3D PRINTING OF MULTI-FUNCTIONAL HYDROGELS

by

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Abstract

3D printing technology has been widely applied to rapid design and fabrication in recent years. Hydrogels fabricated by 3D printing are spotlighted owing to the emerging demands for complicated soft structures and biocompatible devices. The large variety of hydrogels provides the potential to produce multifunctional structures with hydrogels of different formulations and properties. Herein, we reported two works of 3D printing of multifunctional hydrogels by direct ink writing, a 3D printing technology based on the rheological properties of the hydrogel precursor ink. The first work developed a highly stretchable in situ grown metal-organic framework (MOF), overcomes the longstanding challenge of processing MOF materials into the flexible matrix by 3D printing without compromising on the MOF functionality performance. The prepared MOF hydrogel by facile in situ growth of MOF in 3D printed pAAM/alginate double networks hydrogel matrix exhibits high loading of MOF distributed in the whole hydrogel matrix, can be stretched to over 450 % of its original length and shows the best dye adsorption performance among the existing 3D printed MOF-polymer composites. We anticipate that this method would introduce new opportunities fabrication of complex flexible MOF-polymer composite devices for diverse applications such as wearable, implantable biosensors, flexible electronics. The second work introduces 3D printed segmented dual-gel tubes composed of an active thermally responsive swelling gel (poly N-isopropylacrylamide; pNIPAM) and a passive thermally non-responsive gel (polyacrylamide; pAAM). The dual-gel structures are able to achieve reversible shape deformation including uniaxial elongation, radial expansion, bending, and gripping by thermal actuation. The shape changes are programmable, predictable guided by CAD design and finite element simulations. The dual-gel 4D printing opens new avenues such as stimulus-responsive soft robotics

and biomimetic 3D cell scaffold for biomedical engineering, with a high level of customization and tunability in three dimensions.

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Chapter I. 3D Printing of a Highly Stretchable *in situ* Grown Metal-Organic Frameworks Hydrogel

1.1 Introduction

Metal-organic frameworks (MOFs) are a class of emerging crystalline nano-porous materials, that are consisted of metal ions or metal clusters joints and organic ligands linkevrs. MOFs are well-known for their extremely high internal surface area and ordered periodic porosity. Hence, numerous available metal ions and organic ligands enable the high tunability of MOFs structures, resulting in a variety of chemical and physical properties.^{1–3} Owing to its unique properties and diversity, MOFs have been widely used in separation,^{4,5} gas storage,⁶ drug delivery,^{7,8} catalyst,⁹ and sensors.^{10,11} However, the large scale commercial application of MOFs is largely limited despite the massive amounts of achievements in lab-scale applications, because of the disadvantage that most of MOFs are powder shaped, rigid and brittle materials.^{12,13} Tremendous approaches have been explored to tackle this issue, a feasible method to overcome this disadvantage of MOFs is integrating MOFs with substrate materials, such as polymers and ceramics to construct a shapeable and easy-to-handle MOFs composite.¹⁴

MOFs-polymer composite is the most well-studied MOFs composites, owing to the wide variety of polymer matrices and their different properties. Flexible MOFs-polymer composites incorporated MOFs into flexible polymer matrices, given the ability to be stretched or compressed, flexible MOFs-polymer composites extended their application into the emerging fields of wearable devices,¹⁵ implantable sensors,¹⁶ self-folding actuators,¹⁷ supercapacitors,^{18,19} and other This chapter is in preparation for a journal paper titled '3D Printing of a Highly Stretchable in situ Grown Metal-Organic Frameworks Hydrogel' W. Liu, O. Erol, D. H. Gracias applications requiring large deformation or resistance to deformation.^{20,21} But traditional fabrication methods of MOFs-polymer composites often resulted in simple two-dimensional shapes with restricted shape complexity, such as films,^{4,5} filaments,^{22,23} microsphere.²⁴ Therefore, applications of flexible MOFs-polymer composites are limited in fields where required three-dimensional shapes with complex geometries and delicate structures.

The advancement of 3D printing technology allows us to fabricate MOFs-polymer composites into almost any three-dimensional customizable shapes in a rapid manner, greatly broadened the potential application of MOFs-polymer composites in different circumstances. In recent years, several works have been done on 3D printing of MOFs-polymer composite via direct ink writing (DIW), digital light processing (DLP) and fused deposition modeling (FDM) for water treatment,^{25–27} gas storage,^{28,29} drug release,³⁰ and battery.³¹ However, most of the 3D printed MOFs-polymer composites were non-flexible, with rigid, brittle matrices such as ABS, PVA monoliths. Other than lacking flexibility, the existing 3D printing MOFs-polymer composites have critical problems such as harmed performance and low MOFs loading efficiency. To be detailed, the most common method to 3D print MOFs-polymer composite is directly blending of MOFs particles into a polymer solution and 3D print the mixture solution. But this method often suffers from particle aggregation, poor particle-polymer interaction,^{23,32} and the non-porous matrix materials can also block access to the pores of MOFs,³³ leading to reduced MOFs performance. To overcome this problem, in situ growth of MOFs method was investigated, but most of the research 3D printed polymer matrix first and in situ grown MOFs on the surface of the printed scaffold,^{25,26} which evidently reduced the loading efficiency of MOFs, since MOFs only presence

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on the surface. These above-mentioned issues largely limited the development of flexible MOFspolymer composites by 3D printing technology and their applications.

Herein, we first time demonstrate a 3D printing method to fabricate a highly stretchable in situ grown MOF-hydrogel composite. Hydrogel matrix precursor was prepared by homogeneously blending MOF forming ligands into a 3D printable polyacrylamide (pAAm)/alginate double network (DN) hydrogel precursor. pAAm/alginate DN hydrogel was chosen as the flexible matrix as it has been found to form highly stretchable and tough hydrogels, and the mechanical performance of the hydrogel system can be easily tuned by changing the amount of monomer and crosslinking density.³⁴ To turn the hydrogel precursor into a shear-thinning ink required for direct ink writing (DIW) 3D printing, we selected a novel non-ionic shear-thinning agent, hydroxyethylcellulose (HEC), solved the incompatible issue with the MOF forming ligand. The DIW printable precursor allows us to fabricate hydrogel matrix with the desired shape. After 3D printed and primarily cured by UV, the hydrogel matrix was secondarily cured by metal ions, metal ions also *in situ* formed MOF with the pre-added ligands. The facile synthesis method works in aqueous solution at room temperature, doesn't require complicated heating, mechanical stirring, microwave processing in traditional MOFs synthesis.³ In this study, HKUST-1 was selected as a prototypical MOF. Our results suggest the 3D printed HKUST-1 hydrogel composite has HKUST-1 particles distributed in the structures and decorated on the surface. The printed HKUST-1 hydrogel sample can be stretched by up to 450%, with tunable mechanical properties in a wide range, dye adsorption tests indicate excellent MOF performance. This study provides a versatile platform for 3D printing flexible MOFs-polymer composites, significantly improve the fabrication complexity of them, may open a new era for applying flexible MOFs-polymer composites to customizable flexible, wearable, implantable devices.

1.2 Experiment Section

1.2.1 Materials

All the chemicals and solvents were of or above reagent grade, they are used as received without further purification. Acrylamide (AAm), Sodium Alginate (SA, from brown algae, low viscosity), N, N'-methylenebis(acrylamide) (MBAA), trimesic acid (H₃BTC), triethylamine (TEA), methylene blue (MB), rhodamine 6G (R6G), acetone, dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich (USA), Irgacure 2959 (I2959) was purchased from BASF (Switzerland), copper(II) nitrate trihydrate was purchased from Fisher Scientific (Poland), hydroxyethylcellulose (HEC) was purchased from Ashland (USA) with commercial grade of Natrosol 250HHR, Laponite XLG was donated from Southern Clay Production, Inc. (USA). Deionized water (DI water) was used for all experiments.

1.2.2 3D printing ink preparation

To prepare the hydrogel precursor inks for 3D printing, SA (1.5wt% final concentration), H3BTC (0.05 M final concentration) and TEA (0.15 M final concentration) were first dissolved in water by magnetic stirring hotplate at room temperature for a day to form a homogeneous stock solution. Then, AAm (0.0 M, 0.9 M, 1.8 M, 3.6 M) and MBAA (0.03wt%, 0.06wt%, 0.12wt% ratio to AAm) were dissolved in the stock solution to get a series of homogeneous aqueous solutions of various AAm and MBAA concentrations. Photoinitiator 50wt% I2959 DMSO solution was added into the stock solution with final I2959 concentration of 0.4wt% of the pregel ink, DI water was added accordingly to get a series of solutions with desired components concentration. The shear-thinning agent HEC (4wt%, final concentration) was added in the last step, the pregel solutions were stirred

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at 75 °C for 40 minutes to allow the hydration and gelation of HEC. The pregel solutions were rested at room temperature for a day to reach the complete hydration of HEC and remove the air bubbles in the pregel. All pregel solutions were transferred into transferred to UV-blocking cartridges by syringes and centrifuged (IEC CENTRA CL2 centrifuge, Thermo Electron Corporation) to remove bubbles generated during the transferring process in the cartridges. The prepared pregel inks were kept at room temperature for at least 24 hours to achieve the desired shear thinning properties.

