

# Design, Fabrication, and Application of Stimuli-Responsive Hydrogel Actuators

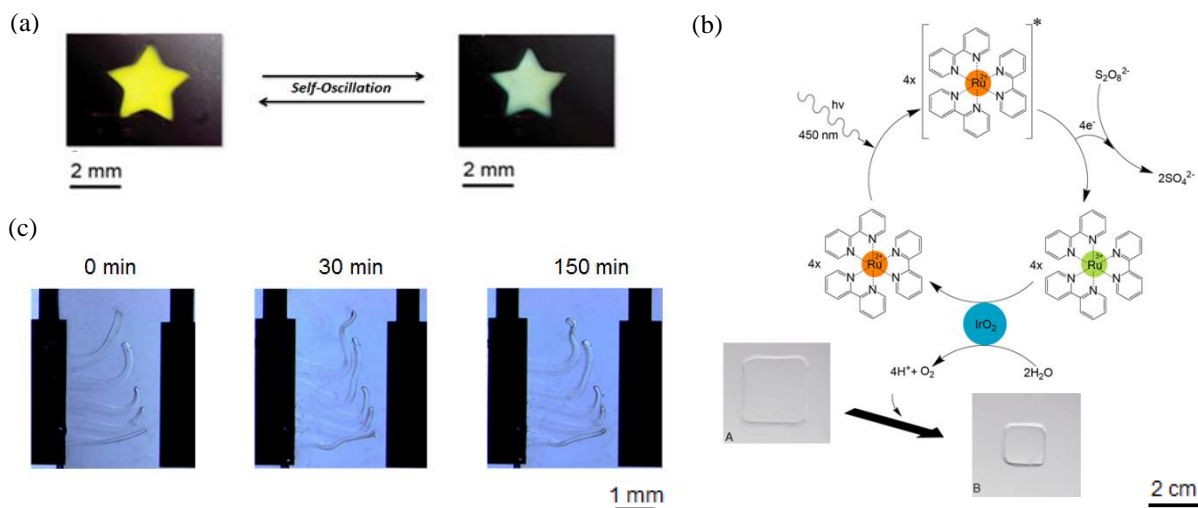
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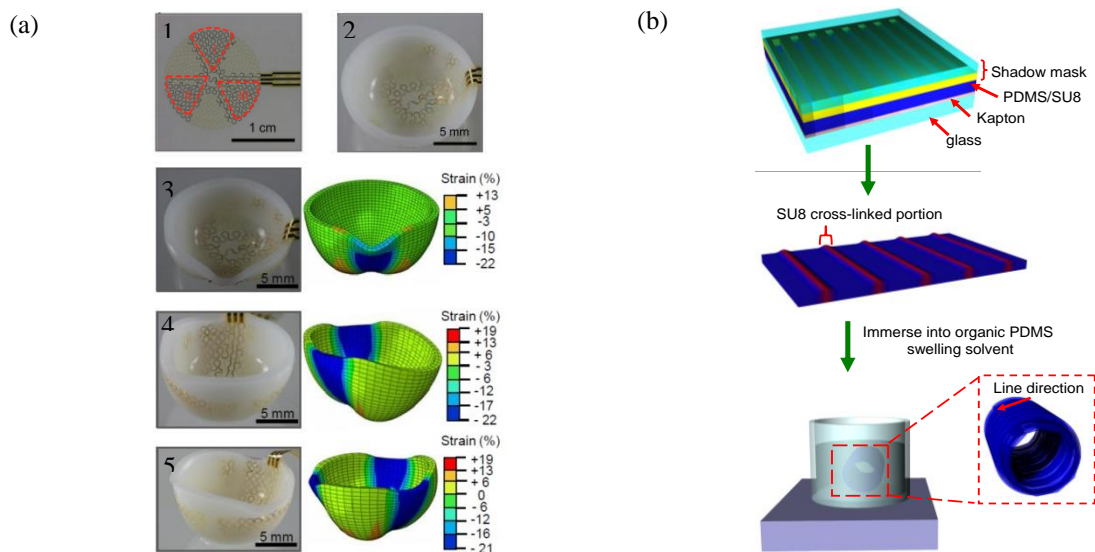
In this thesis, the topics around hydrogel based stimuli-responsive actuators were discussed. In each project, a specially designed stimuli-responsive hydrogel was fabricated. By initiating a corresponding stimuli, swell-deswell changes will be triggered within the hydrogels, and certain mechanical movements can be created by manipulating the patterns and structures of the hydrogels. Stimuli-responsive hydrogels often exhibit sharp volume phase transitions triggered by specific chemical or physical stimuli. Volume phase transitions has been vastly studied due to its potential in triggering the functions of movements, such as deformation<sup>1</sup>, volume change<sup>2</sup>, modulus change<sup>3</sup>, force generation<sup>4</sup> etc., are similar to biological systems in the nature. And there are numerous methods to trigger these responses, such as pH value<sup>5</sup>, electric field<sup>6</sup>, ion concentration<sup>7</sup>, chemical or biological reagents<sup>8</sup> etc. Based on the capability of chemo-mechanical energy conversion, stimuli-responsive polymers have a broad range of applications, ranging from mechanical actuators<sup>9</sup>, soft robotics<sup>1</sup>. We aimed at the designs and applications biomimetic actuators and soft robotics. Among the five projects will be discussed in this thesis, the first three systems are chemically initiated stimuli responsive actuators (chemomechanical actuators); the other two systems are non-chemically initiated.

