# High-Resolution 3D Printing of Stretchable Hydrogel Structures Using Optical Projection Lithography

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Supporting Information

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ABSTRACT: Double-network (DN) hydrogels, with their unique combination of mechanical strength and toughness, have emerged as promising materials for soft robotics and tissue engineering. In the past decade, significant effort has been devoted to synthesizing DN hydrogels with high stretchability and toughness; however, shaping the DN hydrogels into complex and often necessary user-defined two-dimensional (2D) and three-dimensional (3D) geometries remains a fabrication challenge. Here, we report a new fabrication method based on optical projection lithography to print DN hydrogels into customizable 2D and 3D structures within minutes. DN hydrogels were printed by first photo-crosslinking a single network structure via



Step 2. Inducing ionic bonding Step 3. Tensile testing of the Double Network hydrogels structure

spatially modulated light patterns followed by immersing the printed structure in a calcium bath to induce ionic cross-linking. Results show that DN structures made by this method can stretch four times their original lengths. We show that strain and the elastic modulus of printed structures can be tuned based on the hydrogel composition, cross-linker and photoinitiator concentrations, and laser light intensity. To our knowledge, this is the first report demonstrating quick lithography and highresolution printing of DN (covalent and ionic) hydrogels within minutes. The ability to shape tough and stretchable DN hydrogels in complex structures will be potentially useful in a broad range of applications.

KEYWORDS: additive printing, photo-crosslinking, ionic-crosslinking, digital micromirror devices (DMD), double network, stretchable hydrogel

# INTRODUCTION

Hydrogel materials, characterized by their high degree of water content, have been extensively used in areas such as drug delivery and pharmaceuticals, diagnostics and biosensors, soft robotics, flexible electronics, tissue engineering, and organ-ona-chip models.<sup>1-3</sup> However, most hydrogels are mechanically weak and possess poor toughness and low elastic moduli that have limited their usage in applications that require superior mechanical properties, such as tissue engineering and soft robotics.<sup>4-6</sup> To expand the utility of hydrogels for applications that requires a combination of stretchability and toughness, double network (DN) hydrogels, or DN gel, were developed.<sup>7–10</sup> DN gel typically consists of two networks: the first network possesses covalently cross-linked polymer chains that allow for the dissipation of large amount of energy during deformation, whereas the second network is soft and often ionically cross-linked, providing superior toughness and stretchability.<sup>7,10-13</sup>

Over the years, a variety of DN gel with unique mechanical properties have been synthesized.<sup>14-20</sup> For instance, DN gel formed by using ionically cross-linked alginate and covalently cross-linked polyacrylamide (PAAm) have been shown to exhibit remarkable fracture toughness of 9000 J/m<sup>2</sup>.<sup>10</sup> In another study, alginate was replaced by polyvinyl alcohol (PVA) to enable the formation of crystallites upon heating within the intertwined network of PVA/PAAm DN gel.<sup>21,2</sup> Furthermore, Cai et al. have reported the fabrication of porous DN gel with high toughness and stretchability using the freezedrying method.<sup>23</sup> Thermoreversible polysaccharide agar/ PAAm DN gel with excellent recoverability have also been demonstrated.<sup>24</sup> Chen, et al. have developed biocompatible polyethylene glycol (PEG)/agarose DN gel with excellent mechanical strength.<sup>13</sup> In another study, cell-encapsulated DN network hydrogel fiber that showed tunable mechanical strength, and stretching behavior was synthesized using alginate and poly(N-iso-propylacrylamide)/PEG.<sup>25</sup> There are few reports of one-pot synthesis of DN gel such as synthesis of highly mechanical and recoverable agar/PAAm (agar/PAM) DN hydrogels.<sup>26–28</sup> Most current studies choose conventional molding or casting methods to shape DN gel into simple geometries. For instance, clover, snowflakes, and the letters "ICCAA" have been molded using PEG/agarose hydrogel.<sup>8</sup> In