1.2.3 3D printing of hydrogel matrix structure

Cartridges with pregel inks were loaded to a pneumatic extrusion 3D Printer (INKREDIBLE+ 3D Bioprinter, Cellink). The structures were printed with an 18 G (0.8 mm diameter) nozzle on a TeflonTM film covered glass slide at room temperature, the TeflonTM film prevented the adhesion of the printed structures on the substrate. A second printer head was applied when the sacrificial support structure needed, the calibration structure was printed before the actual designs to align the second nozzle with the first one. The printing pneumatic pressure varying from 120 to 150 kPa for the hydrogel inks, and the pressure for the supported ink was 120 to 150 kPa. All the structures are designed by SolidWorks (Dassault Systèmes) and exported as STL files, the STL files were then sliced into G-code by Repetier-Host software via Slic3r slicer, the slicing setting varied based on each design, the G-code was manually edited when necessary.

1.2.4 Post-curing and MOF in-situ synthesis

The curing process of the MOFs hydrogel consists of two steps, photocuring, and metal ions crosslinking, respectively. 3D printed structures were firstly photocured for 15 minutes by an OmniCure

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UV Curing System (LX 500, Lumen Dynamics) to form a polyacrylamide (pAAm) primary polymer network. UV LED heads with 365 nm wavelength operating on its 30% power were placed at a distance of 3 cm from the structure, resulted in a UV intensity of 0.12 W/cm². A rotating platform which rotates slowly at 9.6 rpm was applied for tubular structures to ensure uneven exposure of UV light and consequently uniform curing of the hydrogel structures.

The UV-cured structures were immersed into copper nitrate water acetone (1:1 volume ratio) solution to form a Cu^{2+} cross-linked SA secondary polymer network, the Cu^{2+} reacted with the MOFs forming ligands to *in-situ* synthesize the HKUST-1 as the same time. The UV-cured structures were kept in a series of solutions with various Cu^{2+} concentrations (0.25 M, 0.50 M, 1.0 M) for 24 hours allows the Cu^{2+} diffuse into the hydrogel matrix sufficiently.

1.2.5 Rheology and printability test of the inks

Rheology tests were performed on a rotational rheometer (MCR 302, Anton-Paar Instruments) using a parallel plate measuring tool. The temperature of the plate was kept at 25 °C. Viscosity data were measured by rotational tests with shear rates ramping from 0.01 to 1000 s⁻¹. Viscoelasticity data were obtained by oscillation tests with shear stress ramping from 0.01 to 1500 Pa.

Printability tests were conducted on the 3D printer by printing 30 mm lines on the substrate under different pressure which ramping from 0 KPa to 220 KPa, using different sizes of nozzles (16G, 28G, and 22G which corresponding to 1.2 mm, 0.8 mm and 0.4 mm inner diameter of the nozzle).

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Printed lines were imaged by cellphone, and measured by ImageJ to get the width of lines, 3 lines were printed for each pressure level, all tests were performed at room temperature.

1.2.6 Mechanical test

Uniaxial tensile tests were carried out on a tensile tester (MTS Criterion Series 40, MTS Systems Corporation) equipped with a 100N load cell, ASTM D412 standard was followed whenever possible. Dumbbell shaped hydrogel samples with a designed gauge length of 12 mm, gauge width of 5 mm and 3.2 mm thickness were printed with rectilinear infill aligned with the tension direction. The exact dimensions of each tested sample were measured by a caliper before loading to the clamps. All tests were performed at a constant stretch velocity of 10 mm/min and at room temperature, at least three duplicate measurements were performed for each type of samples. The nominal stress was calculated by the tensile force and the initial cross-sectional area of the sample, the strain is defined as the percentage of clamps displacement to the original clamps separation distance. The initial linear region of the stress-strain curve between 5% to 10% was used to calculate the elastic modulus (E), Fracture energy was measured by integrating the area under the stress-strain curve until the sample fractures.

1.2.7 Characterization

Powder X-ray diffraction (PXRD) patterns were obtained from scanning at room temperature using a Bruker D8 Focus diffractometer with a LynxEye detector using Cu K α radiation (λ = 1.5424 A), samples were freeze-dried and ground before tests. Infrared spectra of the freeze-dried hydrogel samples were obtained using an FTIR spectrometer (Nicolet Nexus 670 FTIR, Thermo Fisher Scientific). Scanning Electron Microscope (SEM, JEOL JSM IT100, JEOL Ltd.) was used

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to take images and study the micromorphology of the prepared materials, all hydrogel samples were freeze-dried by lyophilizer and sputter-coated with a thin layer of gold before imaging. Thermogravimetric analysis (TGA) was carried out with a ramp rate of 10 °C/min from 30 °C to 800 °C, under nitrogen flow at the rate of 40 mL/min, using a thermogravimetric analyzer (TGA 8000, PerkinElmer Inc.).

1.2.8 Dye adsorption of 3D printed MOF hydrogel

The adsorption studies of dyes (MB, R6G and their mixture) aqueous solution by the 3D printed HKUST-1 hydrogel was carried in a batch experiment at room temperature. Tested HKUST-1 hydrogel grid scaffolds are prepared with design dimensions of 20 mm * 20 mm * 4 mm, the weight of the scaffolds were measured by an analytical balance () before the adsorption tests. Typically, one scaffold was added to 10 mL of dye aqueous solution with the initial concentration of 30 μ M, after adsorption for a period of time, the sample bottles were well shaken, and the solution was poured out into a quartz cuvette for analysis, the solution in the cuvette was returned to the sample bottle to continue the test. The adsorption process of the dye molecules was monitored by a UV-Vis spectrophotometer (Lambda 950, PerkinElmer Inc.) for 6 hours. The UV-vis spectra of dye solutions were recorded from 400 to 800 nm wavelength with scanning interval of 5 nm, and the MB, R6G concentrations were quantified by measuring the absorbance at 660 nm and 525 nm, respectively.

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1.3 Results and Discussions

1.3.1 Formulation of hydrogel precursor ink and fabrication of MOF hydrogel

The formulation of the hydrogel precursor ink is depicted in **Figure 1.1A**, hydrogel precursor is prepared by mixing AAm, MBAA, and I2959 as the monomer, crosslinker, photoinitiator for primary polymer network, SA as the polymer for the secondary network, H₃BTC as organic ligand and TEA as deproton agent for HKUST-1 synthesis and HEC as the shear-thinning agent. A key challenge of formulating a pregel ink for DIW printing is the pregel solution must be made into a toothpaste-like ink, with a desired shear-thinning property. The most common way to induce shear-thinning property into a solution system is adding the shear-thinning agent. However, most of the commercial available shear-thinning agents are ionic shear-thinning agents, such as Laponite nanoclay,^{35,36} gellan gum,³⁷ is not compatible in a solution system with the massive amount of ions. With the presence of H₃BTC and TEA in our precursor solution, the common ionic shear-thinning agents in the presence of H₃BTC and TEA in our precursor solution, the common ionic shear-thinning agent into a properties. Our innovation in ink formulating is first time applied the HEC, commercially known as Natrosol, a non-ionic shear-thinning agent into a DIW ink formulation, to solve the incompatibility issue with ions.

