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Multifunctional actuation systems responding to chemical gradients†

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The ability to manipulate the movement of surface microstructures is essential for the development of dynamic, responsive materials. We demonstrate that in addition to bulk actuation upon drying, a unique type of highly localized, directional actuation can be achieved when microstructures embedded in pH responsive gel are exposed to pH gradients. Theory and modelling elucidates the underlying mechanism behind this novel approach to inducing responsive actuation.

Control over the dynamic movement of nano/microstructures is fundamentally important for actuators and sensors, tunable optics, micromanipulation, and the design of “smart” responsive surfaces.^{1,2} Programming the location of response, the direction of movement, and the extent of structural reconfiguration on the microscale are all important characteristics of tunable, dynamic materials. Natural systems have mastered the ability to use chemical cues, often applied not as a uniform stimulus but in the form of chemical or electrochemical gradients, to direct the motion of structures from the nanoscale up. For example, the beating of flagella is driven by proton motive force,³ and the direction of movement of bacteria can be guided by chemotaxis.⁴ The ability of a system to respond to a gradient chemical stimulus rather than a homogeneous environment is accompanied by an inherent directionality, allowing for the chemical stimulus to trigger not only the location of response but also the direction of movement along the gradient.

Although the versatility, tunability, and controllability of artificial responsive actuators would benefit from such directional sensitivity, few systems take advantage of chemical gradients or interfaces to direct the actuation of materials. For instance, chemical gradients have been used to generate the oriented movement of metallic nanorods, similar in concept to chemotaxis.⁵ Recently, there has been significant interest in responsive polymers, such as hydrogels, for chemo-responsive actuators due to their reversible and highly tunable volume change as well as sensitivity to a wide range of stimuli including humidity, temperature, pH, light, and redox state.^{6,7}

Although typically such hydrogels are used and studied in regards to their response to a homogeneous stimulus (*i.e.* the polymer network is either swollen or contracted in a certain state), introducing localized stimuli or gradients of stimuli across a gel can be advantageous for a number of purposes. Cargo transport, for example, was accomplished using gels that swell and shrink in response to oscillations of the Belousov–Zhabotinsky reaction, transporting particles along with the moving interface between swollen and contracted gel regions.⁸ Further exploration of how chemical interfaces and gradients can be used to manipulate hydrogels and induce reversible system directionality is therefore of fundamental interest.

Combination of a chemically responsive material, such as hydrogel, with structures, which can be reconfigured and provide the composite system with unique structural properties, is a powerful concept that we have recently been exploring through the use of hydrogels as a “muscle” to dynamically actuate gel-embedded high-aspect-ratio microstructures.⁹ Patterned gel thickness¹⁰ and asymmetry in the structure geometry itself¹¹ offer some control over the bending direction of structures within such systems. However, in hybrid systems previously reported^{10–14} the structural actuation responds to homogenous stimuli, and the cycling of gel expansion and contraction results in uniform, large-area actuation between pre-programmed configurations inherent to the physical makeup of the surface. To expand the versatility and generate a system that is responsive to a far greater range of stimuli scenarios, both in terms of spatial and directional variations, we aimed to use gradient chemical signals to trigger actuation between numerous configurations. Here, we develop a multifunctional actuation system in which microstructures embedded in a pH-responsive gel can undergo multiple actuation scenarios: (i) highly localized, directional movement of embedded microstructures in response to pH *gradients*, but not to the change in the bulk pH, as in previously described pH-responsive systems,¹¹ (ii) uniform large-area actuation upon hydration/dehydration. We explore the fundamental mechanisms of such novel behavior including investigation of how the chemical gradient is translated to the physical structure of the hydrogel and in turn how the system provides the ability to control the direction of bending, location and area of bending, and degree of bending of embedded structures.