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**Figure 1.** (A) Schematic of the optical projection lithography setup for printing customized 2D and 3D structures. (B) Schematic showing the 3D fabrication of DN hydrogel structure using digital mask-based optical lithography setup. (C) Schematic of the alginate/DMAAm DN hydrogel formed by covalent cross-linking of DMAAm and ionic cross-linking of alginate.

another study, DN gel structures in the geometry of a meniscus have been casted using an acrylamide/PAMPS network.<sup>29</sup> Although DN gel with simple geometries such as sheets, slabs, blocks, discs, and dumbbells have been made, DN gel with user-defined and often complex two-dimensional (2D) or three-dimensional (3D) structures will be necessary for a variety of applications in tissue engineering and soft robotics.

To address the need of creating customized 2D and 3D geometries for a range of application of DN gel, 3D printing methods based on extrusion-based fused deposition modeling have been widely used. Complex shapes, such as human ears and noses, have been fabricated using stretchable alginate/PEG DN gel.<sup>8,9,29-33</sup> 3D printers have also been used to extrude DN gel made from a  $\kappa$ -carrageenan network and PAAm to make structures that can self-heal.<sup>31</sup> Extrusion printing assisted by a heated cartridge was used to print DN structures of PAAm mixed with agar and alginate.<sup>34</sup> However, extrusion-based methods for printing DN gel have low resolution (300-500  $\mu$ m) and are limited in throughput due to the serial nature of fabrication.<sup>8,9</sup> To print DN gel at high resolution and at high speeds, light-based 3D printing methods such as stereolithography, digital light processing lithography, and direct laser writing can be transformative as they allow fabrication of structures with high resolution and improved design flexibility, in a highly automated, assembly-free manner.<sup>35-43,45</sup> However, printing DN gel using light-based methods currently, in general, requires an extremely long cross-linking time (several hours), making these methods impractical.<sup>10</sup>

In this work, we demonstrate quick and high-resolution printing of user-defined 2D and 3D structures made of DN gel using optical projection lithography. The polymer solution, composed of sodium alginate, dimethyl acrylamide (DMAAm), methylenebis-acrylamide (MBAAm), and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), was polymerized by projecting digital patterns of ultraviolet light, followed by immersion of printed structures into calcium chloride solution to undergo ionic polymerization. The quick lithography process (within minutes) and high-resolution printing of DN gel enables customized 3D structures that exhibit high toughness and stretchability. To our knowledge, this is the first report demonstrating fabrication of DN gel into complex 2D and 3D geometries within minutes, and we anticipate that this work will open new avenues in the areas of soft robotics and tissue engineering.

## METHODS

**Preparation of Prepolymer Hydrogel Solution.** Sodium alginate, DMAAm, MBAAm, and calcium chloride anhydrous were purchased from Sigma-Aldrich, USA. LAP was synthesized using an established method as described below.<sup>44</sup> 2,4,6-Trimethylbenzoyl chloride (4.5 g, 25 mmol) was added dropwise to continuously stirred dimethyl phenylphosphonite (4.2 g, 25 mmol) at room temperature and under argon gas. This solution was stirred for 24 h before adding an excess of lithium bromide (2.4 g, 28 mmol) in 50 mL of 2-butanone to the reaction mixture at 50 °C, to obtain a solid precipitate after 10 min. The mixture was then cooled to room temperature, allowed to rest overnight and then filtered. The filtrate

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**Figure 2.** (A) Schematic cartoon showing the fabrication of the 2D (planar) rectangular structure using single exposure in optical projection lithography. (B) Plot showing the tensile stress-strain curve obtained from DN gel structure and its individual parent gel structures. Inset—A dogbone-shaped structure is stretched more than 4 times its original length, and this structure is printed with the laser intensity of 5 mW/cm<sup>2</sup> and exposure time of 5 s. Bar diagrams showing (C-E) elastic modulus, ultimate strain, and ultimate stress for the structure fabricated using DN gel structures, alginate gel structures, and DMAAM gel structures with LAP as an photoinitiator and MBAAm as a cross-linker. ANOVA test showed significant difference among the groups (*p* value < 0.001). Post hoc *t*-tests with Bonferroni correction showed significant differences between two groups at \**p* < 0.016, \*\**p* < 0.001. [Error bars: mean ± standard deviation (SD)]. (F) Plot showing the tearing test for the DN gel representative structures and the individual parent gel structure. (G) Plots showing the stress-strain curve obtained from the DN gel structures exposed to different exposure times.

was washed with 2-butanone  $(3 \times 25 \text{ mL})$  to remove unreacted lithium bromide and dried under vacuum to give LAP (6.2 g, 22 mmol, 88% yield) as a white solid. All chemicals were used as received and were of analytical grade.