The overall fabrication procedure of 3D printed HKUST-1 hydrogel is schematically illustrated in **Figure 1.1B**, the hydrogel precursor is loaded into a cartridge and 3D printed by the DIW 3D printer into the designed shape. Next, the printed structure photocured by a UV curing system. The 12959 is excited by UV and initiated the free-radical polymerization of primary pAAm network, the pAAm, alginate polymer networks are intertwined, and joined by covalent crosslinking between amine groups on polyacrylamide chains and carboxyl groups on alginate chains (represent by red squares and blue triangles in Figure 1a, respectively). ^{34,38} Then, the UV cured structure

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was immersed into a copper nitrate water-acetone solution for ionic crosslinking and in situ HKUST-1 synthesis. Alginate is a copolymer of mannuronic acid (M unit) and guluronic acid (G unit), arranged in blocks rich in G units, M units, and blocks of alternating G and M units. In this Cu²⁺ ions aqueous solution, the G blocks in different alginate chains are jointed by ionic crosslinks through Cu²⁺ ions, resulting in a secondary network.³⁴ At the same time, as the diffusion of Cu²⁺ ions into the hydrogel matrix, HKUST-1 is readily synthesized within the hydrogel matrix at room temperature, with the presence of pre-added Lewis base TEA fed to deprotonate H₃BTC ligands (Cu²⁺ ions represent by light blue dots, HKUST-1 particles represent by dark blue diamonds in Figure 1a). This facile HKUST-1 synthesis method was adapted from Jungho and coworkers,³⁹ it can synthesis MOF distributed in the whole hydrogel matrix in a water environment at mild temperature, preserves the water and flexibility of the hydrogel matrix. Outperformed previous literature which forming a shell layer of MOF on a dehydrated hydrogel and requires a heated organic solution.²³ As shown in Figure 1.1C, The printed hydrogel precursor turned into a transparent soft hydrogel with a slight yellow color after UV cured, and became opaque with a bright blue color after ionic crosslinking and HKUST-1 growth, the prepared HKUST-1 hydrogel is tough and stretchable, able to undergo largely shape deformation such as elongation and twisting.



Figure 1.1. Schematics of the formulation, fabrication process, and the prepared MOF hydrogel. (A) Schematic showing the formulation of hydrogel precursor, polymer structures in the UV cured hydrogel matrix and HKUST-1 hydrogel. (B) Schematic showing the three steps fabrication of MOF hydrogel, 3D printing of precursor structure, UV curing and ionic crosslinking and MOF in situ synthesis. (C) Digital images of UV cured sample and HKUST-1 sample and demonstration of shape deformation of HKUST-1 hydrogel.

1.3.2 Rheological properties and printability of hydrogel precursor ink

Printability and rheological are critical for DIW 3D printing ink, general, an ideal DIW ink should exhibit low viscosity, liquid-like at higher shear rates to allow for extrusion of the ink through the fine nozzles, show high viscosity and paste-like behavior at a low shear rate to keep the shape fidelity of prints after printing.⁴⁰ We firstly investigated printability for a series of ink with different shear-thinning agent (HEC) concentrations, we observed inks with HEC content above 2 wt% is able to retain their shape fidelity after printed (Figure 1.2A). Figure 1.2B shows the printability of inks with feasible HEC concentration under different pressures and nozzle sizes. The blue part in the chart indicate non-extrudable region, the white part stands for the printable region, pink part means the printing extrusion velocity is too high for shape fidelity printing. The ink with 4 wt% of HEC exhibited the biggest printable region under the working pressure of our 3D printer, while the 2 wt% HEC ink showed a smaller printable range at low pressure and the 6 wt% HEC ink was non-extrudable for the fine nozzle to get high-resolution prints. We further studied the fidelity of printed filaments within the printable region for the optimal 4 wt% HEC ink (Figure 1.2C). The printed filaments showed a slightly bigger diameter than the nozzle diameter, and the filaments diameters increased with the printing pressure.

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Figure 1.2. Schematic of the printability tests and plot of printability data. (A) Digital image and schematic of the printability tests. (B) Printability of inks with different HEC concentration under different pressure via different nozzles. (C) The plot of printed filaments under different pressure via different nozzle sizes.

We also characterized the viscosity and viscoelastic properties of the printable ink compositions with different HEC contents. Figure 1.3A shows the viscosities the inks changing as a function under different shear rate. All of the hydrogel precursor inks with HEC exhibited a shear-thinning behavior as observed by their viscosities decrease with the increase of shear rate. Corresponding to the printability test results, inks with higher HEC concentrations exhibited higher viscosity values across the range of shear rates. We further characterized the viscoelastic properties of these inks by oscillation tests, this the viscoelastic behavior is crucial in DIW printing since the inks should have a higher storage modulus (G') at low shear stresses to behave solid-like properties after printing thus retain the shape of prints. In contrast, the loss modulus (G") should be higher than G' at high shear stresses, so inks show liquid-like behavior during extrusion through the fine nozzle.³⁷ Figure 1.3B shows all of the ink with different amount of HEC showed higher G' values at lower shear stresses before the gel point (crossing of G' and G'' curves) and high G'' at higher shear stresses. These results reaffirmed all of these ink formulations are printable. We also characterized the viscosity and viscoelastic properties of inks with different AAm monomer concentrations, as the AAm is the major component in our inks other than water (Figure 1.3C, D). The result suggested the AAm concentration has a negligible influence on the viscosity and viscoelastic properties if inks, the printability is not largely varied by the amount of AAm in the ink within the range studied.

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Figure 1.3. Rheological properties of inks with different compositions (A) Viscosity as a function of shear rate, (B) storage and loss modulus as functions of shear stress of inks with different HEC. (C) Viscosity as a function of shear rate, (D) storage and loss modulus as functions of shear stress of inks with different AAm.

1.3.3 Characterization of MOF hydrogel

We scanned the prepared HKUST-1 hydrogel by PXRD as evidence of *in situ* HKUST-1 growth. The XRD patterns of HKUST-1 hydrogel, HKUST-1 hydrogel after dye adsorption, pAAm/alginate hydrogel, and simulated HKUST-1 are shown in **Figure 1.4**. The XRD pattern of the controls: pAAm/Cu-alginate hydrogel, pAAm/alginate hydrogel doesn't show any peaks,

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indicates no HKUST-1 crystal formed in the controls. The XRD of HKUST-1 hydrogel shows strong peaks align with the simulated HKUST-1 peaks, we attribute the peaks to the diffraction of HKUST-1, it proves the successful synthesis of HKUST-1 in the hydrogel matrix. Furthermore, the peaks of the HKUST-1 hydrogel after dye adsorption is consistent with the peaks of just prepared HKUST-1 hydrogel indicates that the HKUST-1 in the composite is stable during the dye adsorption tests.



Figure 1.4. XRD patterns of samples. The blue line represents HKUST-1 hydrogel, the orange line represents the hydrogel matrix, the grey line represents simulated HKUST-1.

To measure the composition of the HKUST-1 hydrogel, we ran TGA tests for the HKUST-1 hydrogel and hydrogel matrix (**Figure 1.5**), the TGA results suggest the HKUST-1 has a loading

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rate of 7.9 % in the hydrogel composite. The DTG results indicate that the secondary crosslinking and MOF formation improve the thermal stability of the hydrogel composite.



Figure 1.5. TGA results of samples. The pink lines represent HKUST-1 hydrogel, the grey lines represent the hydrogel matrix. (A) Graph showing the thermogravimetric analysis of samples. (B) Graph showing derivative thermo-gravimetric of samples.

We also characterized the FTIR spectra of HKUST-1 hydrogel, hydrogel matrix, and hydrogel precursor ink (**Figure 1.6**), the peaks strengthen at 1350, 1660, 3195 cm⁻¹, and peak weaken at 1251 cm⁻¹ on UV cured hydrogel matrix than the unsure ink indicate the formation of primary polyacrylamide network and covalent crosslinking between polyacrylamide and alginate chains. the results confirm the polymerization of AAm and crosslinking of pAAm chains and crosslinking between pAAm and alginate chains as previous literature reported.³⁴



Figure 1.6. ATR-FTIR spectra of samples. The blue lines represent HKUST-1 hydrogel, the green lines represent the hydrogel matrix and the black represents hydrogel precursor ink.

1.3.4 Morphology and structure of MOF hydrogel

The morphology of the HKUST-1 hydrogel and hydrogel matrix was studied by SEM to investigate the hierarchical structure. The pure hydrogel matrix (**Figure 1.7A**) shows uniform macropores across the whole cross-section, assemble to morphology of previous reported hydrogel with pAAm and HEC.⁴¹ After ionic crosslinking and *in situ* MOF growth, octahedron HKUST-1 particles can be observed all over the surface and external and internal cross-section of the HKUST-1 hydrogel (**Figure 1.7B, C, D**). Small HKUST-1 particles evenly decorate and embed on the surface of the HKUST-1 hydrogel (Figure 3c). Small HKUST-1 particles also densely distributed in the external cross-section of the HKUST-1 hydrogel, the macropores are barely This shorts is in generating for a journal generatited (2D Britting of a Highly Stateholds in sity Group.

visible in the external region due to the high loading of MOF and secondary crosslinking of Cu^{2+} ions. In contrast, bigger HKUST-1 particles loosely distributed in the core region, the macropores are partly preserved in the region. These results are consistent with Jungho and coworkers' report. They attributed this size distribution spectrum of HKUST-1 particles to the differentiated distribution of Cu^{2+} ions and ligands concentration because the firstly formed crystals in the external parts served as a barrier, disrupted the further infusion of Cu^{2+} ions and effusion of ligands.³⁹



Figure 1.7. SEM images of samples. (A) Cross-section of hydrogel matrix. (B) Side view of the surface of HKUST-1 hydrogel. Cross-section of HKUST-1 hydrogel in (C) core region and (D) external region.