The hybrid surfaces used here consist of high-aspect-ratio flexible microstructures embedded in a responsive hydrogel, where the volume change of the hydrogel can drive the movement, or actuation, of the structures. The hydrogel is pH-responsive poly(acrylamide-*co*-acrylic acid), which has a volume phase transition at pH \approx 4–5 corresponding to the pK_a of acrylic acid (4.3), with

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embedded structures made from glycidyl methacrylate-modified epoxy. To fabricate a hybrid surface, hydrogel precursor solution was placed on the structured surface and allowed to spread under confinement of a glass coverslip. The hydrogel was crosslinked by UV-initiated polymerization in this confined state.¹¹ Since the poly(acrylamide-co-acrylic acid) hydrogel precursor solution is quite acidic ($\text{pH} \approx 2$), the hydrogel is polymerized in a contracted state.

By controlling the initial position of the structures (bent *versus* upright) with respect to the initial state of the hydrogel (contracted *versus* swollen), we could generate a system that will either actuate or remain static in response to the bulk pH change (Fig. 1). In particular, we anticipated that if the structures are bent in the initial state of the contracted submerged hydrogel, the structures would actuate into an upright orientation upon the increase in the bulk pH whereas if the structures are oriented upright in the contracted submerged gel, further gel expansion upon pH increase would not change their orientation. The latter system should, however, show significant actuation upon drying. Indeed, when we generated structures that were bent after the polymerization process as previously described¹¹ (Fig. 1b, middle), we observed homogeneous pH-responsive actuation because structures could be pushed to the upright position by the hydrogel swelling in basic conditions (Fig. 1b, right). Upon drying, the original bent structures show only minimal actuation further down to the surface due to the additional contraction of the gel (Fig. 1b, left). When we fabricated surfaces in which the structures in their original state remained upright after hydrogel polymerization by tailoring the initial fabrication and confinement conditions (Fig. 1c, middle) (ESI†), we observed vertical expansion of the gel, but no actuation of the microstructures upon increase of pH (Fig. 1c, right). In this case, however, significant actuation of the microstructures takes place upon dehydration of the gel between the contracted submerged state and the dry state (Fig. 1c, left) as further gel shrinkage upon drying induced structures to buckle.¹⁵ In effect, we were able to shift the homogeneous actuation response from pH to humidity by controlling the initial conditions of the system.

The absence of actuation in response to bulk pH made this particular case an ideal test bed for studying the actuation of structures solely in response to pH gradients. We incorporated hybrid surfaces highlighted by a red box in Fig. 1 into microchannels

(Fig. 2a). Hydrogel was cured only in the area of the microchannel using a photomask, and the microchannel itself was made with double sided adhesive sealed at the top with a layer of polydimethylsiloxane (PDMS). Aqueous hydrochloric acid solution ($\text{pH} = 2$) and sodium hydroxide solution ($\text{pH} = 10$) were pumped into the channel creating a sharp pH gradient at the laminar flow interface (Fig. 2b). We investigated the actuation of both microfins (width = $1.2\ \mu\text{m}$, height = $11.5\ \mu\text{m}$, length = $10\ \mu\text{m}$, side to side spacing = $5\ \mu\text{m}$, front to back spacing = $5\ \mu\text{m}$) and posts (diameter = $1.5\ \mu\text{m}$, height = $10\ \mu\text{m}$, pitch = $8\ \mu\text{m}$) and observed that structures always bent toward the direction of the acid within a “transition zone” of finite width across the interface while preserving an upright position farther from the interface both in the acidic and basic channels (Fig. 2c and d). We could reversibly control the bending direction of the structures and the position of the transition zone by changing the location, shape (Fig. S1†), and gradient direction; for example, as seen in Fig. 2c, structures bent in opposing directions simply by reversing the direction of the pH gradient.

Since the gel at this pH interface was able to significantly shear and bend structures in the direction perpendicular to the acid/base interface, we anticipated that this force, when applied across different axes of an asymmetric embedded structure such as a microfin, may also facilitate control over the degree to which structures were bent over. We therefore rotated the hydrogel-embedded microfins within the microfluidic channel so that the pH interface was positioned at different angles relative to the embedded structures. To approximately calculate the degree of structure bending, we assumed that the structures were bent from the substrate base and were not curved. When the lengths of the structures were oriented parallel to the pH interface (such as in Fig. 2c), structures bent to angles of $30\text{--}35^\circ$; with an interface at a 60° angle, structures' bending angle decreased to $20\text{--}25^\circ$, and with the interface at an 80° angle, structures bent only $10\text{--}15^\circ$ (Fig. 2e). Furthermore, we observed that even surfaces that *did* actuate in response to homogeneous pH stimulus (such as those shown in Fig. 1b) could still be affected by the pH gradient and structures were induced to bend in the opposite direction to what would be normally expected, but only over short distances (Fig. 2f). Of course, such backward-bending behavior only took place where the force generated by the pH gradient opposed the buckling-induced