Optical Fabrication Setup. A custom-built, digital mask-based, optical lithography setup is used to fabricate DN gel 2D/3D structures (Figure 1A). In this optical setup, a femtosecond laser beam (Coherent Inc.) tuned at 800 nm is passed through the secondharmonic generator to obtain 400 nm laser beam. The laser beam is spatially filtered, expanded, and collimated before directing it to a rotating diffuser. The rotating diffuser is used to change the Gaussian intensity profile of the laser beam to a uniform intensity distribution. Next, the laser beam is projected into a digital micromirror (DMD) device, which is an array of micro mirrors that spatially modulate the laser beam. The spatially modulated beam is directed toward the dichroic mirror, which allows the beam to pass toward a projection lens assembly (magnification  $1\times$ ). The projection lens assembly projects the beam onto a prepolymer liquid, resulting in cross-linking of the hydrogel structure. A bright-field imaging arm equipped with a camera (DCC1545M, Thorlabs Inc.) is added to view the region of interest in the sample. The sample holder assembly consists of a

plastic Petri dish, with a hole bored at the center, glued to a 500  $\mu$ m thick polydimethylsiloxane (PDMS) film (the Supporting Information of ref 45). The L-shaped stage is controlled by a linear stage (TRA25CC, Newport) and a controller (EPS301, Newport). A custom-written LabVIEW program is used to synchronize various processes, such as switching the DMD masks, turning the laser on and off, and stage movement in the z-direction.

Fabrication of the DN Gel Structure. Hydrogel prepolymer solution was synthesized by mixing the DMAAm, alginate, MBAAm, and LAP in the aqueous solution (Figure 1B,C). First, a 3D model of any user-defined structures was drawn using AutoCAD and sliced horizontally to create a stack of binary portable network graphics (png) image files using a custom-written MATLAB code. The png files were uploaded to the DMD, which converted the files into a series of digital masks. The mask in the DMD screen can be changed continuously, and the change in mask is synchronized with the upward movement of the stage using a self-written LabVIEW code. The 400 nm laser beam modulated by these masks selectively photocrosslinks the prepolymer solution in a continuous fashion. Postfabrication, the structures were dipped into the calcium chloride



Figure 3. (A) Stress-strain curved measured from the DN gel structure with varying proportion of alginate gel. (B) Elastic moduli were recorded for the DN gel structures with varying concentration of alginate and plotted as scatter diagram. (C) Ultimate strain recorded for the fabricated structures with varying alginate concentration, is depicted in a scatter diagram. (D) Ultimate stress associated with the breaking of the DN gel structure with varying alginate concentration is plotted in a scatter diagram. ANOVA test showed significant difference among the groups (p value < 0.05). Post hoc *t*-tests with Bonferroni correction showed significant differences between two groups at \*p < 0.016, \*\*p < 0.001. (Error bars: mean ± SD).

solution for 72 h to enable the formation of ionic bonds between guluronic acid units in alginate. $^{10}$ 

**Mechanical Properties of the DN Hydrogel.** All mechanical tests were performed in air at room temperature. Post-printing rectangular samples were cut into dog bones using a cutter dye with a gauge length of 6.25 mm and gauge width of 1.50 mm. Samples were placed into a tensile tester with a 25 N load cell and stretched at a rate of 9.375 mm/min until failure. For tearing tests, samples were cut into rectangles of 25 mm length and 10 mm width. A razor blade was used to then cut the samples nominally at the center, along the length of the rectangular sample. The tear path length (TPL) was measured as the distance from the end-tear, to the uncut end of the sample. A trouser tear test was performed at a rate of 10 mm/min. The tearing energy was calculated using eq 1, where *t* is the thickness,  $L_{\text{path}}$  is the TPL, and  $\int_{x_0}^{x_n} F \, dx$  is the area under the force curve.<sup>46</sup>