Despite the different size distribution of HKUST-1 particle with respect to the region in the hydrogel, the local distribution of HKUST-1 particles is quite even. We believe the uniform macroporous structure of hydrogel matrix templated growth of crystals, thus contributes to even local suspension of MOF particles.²¹ Our *in situ* grown HKUST-1 hydrogel composite formed MOF with the whole matrix, even in the core region. The high MOF loading efficiency achieved within the porous hydrogel matrix indicate that we produced a novel 3D printing composite material, which retains the favorable properties of MOF and kept the high loading rate, outperform the existing 3D printing MOFs-polymer composites prepared by directly blending method and surface *in situ* growth method.

1.3.5 Tunable mechanical properties

The pAAm/alginate DN hydrogel system exhibits high tolerability of mechanical properties by varying the material parameters as reported by previous work.³⁴ We tested various HKUST-1 hydrogels fabricated with different materials parameters including the AAm monomer concentration, covalent crosslinker concentration, and ionic crosslinker concentration. The dumbbell-shaped tensile test samples were printed with the design guided by ASTM D412 standard (**Figure 1.8**), the samples were uniaxially elongated until their fracture.

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Figure 1.8. Schematics of micro tensile test samples. (A) Design of the micro tensile sample. (B) As prepared HKUST-1 hydrogel micro tensile sample. (C) Simulation of the stress distribution of the micro tensile sample under uniaxial elongation.

We first studied the influence of AAm monomer concentration on mechanical properties, the stress-strain curves of a series of HKUST-1 hydrogel with different AAm concentration are shown in **Figure 1.9**, it shows the stretchability of HKUST-1 hydrogels increases with the richer amount of AAm in the matrix. The strain at break, strength, tensile modulus and toughness are increasing simultaneously with the of the increasing of AAm in HKUST-1 hydrogel. HKUST-1 hydrogel with 3.6 M AAm in hydrogel matrix exhibited the largest deformation, it can be elongated to 452% of its original length before the break, with the highest 277.6 kPa strength, 152.3 kPa Modulus, 744.7 kJ/m⁻³ toughness. We attribute all improvements on mechanical properties to the higher pAAm content in the hydrogel matrix, leading to an elastomer-like property.

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Figure 1.9. Mechanical properties of HKUST-1 hydrogels with different AAm concentration (A) Stress-strain curves of the samples. (B) Ultimate tensile strength, tensile modulus as functions of AAm concentration. (C) Strain at break as a function of AAm concentration. (D) Toughness as a function of AAm concentration.

Alternatively, the mechanical performance of HKUST-1 hydrogel can also be adjusted by changing the covalent crosslinker concentration. We prepared and tested a series of HKUST-hydrogel with different concentrations of MBAA, and other parameters fixed as control. The stress-strain curves and mechanical properties are charted in **Figure 1.10**. Tensile modulus of the hydrogel slightly increases with the increasing of MBAA concentration, as a result of a higher degree of crosslinking. A critical point exists for the rest of mechanical properties: strength, strain

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at break and toughness, the best mechanical performance present at the 0.06 wt% MBAA to AAm ratio, all mechanical properties drop at the MBAA concentration lower or beyond this point. This trend is observed and well-studied in previous research of pAAm/alginate hydrogel system, it can be explained by that when the MBAA concentration is too low, the polymer network is barely crosslinked, the polymer chains are too compliant to hold the shape deformation. On the other hand, when the MBAA concentration is too high, the polymer network is densely crosslinked, the polymer chains is too high, the polymer network is densely crosslinked, the deformation is too high, the polymer network is densely crosslinked, the deformation is too high, the polymer network is densely crosslinked, the deformation is too high, the polymer network is densely crosslinked, the polymer chain between crosslinking joints is too short, therefore easy to break leading to a decreasing of mechanical performance. ³⁴

We further studied ionic crosslinker concentration's contribution to mechanical performance by testing a series of HKUST-1 hydrogel crosslinked by different concentration of Cu^{2+} solutions. **Figure 1.11** shows the stress-strain curve and all mechanical performance of these hydrogels. We observed the hydrogel matrix became much stiffer and tougher with the inducing of secondary crosslinking and the increasing of Cu^{2+} concentration, we attribute the increase of modulus and decrease of strain at break to the tougher matrix resulting from the higher degree of ionic crosslinking. However, the strength and toughness decrease with the Cu^{2+} concentration after inducing of Cu^{2+} ions. We suggest a reasonable explanation based on the previously mentioned MOF particles distribution regulation. We believe the formation of dense and packed MOF layer formed faster and denser with the higher Cu^{2+} ions in the crosslinking solution, therefore resulting in a less crosslinked core region, leading to the decrease of overall mechanical performance.

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Figure 1.10. Mechanical properties of HKUST-1 hydrogels with different MBAA concentration. (A) Stress-strain curves of the samples. (B) Ultimate tensile strength, tensile modulus as functions of MBAA concentration. (C) Strain at break as a function of MBAA concentration. (D) Toughness as a function of MBAA concentration.



Figure 1.11. Mechanical properties of HKUST-1 hydrogels with different Cu^{2+} concentration (A) Stress-strain curves of the samples. (B) Ultimate tensile strength, tensile modulus as functions of Cu^{2+} concentration. (C) Strain at break as a function of Cu^{2+} concentration. (D) Toughness as a function of Cu^{2+} concentration.

1.3.6 Adsorption performance of MOF hydrogel

Although MOF is intended for various applications, in this study, we test the dye adsorption performance in the aqueous feed of our HKUST-1 hydrogel composite, as a demonstration that the MOF is still functionally working when embedded in pAAm/alginate hydrogel matrix. In the tests, a small piece of 3D printed grid scaffold was placed into 10 mL of an aqueous solution containing 30 μ M certain type of dye. Then we continuously monitored the time-dependent

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adsorption of dye by the UV-vis spectra of the solution. We examined the adsorption of two types of positively charged dyes, MB and R6G, as they have kinetic diameters of 7.0 Å and 13.0 Å, which is slightly smaller and bigger than the window size of HKUST-1, 8.5 Å, respectively.³⁹ The DN hydrogel matrix is able to adsorb dye, and their adsorption rate is dominated by the charge according to previous research. Thus, the R6G with a bigger molecule size than the window of HKUST-1 here served as a control to quantify the non-selective adsorption of the hydrogel matrix, and the MB shows the selective adsorption of HKUST-1.

Figure 1.13A, B shows the digital images and UV-vis spectra of the MB and R6G solution from the initial state to the end of the test. MB solution was dark blue before the test and became almost transparent after the 5 hours adsorption, while the R6G solution remains the same bright pink after the adsorption test. The UV-vis spectra show the trends more clearly, the absorbance of MB at its maximum adsorption wavelength (660 nm) drops from 2.1 to lower than 0.1 within 5 hours (**Figure 1.13C, D**). In contrast, the absorbance of R6G at its maximum adsorption wavelength (525 nm) only decrease from 2.2 to 1.5. We convent the absorbance to dye concentrations in solution by the preset baseline equations for each dye (see details in **Figure 1.12**), and further calculated the removal rates. The quantitative data are shown in **Figure 1.13E, F**, the MB concentration dropped from 30.4 μ M to 1.1 μ M with 96.3% of removal rate by the HKUST-1 hydrogel composite, while the R6G concentration dropped from 30.3 μ M to 20.2 μ M with a removal rate of 33.4%. The results suggest the HKUST-1 hydrogel has an extraordinary dye removal performance, without being compromised by embedded into the matrix. We significantly attribute this good performance to the hydrogel matrix's hierarchical porous structure, with the

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combination of easy accessibility through macropores, and capillary effect of mesopores, enable for fast water uptake and contact between the MOF micropores and the dyes.

To illustrate the selective adsorption of the dyes by HKUST-1, we further added an adsorption test for the mixture of MB and R6G solution. The mixture of the blue and pink dyes presents a dark purple color initially, and the mixture became pink after 5 hours adsorption (**Figure 1.14A**). The time-dependent UV-vis spectra in Figure shows this result more obviously, the peaks of MB almost disappeared after adsorption, but the peaks of R6G remain high. HKUST-1 exhibits a similar removal rate for the mixture dyes solution compare to the individual dye solutions (**Figure 1.14B**, **C**, **D**).