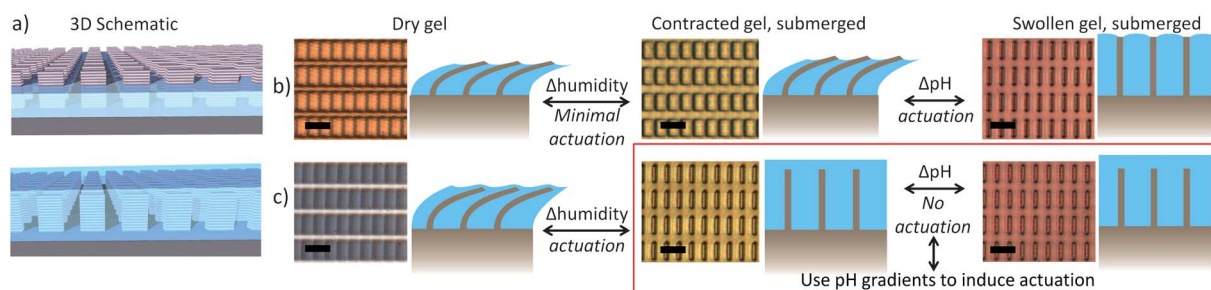


Fig. 1 Tuning actuation response with humidity and pH. (a) Schematic 3-D representation of an array of microfin structures embedded in hydrogel. (b and c) Each panel contains a top-view optical image along with a schematic side-view cross-section. The coloration in the optical images arises from bromophenol blue pH indicator added to the solution. (b) For surfaces in which structures are bent in a contracted gel in acidic conditions (middle), we observe pH-responsive actuation (between middle and right), but minimal actuation between the contracted, acidic state and dry state (middle and left). (c) For surfaces in which structures are upright in the contracted gel in acidic conditions (middle), we do not observe pH-responsive actuation (between middle and right), but we can still observe pronounced humidity-responsive actuation (between middle and left). The red box highlights the conditions under which we used pH gradients to actuate structures. Scale bars = $10\ \mu\text{m}$.