Tearing energy = 
$$\frac{1}{(t \times L_{\text{path}})} \times \int_{x_1}^{x_n} F \, \mathrm{d}x$$
 (1)

**Digital Optical Microscope Imaging.** The fabricated structures were imaged and characterized using a digital optical microscope (HIROX, KH-8700). An MX(G)-2016(z) objective lens was used to image the fabricated structures, which provided a resolution of 1.16  $\mu$ m.

**Statistical Analysis.** Statistical analysis was performed using analysis of variance (ANOVA) with three independent samples for each test. Post hoc *t*-tests with Bonferroni correction were also performed between two groups to determine significant differences.

## RESULTS

Fabrication and Characterization of Planar DN Gel Structures. First, we printed a planar slab structure using a single exposure of light pattern and characterized its mechanical properties (Figure 2). The L-shaped stage was placed at a desired height from the PDMS film. A rectangular shaped patterned fs laser beam of wavelength 400 nm with a laser intensity of 5 mW/cm<sup>2</sup> was exposed for 5 s to print planar rectangular shaped structures. The hydrogel prepolymer solution consisted of DMAAm (22 wt %), alginate (2.4 wt %), MBAAm (0.07 wt % or 0.2 mol MBAAm/mol DMAAm), and LAP (0.33 wt %). Next, we studied the swelling behavior of the structures after submerging them to the calcium solution (Figure S1, Supporting Information). These structures swelled to 208% of its original dimension during the first 24 h of immersion and further swelled to 248% at the end of fourth day. As a result, all mechanical property characterizations, such as stress—strain relationships, tearing resistance, and tensile properties such as elastic modulus, strain, and maximum stress, were performed 72 h post-immersion to ensure repeatability and minimal influence of swelling on the tests.

The stress-strain plots for the DN gel structure and structures printed using its individual parent gel (acrylamideonly and alginate-only) show that the DN gel structure stretched more than four times its original length without rupture (Figure 2B and inset). The acrylamide gel structure was softer and more stretchable compared to the DN gel structure; however, the alginate structures were more tough and less stretchable than that of the DN gel structure (Figure 2B).

Tensile parameters (elastic modulus, ultimate strain, ultimate stress) of the structures printed using DN gel, alginate-only gel and acrylamide-only gel are plotted (Figure 2C-E). The modulus of elasticity was 124  $\pm$  17 kPa for alginate structure, 49  $\pm$  4.3 kPa for the DN gel structure, and 5.3  $\pm$  0.15 kPa for DMAAm structure. It required stress of 65  $\pm$  4 kPa to stretch the DN gel structure by 4.10  $\pm$  0.5 times of its original length (Figure 2D,E). The stress and associated strain for the acrylamide gel structure was 6.6  $\pm$  0.5 kPa and 6.25  $\pm$  0.44 and for the case of the alginate gel, and the



**Figure 4.** (A) Stress-strain curve recorded from the DN gel structure printed with varying proportions of the cross-linker (0.035, 0.07, and 0.14 wt %). (B) Elastic moduli for the structures printed with varying amount of MBAAm. (C) Ultimate strain of the fabricated structures is depicted. (D) Ultimate stress associated with the breaking (rupture) of the structures with varying MBAAm concentration is shown as a scatter diagram. ANOVA test showed significant difference among the groups (*p* value < 0.05). Post hoc *t*-tests with Bonferroni correction showed significant differences between two groups at \**p* < 0.016, \*\**p* < 0.001. (Error bars: mean  $\pm$  SD).

ultimate strain was  $1.54 \pm 0.23$ , with a corresponding ultimate stress of  $118 \pm 22$  kPa (Figure 2C–E). The elastic modulus of the DN gel structure is close to the average of the elastic moduli of the DMAAm and alginate gel (Figure 2). A similar trend is also observed in the ultimate stress and ultimate strain of the fabricated structures (Figure 2). Essentially, these results show that the DN gel structure acquires its stretching properties from the acrylamide gel and stiffness properties from the alginate gel.