We further explored the influence of the amount of AAm in hydrogel matrix to the adsorption performance of the HKUST-1 hydrogel. The time-dependent adsorption results of HKUST-1 hydrogel with 0.9, 1.8, 3.6 M AAm (**Figure 1.15**)suggest the AAm concentration in the matrix doesn't impact the final removal rate, mean these hydrogels have very similar MOF loading rates. The time needed to reach the adsorption decreases with the increasing AAm concentration, we attribute this trend to the hydrophilicity of the composite increases with the increasing of hydrophilic AAm in the matrix, results in a faster water update from the dye solution.

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Figure 1.12. Baseline setup of dyes. UV-vis spectra of a series of dye solutions with different concentrations (A) MB and (C) R6G solution. Baseline equation polts for (B) MB and (D) R6G solutions.



Figure 1.13. Dyes adsorption performance of HKUST-1 hydrogels. Digital images of dyes solution before and after adsorption for (A) MB (B) R6G. Time-dependent UV-vis spectra of (C) MB and (D) R6G solution. Time-dependent (E) dye concentration and (F) dye removal rate of MB and R6G solutions.



Figure 1.14. Selective dyes adsorption performance of HKUST-1 hydrogels. (A) Digital images of dyes mixture solution before and after adsorption. (B) Time-dependent UV-vis spectra of MB and R6G mixture solution. Time-dependent (C) dye concentration and (D) dye removal rate of MB and R6G mixture solution.



Figure 1.15. Dyes adsorption performance of HKUST-1 hydrogels with different AAm concentration. Time-dependent (C) dye concentration and (D) dye removal rate of MB solution by HKUST-1 hydrogel with different AAm concentrations.



Figure 1.16. Images of 3D printed HKUST-1 samples with various shapes. (A) Dogbone, (B) Pyramid, (C) Gird scaffold at cured state and HKUST-1 grown state.

1.4 Conclusion

In conclusion, we have demonstrated a novel 3D printing fabrication method of a highly stretchable *in situ* grown MOF hydrogel composites. The pAAm/alginate DN hydrogel acts as a

3D printable porous matrix for the facile MOF in situ synthesis, the prepared prototypical HKUST-1 hydrogel exhibits excellent mechanical performance, it can be stretched up to 452% of its original length, with the highest 277.6 kPa strength, 152.3 kPa Modulus, 744.7 kJ/m-3 toughness, the mechanical properties are easily tunable by adjusting the fabrication parameters. 7.9 wt% MOF loading was reached in this study, the loading rate can be further improved by tailoring the concentration of ligands in the matrix. We highlight this method's ability to fabricate flexible MOF composite with complex shape (Figure 1.16) and preserve the performance of MOF by 3D printing, more detailed prints can be achieved by slightly modify this hydrogel formulation to an SLA or DLP printer with a higher resolution of few microns. The MOF functionality performance was demonstrated by water treatment experiments, the HKUST-1 hydrogel can remove about 97% MB contaminant from water, and presents a good selectivity to molecules with the size of MOF's micropores. This method provides a versatile platform for 3D printing of flexible MOF composites, various types of MOFs can be synthesis by changing the ligands and metal ions, application of these 3D printed flexible MOFs hydrogel may extend to novel wearable, implantable sensors, soft actuators, etc.

Chapter II. Dual-Gel 4D Printing of Bioinspired Tubes and Studies of Their Periodic Buckling

2.1 Introduction

The radial or bilateral distribution of chemicals during growth and morphogenesis is a widely observed feature in biology, seen in more than 99% of modern animals, and across diverse species ranging from humans to microorganisms.⁴² Tubular biological species and their functional components including nematodes, flowers, marine animals and elephant trunks also show symmetric and/or periodic arrangements of different material segments. The organisms exploit the swelling mismatch and mechanical instabilities inherent in these structures to enable complex shape change and motion. It is noteworthy that tubular shapes are essential in human engineering due to the need for bioimplants such as vascular grafts⁴³ and continuum robots.⁴⁴ Apart from static designs, controllable shape change in tubular shapes such as elongation, lumen expansion, and bending could facilitate smart or autonomous behaviors, but such features are challenging to incorporate especially in an unwired, external-power-free, and customizable manner.^{45,46}

Stimuli-responsive polymers offer significant opportunities for implementing a range of smart, adaptive and dynamic behaviors in response to temperature, light, electromagnetic fields, and chemicals.^{47–53} As one of the most widely used stimuli-responsive materials, thermally responsive poly N-isopropylacrylamide (pNIPAM) has been utilized to create a range of shape-changing structures including grippers,^{54,55} propellers,^{56,57} and actuators.^{58–60} When coupled with 3D printing, a high level of customization, tunability, and adaptability can be achieved.

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The 4D printing which introduces a new dimension of time^{61–67} has been previously utilized to create shape change devices.^{68–81} Besides the well-recognized advantage of easy programmability as a path-based additive manufacturing method, 3D printing also offers excellent potential in material integration and switching of dissimilar materials on demand (similar to weaving). Among the different types of 3D printing, direct ink writing (DIW) of gels has notable advantages over alternate 3D gel printing methods such as stereolithography including low-cost implementation and the ease of incorporating multiple gels at the same time.

Inspired by symmetrical and periodic tubular structures in biology and motivated by the need to create untethered, thermally responsive bioimplants and continuum robots, we explored the 4D printing of tubes with direct written alternating segmental patterns of an active thermoresponsive gel pNIPAM and a passive thermally non-responsive gel (polyacrylamide; pAAM). The essential challenge in our work was to elucidate, rationalize and validate design principles by which sequential arrangements of segments of high and low swelling stimuli-responsive gels could elicit dramatically different shape change of functional importance.

The similar acrylamide composition of the gels is essential to ensure interfacial adhesion in segmented designs. First, printable inks were made by blending monomers of these gels with a clay (Laponite) that alters the rheological characteristics of the gels and enables shear-thinning behaviors. Using finite element modeling and bioinspiration, we generated standard tessellation language (STL) to design tubes with different periodic vertical and horizontal arrangement of active and passive segments that could generate a diverse range of shape changes including uniaxial elongation, bending, radial expansion, and gripping. Further, inspired by coral polyps, we designed and printed tubes with self-folding fingers at one end, and these structures display more

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complex dual-function thermally responsive shape change involving both uniaxial expansions of the tube and finger gripping. We anticipate that this novel bio-inspired approach that utilizes just segmented placement of active and passive stimuli-responsive materials, when combined with finite element simulations and the versatility of customizable 3D printing designs offers the possibility of producing a range of multi-functional shape change structures with broad applicability.

2.2 Experiment Section

2.2.1 Materials and formulation of the active NIPAM and passive AAm pregel inks

Active NIPAM ink: Laponite XLG (Southern Clay Products) was first mixed with DI water using magnetic stirring, followed by a planetary mixer (Mazerustar KK-250S, Kurabo Industry Ltd.) 10 vol% of a 0.12 mg ml⁻¹ solution of Methacryloxyethyl thiocarbamoyl Rhodamine B (Polysciences, Inc.) was used as the dye for fluorescence imaging. The aqueous dye solution was added to the Laponite solution and mixed with the planetary mixer. Subsequently, N-Isopropylacrylamide (NIPAM, Scientific Polymer Products Inc.) monomer and Irgacure 2959 (BASF) as a UV photoinitiator was added to the Laponite-dye solution and mixed again using the planetary mixer. The final concentrations (by weight) of each component in the active NIPAM ink were as follows: 84.6% DI water, 8.46% NIPAM, 6.77% Laponite, 0.17% Irgacure, 0.001% Should be Methacryloxyethyl thiocarbamoyl Rhodamine B.

Passive AAM ink: Laponite solution was prepared the same way as the active ink. 10 vol% of a 0.3 mg ml⁻¹ solution of Fluorescein o-methacrylate (97%, Sigma-Aldrich) was used as the dye for the passive ink. The dye solution also contained 2 mg ml⁻¹ NaOH (Fisher Scientific) since the dye

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monomer is dissolvable in base conditions, and was mixed by magnetic stirring. Subsequently, acrylamide (AAM, Sigma-Aldrich) monomer, Irgacure 2959 and N,N'-methylenebisacrylamide (BIS, Sigma-Aldrich; BIS functions as a crosslinker) was added to the Laponite-dye solution and mixed using the planetary mixer. The final concentrations (by weight) of each component in the passive ink were: 82.97% DI water, 7.88% AAM, 6.64% Laponite, 0.83% Irgacure, 1.66% BIS, 0.0025% Fluorescein o-methacrylate, 0.017% NaOH.