In the chemomechanical systems, we explored relationships between different chemical systems and hydrogels, as well as the conversion of chemical energy into mechanical movements in a biomimetic fashion.



**Figure 1:** (a) Swell-deswell of a PAAM based self-oscilating gel. The yellow gel is PAAM at reduced state (swollen), the green gel is PAAM at oxidized state (unswollen) (b) Illustration of water-splitting reaction and its proton release caused deswell of PAA gel. Insert figure A is the PAA at pH=9, figure B is the PAA after exposed under water-splitting reaction. (c) PAA's responses to ORR. The pictures represent the PAA gel at initial state (0 min), elongated state (apply 30 mins of ORR), restored state (ceased ORR for another 120 mins).

Firstly, we described a new planar processing chemistry that allows the synthesis and patterning of dynamically self-actuating gels of diverse form. The chemical reaction covalently incorporates a methacrylate-modified ruthenium trisbipyridine ( $\text{Ru}(\text{bpy})_3^{2+}$ ) monomer within a poly acrylamide (PAAm) gel, modified to provide a flexible chemistry for UV-curable, self-oscillating Belousov-Zhabotinsky (BZ) gels. PAAm has been reportedly utilized as a backbone for self-oscillating B-Z gels<sup>10</sup>. For this system, sample size decreases upon the catalyst oxidation; they attributed these effects to the formation of additional reversible physical crosslinks, which were broken when the catalyst was in the reduced state. (Fig. 1a) Then, inspired by the photosensitizing capability of ( $\text{Ru}(\text{bpy})_3^{2+}$ ) from the first project, we successfully achieved using visible light to trigger macroscopic movements of polyacrylic acid (PAA) (Figure 1b) based pH sensitive hydrogels through photo catalytic water-splitting reaction system, which contains  $\text{Ru}(\text{bpy})_3^{2+}$  as photosensitizer and iridium dioxide ( $\text{IrO}_2$ ) nanoparticles as catalyst. As a pH sensitive hydrogel, PAA protonation and de-protonation could create a difference in concentration of mobile ions in the hydrogel interior relative to external solution (osmotic pressure) drives the volume change, with consistent theoretical predictions of experimental results<sup>11</sup>. (Fig. 1b) Thirdly, inspired by the pH sensitive materials PAA from the second project, we achieved electrochemistry-induced micro and macro scaled chemomechanical hydrogel actuators. The actuation from pH sensitive polyacrylic acid (PAA) hydrogel have been achieved through the electrochemically induced oxygen reduction reaction (ORR), during which protons are produced at the anode yet consumed at the cathode, forming a pH gradient between the two electrodes. (Fig. 1c)



**Figure 2:** (a-1) Optical image of a fan-shaped heater mesh, with separately addressable segments, marked I, II, and III. (a-2) Image of a hydrogel in the shape of a hemispherical shell with an embedded fan-shaped heater mesh. (a-3,4,5) Optical images and computational simulations of programmed shapes induced by activating one, two, and three heaters, respectively. (b) Schematic depiction of the light programming step and folding process.

Among the non-chemical triggered actuator systems, by adapting the fast-responsive and vast volume change of the hydrogel due to thermal change or solubility change, we aimed to explore the hierarchical programmability of matters through strain in a 3D fashion. In the fourth

project, we show the controlled nonuniform swelling and de-swelling of one 3D hydrogel based on integrating electronic meshes, utilized as local heating agent, into thermal responsive poly N-isopropyl acrylamide (PNIPAAm). Such hydrogel yields from embedding electronic meshes with functionalities and controlling abilities to locally program the shape of the hydrogel (Fig. 2a). In the last project, we used light to “program” the folding mechanics of a flat, two-dimensional material. Mixtures of polydimethylsiloxane (PDMS) and SU-8 photoresist are exposed to different photomasks, creating a disparity in cross-linked SU-8 density between the exposed and unexposed portions. Upon immersion in nonpolar organic solvent, strain gradients are formed into the folding configuration, due to the swelling difference of PDMS and SU-8. The photomasks in the fabrication process can be varied to tailor the strain and direct folding into different 3D configurations upon immersion into nonpolar solvent. By changing the exposure pattern, different folding configurations can be generated from the same two-dimensional precursor. (Fig. 2b).

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