Furthermore, tearing tests were performed to characterize the tear resistance of the printed structure (Figure 2F). In the case of the DN gel structure, the position moved by the upper clamp was 26 mm, whereas for case of the alginate sample the clamp moved 24 mm, and for acrylamide the clamp only moved 5 mm. The tearing energy was 92 J/m<sup>2</sup> for the DN hydrogel structure, 0.4 J/m<sup>2</sup> for the acrylamide-only structure, and 98 J/m<sup>2</sup> for the alginate-only structure. This study suggests that the tearing resistance for the DN gel structure is similar to that of the alginate sample and higher compared to that of the acrylamide structure.

Effect of Light Dose on the Tensile Properties of DN Gel Structures. To investigate the effect of light dose on the tensile properties of DN gel structures, we varied the exposure time from 3 to 10 s while keeping a constant light intensity of 5 mW/cm<sup>2</sup> (Figure 2G). For the sample exposed less than 3 s, no cross-linking was detected; therefore, we used exposure times of 3, 5, 8, and 10 s. Samples exposed to 3 s were partially cross-linked, and the structures were partially formed. However, 5 s exposure was able to completely cross-link the structure. The strain was highest for the structure which is exposed for 5 s (Figure 2G). The structures fabricated with exposure times of 8 and 10 s were considered overexposed, as

they exhibit less stretchability and break with lower ultimate stress as compared to the sample exposed to 5 s.

Effect of Composition of Alginate/acrylamide on the Tensile Properties of DN Gel Structures. In this set of experiments, the laser intensity and exposure time were kept constant at 5 mW/cm<sup>2</sup> and 5 s, respectively. Samples were prepared using a constant amount of DMAAm (22 wt %), and the amount of alginate was varied (1.2, 2.4 and 4.8 wt %) to change the acrylamide/alginate ratio of the printed samples. The amount of the cross-linker and photoinitiator was fixed to 0.07 and 0.33 wt %, respectively. A stress-strain curve is plotted for one representative structures. An increase in the concentration of the alginate increases the modulus of elasticity and maximum stress, while the stretchability of the structure decreases (Figure 3B–D). The elastic modulus of the structure decreases from 148.5  $\pm$  12.5 to 12  $\pm$  1.88 kPa, when the concentration of alginate was decreased from 4.8 to 1.2 wt %. Next, the strain of the structure was  $3.7 \pm 0.38$  for the structure with alginate concentration of 4.8 wt %. There was a small increase in ultimate strain when the alginate concentration is 2.4 wt % and the ultimate strain of 4.76  $\pm$  0.30 is obtained for the structure printed with the alginate concentration of 1.2 wt %. Ultimate stress follows the decreasing trend similar to the elastic modulus. The stress decreases from the 159.3  $\pm$  14.5 to 21.33  $\pm$  1.5 kPa, when the alginate concentration is decreased from 4.8 to 1.2 wt % (Figure 3B–D).

Effect of Cross-linker Amount on the Tensile Properties of DN Gel Structures. Tensile properties of the DN gel structures were studied by varying the MBAAm cross-linker concentration (0.035, 0.07, and 0.14 wt %) while keeping the amounts of the acrylamide, alginate, and photoinitiator constant at 22, 2.4, and 0.33 wt % respectively. Structures



**Figure 5.** (A) Stress-strain curve recorded from the DN gel structure printed with varying proportion of LAP photoinitiator (0.165, 0.33 and 0.66 wt %). (B) Elastic modulus was recorded for the DN gel structures printed with varying amount of LAP. (C) Scatter diagram showing the ultimate strain for DN gel structures printed using different LAP concentration. (D) Ultimate stress associated with the breaking (rupture) of the structures with different LAP concentrations is shown as a scatter diagram. ANOVA test showed significant difference among the groups (*p* value < 0.05). Post hoc *t*-tests with Bonferroni correction showed significant differences between two groups at \**p* < 0.016. (Error bars: mean  $\pm$  SD).