2.2.2 3D printing of NIPAM and AAm dual-hydrogel structures

The NIPAM and AAM inks were loaded into syringes, transferred to UV-shield cartridges and centrifuged to remove any bubbles present in the cartridges. The inks were kept at room temperature for at least 24 hrs to allow thorough hydration needed to achieve the desired shear thinning properties. The cartridges were then attached to the Direct Ink Writing 3D Printer (Inkredible+ 3D Bioprinter, Cellink) and connected to an air pump pressure control. We chose nozzles 22G (diameter 0.41 mm) which ensures smooth and clog-free printing.

All the computer-aided-design (CAD) and STL files were generated in Solidworks (Dassault Systèmes). Then, the G-code for each design was generated using the software Slic3r (layer height 0.4 mm, printing speed 10 mm s⁻¹). Before printing the final designs, we printed test structures to calibrate the two printing nozzles so that they were perfectly aligned with each other. The structures were printed on silicon wafers at room temperature in air. The printing pressures were optimized for each ink to ensure smooth printing at a speed of 10 mm s⁻¹. The pressures used for printing active and passive inks were 90-100 kPa and 110-130 kPa respectively.

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2.2.3 UV photo-curing

After 3D printing, we photocured the structures using an Omnicure UV source (LX 500, Lumen Dynamics). We designed a rotating platform that rotates slowly at 9.6 rpm to enable relatively uniform exposure of UV light and consequently uniform curing of gel tubes (see details in Note S1). Two UV LED heads with 365 nm wavelength were used to cure the tubular structures, and we used a lens of diameter 12mm for each UV LED head and a resulting intensity of 0.4 W/cm² at a distance of 3 cm. We cured the tubular structures with 100% power and section by section depending on the structural height. Each section was cured for 9 mins using two UV LED heads at the same time.

2.2.4 Rheological characterization of pregel inks

The rheology of the inks was measured using a rheometer (Modular Compact Rheometer MCR 302, Anton Paar, Austria) with a 1° cone-plate geometry. The temperature of the plate was kept at 23°C. Ink viscosities were measured via a logarithmic sweep of shear rates ranging from 0.01 s^{-1} to 1000 s⁻¹. Oscillatory experiments were performed at a constant frequency of 1 Hz.

2.2.5 Mechanical test of the printed 3D printed and photocured hydrogels

Active and passive hydrogel square plates with a side length of 10 mm and a thickness of 2 mm were 3D printed and UV cured using the methods described above. After curing, the hydrogel samples were kept in DI water at room temperature for 24 hours so that they could reach their equilibrium swollen state. We used DMA (Dynamic Mechanical Analyzer Q800, TA Instruments) to conduct unconfined compression tests on the samples in air. Three samples were tested for each hydrogel and the engineering stress-strain curves were calculated (Figure S3). Young's moduli of

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the active and passive hydrogels were calculated from the slopes of the engineering stressengineering strain curves.

2.2.6 Macro-Imaging and images analysis

All optical images were taken with a digital camera (Canon EOS 70D) and a broad spectrum UV light source (Spectroline Model EF-160C, Spectronics Corporation, USA) to excite the fluorescent dyes in the inks. The images of photocured tubes were taken at room temperature in the air after UV curing. Then, the structures were placed in DI water and put into an incubator (MODEL 1575, Sheldon Manufacturing, INC., USA) set at the desired temperatures for 24 hours to reach the equilibrium swollen state at each temperature. The photographs of transformed structures were taken in DI water.

2.3 Results and Discussion

2.3.1 Development of active and passive hydrogel inks and 3D printing of homogeneous tubes

To be 3D printed via Direct Ink Writing (DIW), a material must display unique rheological or shear thinning characteristics.^{82,83} Hence, the first step was to create thermoresponsive and non-thermoresponsive NIPAM and AAM inks for DIW. pNIPAM has a lower critical solution temperature (LCST) above which it transforms from a hydrophilic to hydrophobic state and expels water with a significant reduction in volume.⁸⁴ pAAM lacks the critical isopropyl group and shows no LCST.

Both NIPAM and AAM have previously been printed using stereolithography⁶⁵ and nozzle-based approaches.^{61,62,64,66} We blended the monomer NIPAM with different shear-thinning agents

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including Xanthan Gum, Gellan Gum, and Laponite nanoclay. All of the three agents showed shear-thinning properties (the rheology measurements of our NIPAM inks are shown in Figure S1) and could be printed by direct ink writing. We attribute this observation to dissociation of the ink network under applied shear stress. Consequently, the ink could be extruded out of the printing nozzle, and when the shear stress was removed after printing the network reassembled and the extruded ink retained its shape.⁸²

We observed, however, that the Laponite-blended ink had a higher storage modulus than the other two inks (modulus measurements for NIPAM inks are shown in Figure S1(B)), and could be used to print taller structures. The AAM-blended inks showed similar rheological and modulus trends. Therefore, we chose Laponite as the shear-thinning agent for both our active NIPAM and passive AAM inks. Also, a free radical curing agent Irgacure was added to both inks to facilitate photocuring with ultraviolet (UV) light. It has been previously reported, and we confirmed, that the Laponite-NIPAM-Irgacure mixture was photocrosslinkable and retained its shape in the water.^{85,86} However, it was necessary to add a crosslinker, N,N'-methylenebis(acrylamide) (BIS) to the AAM inks, so that they did not dissolve in water after printing and curing (**Figure 2.2**).

Printing dual-material 3D structures present unique challenges even with the two-nozzle printer used in our experiments. Briefly, we developed a calibration methodology to reduce misalignment between nozzles during the approximately 50-100 print layers required for our structures. We also designed a rotary photocuring stage to ensure homogeneous crosslinking of the pNIPAM and pAAM gels. After printing and photocuring in air, the structures were soaked in deionized (DI) water which induced swelling and release from the substrate. The conceptual schematic of the 4D Printing process is shown in **Figure 2.1A**.

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Figure 2.1. Schematics of the 4D Printing process and experimental characterization of the swelling of printed active and passive hydrogel tubes. (A) Schematic showing the microstructure of the active NIPAM and passive AAM inks and different steps in the process including the formulation of the inks, 3D direct ink writing, and photocuring. (B) A plot showing the experimentally measured normalized diameter change ($\Delta D/D0$) in the water at different temperatures between 25 °C and 50 °C for 3D printed and photocured tubes composed of pNIPAM and pAAM. D0 is the diameter of the 3D printed and photocured tube in air. Bars indicate standard

deviation with a sample size of three and data at each temperature was taken at equilibrium after 24 hours. Inset shows several snapshots of the pNIPAM (yellow) and pAAM (green) tubes recorded at different temperatures. Scale bars indicate 1 cm.



Figure 2.2. Schematic representation of the molecular and microstructure of the inks. (A) active NIPAM ink and (B) passive AAM ink.

2.3.2 Mechanical properties and temperature-responsive behavior

We first verified the swelling of the active pNIPAM, and non swelling of the passive pAAM by measuring the diameter change of homogeneously printed single component pNIPAM and pAAM tubes by placing them in DI water at different temperatures (25°C, 33°C, 41°C, and 50°C) where they were allowed to reach an equilibrium shape over 24 hours (**Figure 2.1B**). We observed dramatic increases (38%) and decreases in the diameter ($\Delta D/D_0$) of the pNIPAM tubes on cooling and heating, respectively, while there was no significant change (1.2%) in the diameter of pAAM tubes. This swelling behavior agrees with prior swelling data from photolithographically patterned pNIPAM and pAAM gels.^{50,87} Consequently, we consider the pNIPAM portion of the structure to

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be the active gel that drives shape change by swelling or deswelling, while the pAAM portion is largely passive.

We measured Young's moduli of 3D printed and photocured pNIPAM and pAAM square plates using a Dynamic Mechanical Analyzer and found them to be 2.53 kPa and 60.3 kPa respectively (Figure 2.3). Using these modulus values and measured volumetric swelling from the completely dry to the equilibrium swollen state at room temperature, the Flory-Huggins interaction parameter was obtained by fitting the swelling of homogeneous pNIPAM and pAAM tubes obtained from the model to that measured in the experiments (Figure 2.1B). We applied these parameters to the finite element model for predicting the complex shape transformation of the dual-gel tubes.



Figure 2.3. Results of stress-strain measurements of 3D printed and photocured pNIPAM and pAAM hydrogels. Elastic moduli measurements were obtained for fully hydrated hydrogel square plates to determine the stiffness of the active and passive hydrogels used in this study. (A) The elastic modulus of the pNIPAM gel sample was measured using unconfined compression test at room temperature (DMA Q800; TA instruments) with a maximum applied static force of 6 mN at a rate of 1 mN min⁻¹. (**B**) The elastic modulus of the pAAM gel sample was measured using the unconfined compression test at room temperature with a maximum applied strain of 5% at a rate of 0.1% s⁻¹. Static force and displacement data of the compression test were used to generate engineering stress and engineering strain curves. The elastic modulus was measured as the slope of the best-fit line to the stress-strain curves.

