, this is the first report of the batched production of many patterns on a large-sized hydrogel sample. Therefore, this ion inkjet printing technique might be suitable for commercial applications. In addition, this ion inkjet printing technique can be extended to hydrogels containing other polyelectrolytes and other types of metal cations. Furthermore, some other inkjet printing techniques can also be developed by the proper choice of the physical interactions, such as hydrogen bonding, electrostatic and host–guest supramolecular interactions, or even chemical reactions between the polymers and chemical inks. Similar to other shape deformable hydrogels, these hydrogels patterned with IIP technique can be used to fabricate soft machines, microfluidics, optical devices, drug delivery systems, and artificial muscles.

4. Experimental Section

Materials: Poly(N-vinylpyrrolidone) (M\(_w\) = 4 × 10\(^4\)) and AAm were purchased from Amresco Inc. (OH, USA); acrylic acid (AAC) was purchased from Aladdin (Shanghai, China); MBA and potassium persulfate (KPS) were from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China); sodium hydroxide (NaOH), ferric nitrate nonahydrate (Fe(NO\(_3\))\(_3\) · 9H\(_2\)O), and ethanol were from Beijing Chemical Works Co., Ltd. (Beijing, China); Rhodamine B was from Alfa Aesar (Tianjin, China); AAc was from Acros (Geel, Belgium). AAm was redistilled before usage, while the other reagents were of A. R. grade and used without further purification. NaAAc was prepared by mixing equimolar amounts of acrylic acid and sodium hydroxide in deionized water.

Hydrogel Preparation: The pre-existing polymer PVP (43 mg mL\(^{-1}\)), the monomers AAm (3.0 mol L\(^{-1}\)) and NaAAc (0.5 mol L\(^{-1}\)), the initiator KPS (3.5 × 10\(^{-3}\) mol L\(^{-1}\)) and MBA (3.5 × 10\(^{-3}\) mol L\(^{-1}\)), and sometimes Rhodamine B (3.0 × 10\(^{-4}\) mol L\(^{-1}\)) (as a dye) were thoroughly dissolved in deionized water. The solutions were deaerated by bubbling high-purity nitrogen for 10 min in an ice-water bath and then were transferred into molds made by placing a silicone spacer with a height of 1 or 15 mm between two glass plates. Finally, the molds were placed at 50 °C for 12 h to ensure the completion of polymerization. The as-prepared hydrogels were directly used in this work. Mostly, the thickness of the hydrogel strips or sheets was 1 mm, if not otherwise stated.

Inkjet Printing on the As-Prepared Hydrogel Surfaces: A modified inkjet printer (DF-FA3A) with a movable platform was purchased from Dijiafu Electromechanical Corp. (Zhejiang, China). A Fe(NO\(_3\))\(_3\) aqueous solution (2 mol L\(^{-1}\)) was used as the ink. An as-prepared hydrogel sheet was placed on the printing platform, whose height was adjusted to ensure the completion of printing. And then different patterns designed were inkjet printed on only one or both surfaces of the hydrogel sheet with the aid of a computer, and the printing process could be repeated for several times.

Characterizing Patterned Hydrogels: The micropatterns printed on the hydrogel surfaces and the cross-sectional distribution of ferric ions along the thickness were observed with a microscope (SMART-POL, OPTEC, China) equipped with a digital camera. To measure the amounts of ferric ions printed on the hydrogel surfaces, square patterns (1 cm × 1 cm) were inkjet printed on the hydrogel surfaces for 1, 3, or 5 times, then the printed hydrogels were immersed in 0.1 mol L\(^{-1}\) ethylenediaminetetraacetic acid (EDTA) solution for two weeks, and then the solutions were measured by inductively coupled plasma atomic emission spectroscopy on an SPECTRO ARCOS EOP instrument (SPECTRO Analytical Instruments GmbH, Germany). Similarly, distribution of ferric ions on hydrogel surfaces (1.5 cm × 7.5 cm) with gradient patterns was also measured from the hydrogel sections (1.5 cm × 1.5 cm) equally divided from the hydrogel sample.

Measuring Swelling/Deswelling and Deformation Behaviors: The cubic samples (1.5 cm × 1.5 cm × 1.5 cm) of as-prepared hydrogels and the hydrogels with all surfaces printed for different times were immersed in deionized water for 5 min or in ethanol for 40 min. The
swelling/deswelling ratios of the hydrogel samples were measured from the change of their volumes. The bending deformation of hydrogel strips soaked in water or ethanol was recorded by a digital video camera, and their bending angles were measured according to the previous reported work.\(^\text{[11c]}\) In addition, the expanded/contractive deformation of the hydrogels with both surfaces printed was measured by recording the change in the diameters of round samples soaked in water or ethanol. The more complex shape deformations of patterned hydrogel samples were also recorded with a digital video camera.

**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.

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