**Figure 6.** (A) Schematic cartoon showing the fabrication of 3D rectangular structure using optical projection lithography. (B) Stress-strain curve for DN gel structure printed at fixed fabrication speed and varying laser power. (C) Scatter plot showing modulus of elasticity, ultimate stress (kPa), and ultimate strain of the DN gel structure fabricated with different laser intensity and constant fabrication speed. (D) Stress-strain curve for DN gel structure printed at varying fabrication speed and fixed laser power. ANOVA test showed significant difference among the groups (\**p* value < 0.05, \*\**p* value < 0.001). (Error bars: mean  $\pm$  SD).

were printed using a laser power of 5 mW/cm<sup>2</sup> and an exposure time of 5 s. The fabricated structures were loaded into the tensile tester, and the stress strain curve was recorded (Figure 4). Results show that the elastic modulus of the structure is highest (51.31  $\pm$  1.75 kPa) for the structure printed with MBAAm concentration of 0.07 wt %, and the modulus decreases when the concentration of MBAAm

increases to 0.14 or decreases to 0.035 wt %. Similarly, the ultimate strain is also highest  $(3.85 \pm 0.55)$  for the structure printed with the MBAAm concentration of 0.07 wt %. The strain is decreased to  $1.9 \pm 0.06$  and  $2.65 \pm 0.26$ , when the MBAAm concentration is 0.14 and 0.035 wt %, respectively. A similar trend is also shown in the ultimate stress. The stress is highest  $(65 \pm 4 \text{ kPa})$  for the DN gel structures fabricated with



**Figure 7.** (A1) Illustration cartoon of 2D structure (auxetic shaped). (A2) Fabricated DN gel structure before stretching and (A3) after stretching. Structure was printed using optical projection lithography and dipped into calcium solution for 72 h. (B) 2D printed "Syracuse University" before dipping into calcium solution. (C) Log-pile structure demonstrating the smallest feature size/resolution of 120  $\mu$ m. (D,E) 3D printing of tough and stretchable hydrogel. (D1,D2) Empire State Building structure before and after dipping into the calcium solution. (E) Mayan pyramid structure printed using DN gel structure and image was recorded after the structures are dipped into calcium solution for 72 h. The fabricated images shown in Figure 7A,D,E were acquired using a digital SLR camera and 7B,C are recorded using HIROX microscope.

MBAAm concentration 0.07 wt % compared to that of the structures printed with the MBAAm concentration of 0.14 and 0.035 wt %.

Effect of Composition of Photoinitiator on the Tensile Properties of DN Gel Structures. DN gel slab samples were prepared with three concentrations of LAP photoinitiator (0.165, 0.33, and 0.66 wt %). The amount of the acrylamide, alginate and cross-linker was fixed to 22, 2.4, and 0.07 wt %, respectively. Structures were printed using a DMD based fabrication with the laser power of 200 mW (=laser intensity of 5  $mW/cm^2$ ) and exposure time of 5 s. The concentration of the LAP also strongly affects the stretchability and stiffness of the DN gel structures (Figure 5). The highest elastic modulus of  $60.91 \pm 2.91$  kPa is obtained for the structure fabricated with the LAP concentration of 0.66 wt % (Figure 5B). This figure also shows that the modulus remains at the similar level for the LAP concentrations of 0.33 and 0.16 wt %. However, the ultimate strain of  $3.89 \pm 0.51$  is obtained for the structure printed with the LAP concentration of 0.33 wt % and is highest among the structures printed with the three different concentrations of the LAP photoinitiator (Figure 5C). Similarly, the ultimate stress is  $65 \pm 4$  kPa, which is obtained for the structures fabricated using a DN gel with a LAP of 0.33 wt % (Figure 5D).