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2.2.3 4D printing of symmetrically patterned tubes

Applying the FEA model and experiments, we explored the rational design of shape change gel tubes by the symmetric placement of horizontal (**Figure 2.4**) or vertical (**Figure 2.7**) segments of active pNIPAM gels interspaced with passive pAAM gels. After 3D printing and photocuring, the structures were soaked in DI water at 25°C, 35°C, and 50°C for 24 hours to reach the equilibrium state. Bilaterally symmetric tubes with equally spaced, alternating cylindrical-disk-shaped segments of pNIPAM (three segments), and pAAM (four segments) showed elongation as high as 32%, with good agreement between FEA simulations and experiments (**Figure 2.4A-B** and **Figure 2.5**). As compared with homogeneous tubes of pNIPAM that elongate by approximately the same extent (38%, **Figure 2.1B**), the introduction of passive segments constrained radial expansion of the tube, so that its predominant shape change was uniaxial elongation.

When the same number of alternating pNIPAM and pAAM segments were placed at angles with respect to each other (**Figure 2.4C-D** and **Figure 2.6**), like cylindrical wedges, the tube bent by approximately 25°. The bending angle decreased as we increased temperature, and at 50°C, it reversed to the photocured state ($\theta = 0^\circ$), in agreement with simulation snapshots.

We next printed tubes with twelve alternating vertical segments of pNIPAM and of pAAM (six of each), on top of a constraining ring of pAAM. The tubes expanded radially by 75% but did not elongate. Constrained by the non-swelling strips of pAAM, the tube buckled and folded downwards to accommodate the elongation of the pNIPAM strips by swelling (**Figure 2.7A-B** and **Figure 2.8A**). The tubes recovered their original shape when we increased the temperature to 50°C.

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Figure 2.4. Bilaterally symmetric tubes with horizontal, periodically-spaced segments. (A- B) Results showing thermoresponsive uniaxial elongation of tubes with alternating cylindrical discs of active pNIPAM (red) and passive pAAM (green) segments. (A) Optical and FEA snapshots of shape change of tubes at different temperatures. H indicates the height of the tube which is plotted against temperature in panel (B). (C-D) Results showing thermoresponsive bending of tubes with alternating cylindrical wedge-shaped segments of active pNIPAM (red) and passive pAAM (green) segments. (C) Optical and FEA snapshots of shape change of tube at different temperatures. θ indicates the bending angle of the tube which is plotted against temperature in panel (D). The experimental snapshots of all tubes were obtained after soaking them in the water at the desired temperature and allowed to equilibrate over 24 hours. The simulation snapshots and plots are in agreement with the experiments. All Scale bars are 1 cm.



Figure 2.5. Shape change snapshots of the uniaxial elongation tube with different aspect ratios. h_{pNIPAM} and h_{pAAM} represent the height of the active and passive rings respectively. Increasing the aspect ratio from 1 (bottom) to 3 (top) resulted in an increase of elongation () from 15.5% to 32.4%. Scale bars are 1 cm.



t = 0 hr

t = 6 hr

Figure 2.6. Time-lapse shape change snapshots of the bending tube in DI water at room temperature. Scale bars are 1 cm.

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We also designed tubes with wedge-shaped alternating pNIPAM and pAAM vertical segments and overhanging pNIPAM 'fingers' constrained by pAAM edges. The pNIPAM 'fingers' are more constrained at their bottoms than at their tops. As a result, the 'fingers' bent by approximately, ω = 35° when the pNIPAM gel swelled at 25°C (**Figure 2.7C-D**, **Figure 2.8**).



Figure 2.7 Radially symmetric tubes with vertical, periodically-spaced segments. (A- B) Results showing thermoresponsive radial expansion of tubes with alternating vertical segments of active pNIPAM (red) and passive pAAM (green) segments. (A) Optical and FEA snapshots of shape change of tubes at different temperatures. D indicates the diameter of the tube at the point of maximal expansion which is plotted against temperature in panel (B). (C - D) Results showing thermoresponsive folding of fingers on tubes with vertical segments of active pNIPAM (red) and passive pAAM (green) segments. (C) Optical and FEA snapshots of shape change of the tube at different temperatures. ω indicates the folding angle of the fingers which is plotted against temperature in panel (D). The experimental snapshots of all tubes were obtained after soaking them in water at the desired temperature and allowed to equilibrate over 24 hours. The simulation snapshots and plots are in agreement with the experiments. All Scale bars are 1 cm.

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Figure 2.8. Time-lapse shape change snapshots of the (A) radial expansion tube, and (B) the gripper in DI water at room temperature. Scale bars are 1 cm.

2.3.4 3D Printed Dual Shape-Change Tubes

Advanced biomedical or soft robotics applications often require a library of parts that may transform in shape. Nature is replete with such complex shape change organisms. For example, the coral polyp is an aquatic animal with a cylindrical vase-shaped body with radially distributed tentacles capable of capturing prey (**Figure 4A**).⁸⁸ Our design, simulation, and the 3D printing approach is amenable to the creation of more such complex shape-change devices. Inspired by the coral polyp, we designed dual shape-change tubes, composed of a uniaxial elongation tubular base (**Figure 2A**) and a bending three-finger gripper module (**Figure 3C**). A 3D printed passive ring at

the bottom of the base served as a handle (Figure 4B-C). After 3D printing and photocuring, the This chapter has been adapted from 'Dual gel 4D printing of Bioinspired Tubes' J. Liu, O. Erol, A. Pantula, W. Liu, Z. Jiang, K. Kobayashi, D. Chatterjee, N. Hibino, L. H. Romer, S. H. Kang, D. H. Gracias, ACS Applied Materials and Interfaces (2019). and 'Periodic Buckling of Soft 3D Printed Bioinspired Tubes' J. Liu, W. Liu, A. Pantula, Z. Wang, D. H. Gracias, T. D. Nugyen, Extreme Mechanics Letters (2019)

structure was suspended in the air on top of a cuboidal object placed at the bottom of the tank (**Figure 4D**). When the tank was filled with water at 25°C, the polyp-inspired tube showed two shape change events by simultaneously elongating and bending its fingers to grab onto the cube (**Figure 4E**). It is noteworthy that the fingers were able to firmly grasp the cube so that it could be lifted off of the bottom of the tank (**Figure 4F**). Upon heating to 50°C, the fingers opened up, the base contracted and the part was released (**Figure 4G**).



Figure 2.9. Dual-shape change tubes. (A) Schematic of the basic anatomy of the coral polyp; the image was created based on encyclopedic depictions of the polyp.⁴⁷ (**B-C**) CAD model and image of a 3D printed and the photocured tube with a cylindrical base and three fingers. (**D-G**) Optical snapshots of shape change of the tube at different temperatures. The tube was suspended over a part placed in a tank. When water was added to the tank, the tube shows uniaxial elongation and gripping of the part. Upon heating to 50°C, the tube shortened and the fingers opened to release the part back to the bottom of the tank. Scale bars are 1 cm.

2.3.5 Periodic buckling of soft 3D printed bioinspired tubes

We further designed stimuli-responsive periodic buckling tubes composed of alternating soft active segments and stiff passive segments. We investigated the buckling modes of the tube using a combination of theoretical and finite element modeling and verified the buckling modes with 4D printing experiments. The model included six dimensionless design parameters that describe the geometry and material properties of the active and passive segments. From the simulations, we observed that the number of half-sine waves at buckling varied with three design parameters individually: slenderness ratio B/L, diameter ratio B/A, and modulus ratio Ep/Ea. The other three design parameters, segment width ratio Wp/Wa, number of alternating segments B/(Wp+Wa), and volumetric swelling ratio $\Delta\theta$, did not affect the buckling modes. Approximating the buckled segment as the buckling of a bar on an elastic foundation, we developed a universal design parameter, W_{tube}, that combines the effects of geometry dimensions, modulus, and swelling ratio, and constructed a phase diagram of the periodic buckling modes of the tubes, that was validated by experiments.

The modeling outcomes were validated by 3D printing three selected cases from the parameter study and performing the swelling experiments in DI water at the room temperature (**Fig. 2.10**). The three cases were: B/L = 0.5, B/A = 1.04, and Ep/Ea= 5 (**Fig. 2.10a**); B/L= 0.33, BA= 1.1, and Ep/Ea = 5 (**Fig. 2.10b**); and B/L= 0.25, B/A = 1.1, and Ep/Ea= 5 (**Fig. 2.10c**). The printed tubes were immersed in DI water for 24 hours and the deformed configuration showed the same buckling mode with the same number m of half-sine waves as predicted by the FEA simulations and the critical buckling coefficient W_{tube} . The experiment was repeated 2-3 times for each case with the same result.