Results showed that the optimized prepolymer composition of DMAAm (22 wt %), alginate (2.4 wt %), MBAAm (0.07 wt %), LAP (0.33 wt %), and laser parameters (laser intensity of 5 mW/cm<sup>2</sup>, exposure time of 5 s) can result in mechanically robust yet stretchable structures.

**Printing and Characterization of 3D DN Gel.** Optimized prepolymer composition and printing conditions were used to demonstrate the ability to print complex 3D structures using DN gel. The schematic of strategy for printing the 3D rectangular structure is depicted (Figure 6). This optical setup allows us to continuously print a 3D structure in a layer-by-layer approach. One of the key components of this setup is the use of a oxygen-permeable PDMS membrane that creates a cross-linking inhibition zone due to oxygen permeation between the cross-linking part and fabrication window, and the inhibition zone prohibits the cross-linking of the prepolymer to the fabrication window and allows to draw the prepolymer liquid into the fabrication area for continuous printing. In the case of the 3D fabrication, an UV absorber quinoline yellow (QY) dye was used to limit the light scattering and penetration of depth of the light. We observed that the QY dye washed away when the sample was dipped into the calcium solution. First, the stress-strain curve was obtained by fabricating the DN gel rectangular slab structures with varying the laser intensity of 0.65  $mW/cm^2$  (=laser power of 40 mW), 1 mW/cm<sup>2</sup> (=laser power of 60 mW), 1.35 mW/ cm<sup>2</sup> (=laser power of 80 mW), and 1.65 mW/cm<sup>2</sup> (=laser power of 100 mW) at a constant fabricating speed of 0.02 mm/s (Figure 6B). The elastic modulus does not vary significantly for the fabricated structures with different laser intensities (Figure 6C). It is also evident from the figure that the ultimate stress is 35 kPa for the structure fabricated with a laser intensity of 0.6  $\,mW/cm^2$  and the stress increases to highest (66 kPa) for the laser intensity 1 mW/cm<sup>2</sup>; however, further increase in laser intensity leads to decrease in the stress (Figure 6C). The structure printed with a laser intensity of 1  $mW/cm^2$  stretches almost 480% of its original length, and the ultimate strain is decreased for the structure printed with laser intensity lower and higher than 1 mW/cm<sup>2</sup> (Figure 6C).

Further, the effect of the fabrication (scanning) speed on the tensile properties of the DN gel structure was also studied. To perform a test, DN gel structures were printed by a constant laser intensity of 1.65 mW/cm<sup>2</sup> and varying scanning speed of 0.045-0.09 mm/s. The exposure laser dose for fabrication speed of more than 0.075 mm/s was not able to fully cross-link the AAm hydrogel. These printed structures were stretched to

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obtain a stress-strain curve (Figure 6D). Increasing the fabrication speed from 0.045 to 0.06 mm/s, the ultimate strain increases from 150 to 290% and decreases when the printing speed is increased to 0.075 mm/s and above (Figure S2, Supporting Information). The trend is also consistent with the result obtained in stress-strain curve obtained from structure with different laser powers (Figure 6B) and stress-strain curves obtained from the 2D structure printed with different exposure time (Figure 3D).

**Fabrication of User-Defined 2D/3D Structure of DN Hydrogel.** Next, we demonstrate the printing of user-defined 2D DN gel structures using an "auxetic" shape design. A cartoon of auxetic shape with re-entrant cell structure before and after stretching is shown (Figure 7A1). The auxetic structure was printed using the DN gel with the laser intensity of 5 mW/cm<sup>2</sup> and exposure time of 5 s (Figure 7A2). This structure did not lose its breadth when stretched to 200% of its original length (Figure 7A3). Next, we also fabricated the 2D structure of DN hydrogel by writing "Syracuse University" using a laser intensity of 5 mW/cm<sup>2</sup> and exposure time of 5 s.

We further tested the smallest feature size of DN gel structures fabricated using our optical lithography system (Figure 7C). The smallest feature size of the printed structure is mostly influenced by the size of a mirror in DMD (~12  $\mu$ m) and the material properties of DN gel. In this experiment, we designed masks of intersecting lines and the linewidth of the lines were varied to 3, 5, and 10 pixels, with a laser intensity of 5 mW/cm<sup>2</sup> and exposure time of 5 s. No observable cross-linking was observed in the case of 3 pixels' line. Only partial cross-linking was observed for 5 pixels' line, and the partially cross-linked structures were easily destroyed during the subsequent washing steps. The smallest linewidth of printed stable line of the DN gel was 120  $\mu$ m using a mask of 10 pixels lines.

Further, 3D printing of the DN hydrogel structures is demonstrated (Figure 7D,E). This is done by printing the Empire State Building printed using digital mask-based optical lithography. Post-printing, the structure is dipped into the calcium chloride solution for 72 h (Figure 7D). In order to fabricate the structure, a laser power of 60 mW (=laser intensity of 1 mW/cm<sup>2</sup>) and stage speed of 0.02 mm/s was used. Mayan pyramid printing is also demonstrated using DN gel hydrogel, and the structure was printed using the laser power of 1 mW/cm<sup>2</sup> and scanning speed of 0.02 mm/s (Figure 7E).

#### DISCUSSION

In this work, DN gel structures were fabricated using digital mask-based optical projection lithography followed by subsequent dipping of the structure into an ionic solution. During the process of fabrication, the UV exposure induced cross-linking of acrylamide by covalent bonding; at this stage, the alginate within the acrylamide network does not form a network. When UV-crosslinked structures are subsequently immersed into the 100 mM calcium chloride solution, ionic cross-linking of alginate occurs. Alginate chains consist of mannuronic acid (M unit) and guluronic acid (G unit), and the introduction of the divalent cations results in cross-linking of G units in different alginate chains forming an ionic network.<sup>10</sup>

As evidenced by tensile results, the fabricated DN gel structures stretched four times of its original length without rupture (Figure 2). Compared to the acrylamide gel structure,

these structures were tougher and less stretchable. When compared to alginate structures, the DN gel structures were much softer and more stretchable. In essence, it is suggested that the DN gel structure acquires its stretching properties from the acrylamide gel and stiffness properties from the alginate gel.

The effect of the laser intensity and composition of the MBAAm and LAP to the tensile properties of the structure were investigated (Figures 2G, 4, and 5). The highest ultimate strain and stress were obtained for an intermediate concentration of cross-linker, photoinitiator, and light dosage. Structures that were fabricated with long exposure times and/ or with the high concentration of cross-linker and/or high concentration of photoinitiator exhibited less stretchability and broke with lower ultimate stress. Increase in the amount of the cross-linker, photoinitiator, or light dose increases the covalent cross-linking of the acrylamide. The covalent cross-linking is too high; hence, the bond between the individual PAAm chain is short. Breaking of the chain leads to the dissipation of the energy stored to the entire chain, which leads to low fracture energy. Structures exposed to low dose of the light and/or low amount of the cross-linker and/or low amount of photoinitiator were weak and exhibited less stretchability. In this case, the covalent cross-linking density in these structures is low and the partially cross-linked acrylamide gel structure is not able to stabilize the deformation of gel as the DMAAm network becomes too compliant.<sup>10</sup>

Next, fabrication of the user-defined 2D DN gel structures were demonstrated by writing "Syracuse University" and by printing honeycomb shaped auxetic structure. The smallest feature size of 120  $\mu$ m was demonstrated by printing intersecting lines using a mask of 10 pixels' lines. 3D printing of the DN hydrogel structures was shown (Figure 7D,E) by fabricating the Empire State Building and the Mayan pyramid using digital mask based optical lithography.

## CONCLUSIONS

In summary, we have demonstrated the 3D additive printing of tough and stretchable DN gel structures using digital maskbased optical projection lithography. To the best of our knowledge, this is the first report of 3D additive printing of tough and stretchable complex 2D and 3D DN gel (ionic and covalent network) structures using optical projection lithography within minutes. This new method can be extended to other material compositions with broad implications in the areas of soft robotics and tissue engineering.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b19431.

Detailed description of measurements and additional data (PDF)

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## Notes

The authors declare no competing financial interest.

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