Figure 2.10. Images from the photocured and the actuated tubes exhibiting different periodic buckling modes along with simulation snapshots. Tubes with different design parameters were printed: (a) B/L = 0.5, B/A = 1.04, and Ep/Ea = 5; (b) B/L = 0.33, B/A = 1.1, and Ep/Ea = 5; and (c) B/L = 0.25, B/A = 1.1, and Ep/Ea = 5. In the experimental pictures, the active pNIPAM and passive pAAM hydrogels show fluorescent orange and green colors, and the scale bar indicates 1 cm. In the simulation snapshots, the contour plots of the volumetric swelling ratio q of the hydrogel are shown for the deformed equilibrium configuration at 25 °C.

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2.4 Conclusion

We utilized bioinspired principles of symmetric arrangements of high-swelling and low-swelling gels in tubular geometries to achieve uniaxial elongation, radial expansion, bending, and gripping. The use of symmetry combined with numerical modeling enables the rational design of shapechanging primitives and their combinations to produce significantly complex motions of practical importance. We designed a dual-function tube capable of simultaneous elongation and gripping; this polyp inspired tube can reach into a tank and grab an object. We incorporated advanced multimaterial integration in the direct ink writing process to achieve interweaving of active and passive materials with a 3D structure and with a high spatial resolution of approximately 400 microns. Additive manufacturing with multi-material integration permits direct printing of the assembly shape-changing primitives and potentially of functional grading. It is conceivable that this approach could be extended to the 4D printing of more complicated assemblies, including those with soft and rigid segments⁸⁹ or those with multiple temperature-responsive gels⁹⁰ to enable sequential motions for more complicated tasks. For example, shape change tubular constructs which elongate, bend or increase in size are important for pediatric tissue and vascular implants to accommodate and adjust to the effects of the growth of the surrounding tissues^{91,92}. Alternatively, tubes that elongate and grip are important for soft-robotic endoscopic applications⁹³. We further explored the design parameter provides an efficient rule for the design of self-morphing tubes that can expand radially with a negligible axial elongation that have potential applications to deployable and morphing biomedical implantable devices and actuators for soft robotics. The combined theoretical and computational approach represents a powerful framework to develop analytical design parameters for tailoring buckling instabilities of active hydrogel structures. Coupling our methodology to materials that respond to alternative stimuli such as biochemicals,⁵⁰

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light,⁹⁴ or magnetic fields^{79,95} would further enhance their programmability and complexity to realize multistage, goal-oriented control of broad relevance to soft-robotics and biomedical engineering.

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Curriculum Vitae

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Education

M.Sc. in Chemical and Biomolecular Engineering
Johns Hopkins University (GPA: 3.80)
B.Eng. in Chemical Processing Engineering of Forest Products
Beijing Forestry University

Research Experience

Gracias Laboratory, Johns Hopkins University

Baltimore, MD, US 09/2017 - Present

07/2016 - 06/2017

2017 - 2019

2013 - 2017

Beijing, China

Baltimore, MD, US

Research Assistant (Advisor: Prof. David Gracias)

• Work in a multidisciplinary team including chemical, mechanical engineering researchers, and clinicians for projects focusing on 3D printing functional photopolymer materials for soft robotics and biomedical application.

•Develop an Alginate-Acrylamide based Interpenetrating polymer network printable hydrogel with in-situ grown Metal-Organic Frameworks (MOFs) for biomedical engineering.

• Formulated Laponite based thermo-responsive UV curable hydrogel ink for 4D printing shape-changing soft robotics.

• Tested rheology properties of prepared inks, optimized the printing and curing conditions for developed inks.

• Characterized the chemical, physical and mechanical properties of printed gels via tensile tester, DMA, FTIR, SEM,

XRD, etc., studied the actuating motion of printed soft robotics by fluorescent imaging and image processing.

• Designed and modeled printing structures by CAD software, processed G-code for complex structures.

MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy Beijing, China

Research Assistant (Advisor: Prof. Jiandu Lei, Assoc. Prof. Luying Wang)

• Fabricated sustainable biomaterial-based nanofiltration (NF) membrane for water softening via layer-by-layer polyelectrolytes self-assembly from underdeveloped industrial lignin waste.

• Developed MOFs-polymer composite membrane with ZIF-8 core-shell microspheres (SMM) in PPSU mixed matrix for solvent-resistant NF; Synthesized a novel ZIF-67@SMM adsorbent for removing pollutants in wastewater.

• Tested the separation performance of prepared NF membranes and adsorbent by conductivity meter and UV-vis.

• Studied the properties of prepared composites by SEM, AFM, XRD, FTIR, Zeta-potential Analyzer, etc.

Biopharmaceutical and Fine Chemical Engineering Laboratory, Beijing Forestry University Beijing, China *Leader of College Students Innovation and Entrepreneurship Program (National Grant Awarded)* 03/2015 - 06/2017 •Led a team of undergraduate students to study the subcritical water extraction (SWE) methods for extracting anticancer and antioxidant drugs from plant materials.

• Extracted drugs and oils from multiple plants via SWE with varied extraction parameters, purified extractions by GPC, analyzed the yielding of drugs by HPLC, GC, GC-MS, UV-vis.

• Collected and modeled yielding data under different conditions, optimized the parameters by response surface methodology modeling. Examined the extracted drugs antioxidant performance by ABTS radical cation.

•Worked with a Ph.D. to develop a carboxymethylcellulose based biodegradable nanoparticle for anticancer drugs delivery

Publications

Journal Publications (# indicates equal contribution)

- 1. W. Liu, J. Dai, J. Lei, L. Wang, (2019). "Facile fabrication of novel positively charged ligninsulfonates-based ultra-thin composite film membranes for water treatment by nanofiltration," (under review in *Green Chemistry*)
- **2.** W. Liu, Q. Qi, X. Hu, J. Liu, J. Lei, (2019). "Extraction of polysaccharide from Dendrobium nobile Lindl. by subcritical water extraction," *Journal of Integrative Agriculture*
- **3.** J. Liu, **W. Liu**, A. Pantula, Z. Wang, D. Gracias, V. Nguyen, (2019) "Periodic Buckling of Soft 3D Printed Bioinspired Tubes", *Extreme Mechanics Letters*
- **4.** O. Erol., A. Pantula[#], **W. Liu[#]**, D. Gracias, (2019). "Transformer Hydrogels: A Review", *Advanced Materials Technologies*
- 5. J. Liu, O. Erol, A. Pantula, W. Liu, Z. Jiang, K. Kobayashi, D. Chatterjee, N. Hibino, L. H. Romer, S. H. Kang, D. Gracias, (2019). "Dual-gel 4D Printing of Bioinspired Tubes," *ACS Applied Materials & Interfaces*

Patents

- 1. Preparation method of polyethylene imine/sodium lignin sulfonate composite membrane, CN107261871A
- 2. Preparation method of supportive electrolyte optimization-based layer-by-layer self-assembled composite nanofiltration membrane, CN107252637A
- 3. Method for simultaneously extracting ursolic acid and oleanolic acid in hawthorn by means of subcritical water, CN105232679A
- 4. Method for extracting Triptolide from Tripterygium wilfordii by subcritical water extraction, CN104861081A
- 5. Method for extracting Ursolic Acid and oleanolic acid from *Hawthorn* by subcritical water extraction, CN105198956A

Skills

• Characterization and Fabrication: FT-IR, SEM, TEM, AFM, NMR, GC, GC-MS, HPLC, UV-Vis, XRD, TGA, DSC, DMA, Rheometer, Tensile tester, Electrokinetic Analyzer, 3D Printing, Photolithography, Mask Aligner

- Design, Modeling and Analysis Tools: AutoCAD, SolidWorks, Solid Edge, Matlab, R, MS Office, OriginLab
- Photography, Video Postproduction: Experienced in DSLR, Adobe Premiere, After Effects and Photoshop
- Language: Chinese, English, Japanese

Awards and Honors

- Second-year Master of Science in Engineering Scholarship Johns Hopkins University, 2018
- Best Biotechnology Poster American Institute of Chemical Engineers (AIChE), 2018
- Excellent Dissertation of Bachelor's Degree Beijing Forestry University, 2017
- Gold Medal Patent Beijing Association for Science and Technology, 2015
- National Grant for College Students Innovation and Entrepreneurship Program Ministry of Education, 2015
- First-class Academic Scholarship Beijing Forestry University, 2014
- Outstanding Student Cadre Beijing Forestry University, 2014