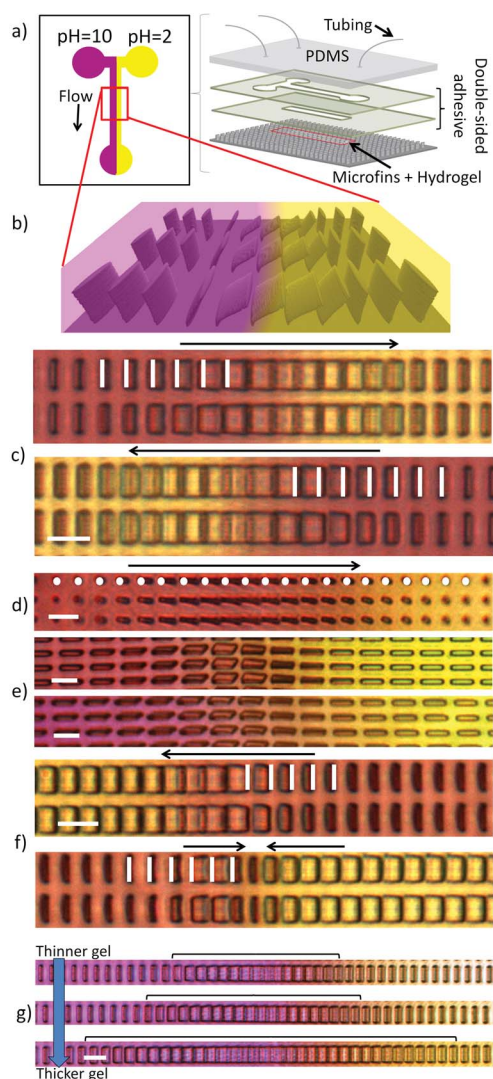


Fig. 2 Patterned actuation of microstructures driven by a pH-responsive hydrogel induced by a pH gradient, which was created by flowing acid and base in a microfluidic channel. (a) Schematic representation of experimental setup. (b) 3-D schematic showing an orientation of microfins within such a microfluidic channel, as demonstrated in (c). (c–g) Optical microscope images of actuated microstructures taken normal to the surface, showing that the direction of microstructure bending is always towards the acid. White lines or dots are place markers for the base of the structures to help visualize bending directions; bending directions are also marked with arrows above the micrographs. Color in all micrographs arises from pH indicator, bromophenol blue. Scale bars = 10 μm . (c) Bending direction can be switched by pH interface reversal: microfins are bending to the right when the acid is flowed on the right side of the channel (top), and the same fins are bending to the left when the acid is flowed on the left side of the same channel (bottom). (d) Micro-posts showing the same behavior as the microfins and bending toward lower pH. (e) Microfins like those in (c) but placed at different angles relative to the laminar flow interface exhibiting torsion and, therefore, different bending angles. (f) When a sample, which actuates in response to homogeneous pH as shown in Fig. 1b, is put in a pH gradient, it exhibits either a uniform bending direction corresponding to the bending direction of the original structures (e.g. to the left in the top image, when the acid is flowed to the left), or unique backward-bending at the base/acid interface, when the acid is flowed against the original bending direction, to the right. (g) A surface in which there is gradient hydrogel

actuation direction; in Fig. 2f, we saw that when structures already preferentially bent in the direction facing the acid, the actuation pattern was undisturbed, but backward-bending was induced when the preferred bending direction was toward the base.

The pH gradients used here were quite sharp and spanned only a few microns, but we observed the areas over which the structures bent (the transition zone) to be significantly wider than the pH gradient itself. We hypothesized that this discrepancy may be due to the fact that the gel cannot immediately conform to the chemical signal due to physical constraints. Thicker gels would then require larger distances to reach their equilibrium swollen and contracted states on either side of the interface than a thinner gel. To test the correlation of gel thickness with transition zone width, we created a surface with increasing hydrogel thickness along the length of the channel. As pictured in Fig. 2g, we observed that the width of the transition zone indeed increased along with hydrogel thickness even while under the influence of the same pH interface.

We used confocal microscopy to quantify this influence of the hydrogel thickness on structure actuation and investigate the hydrogel profile at the pH interface. To visualize both the actuation of the microfins and the topography of the hydrogel at the same time, epoxy microfins were fluorescently dyed with pyromethene 546 and 1 μm red fluorescent microspheres were adhered to the surface of the hydrogel. Overlaying a confocal Z-stack cross-section showing both the fluorescent microfins and gel-adhered microspheres with a bright field optical image to clearly show the extent of structure actuation (Fig. 3a) revealed that structure bending in the transition zone correlated to the region over which the thickness profile of the gel was sloped. We could tune the transition zone from widths of <50 μm (less than 10 consecutively bending structures) to nearly 500 μm (~100 consecutively bending structures) simply by changing hydrogel thickness (Fig. 3b).

To gain insight into the fundamental mechanism of how the pH gradient at the acid/base interface actually causes the bending of the structures, we modeled the surface deformation using a nonlinear field theory of hydrogels which was implemented as a user subroutine in the commercial software ABAQUS.¹⁶ The crosslink density of the hydrogel was chosen such that the ratio of the shear modulus of the gel in acidic conditions over that of the epoxy matched the experimentally measured value $G_{\text{gel}}/G_{\text{epoxy}} = 0.37 \times 10^{-3}$. Since the behavior of pH-responsive gels can be also understood in terms of the osmotic pressure,¹⁷ we simulated the changes in the pH by prescribing a corresponding change in the osmotic pressure. Under homogeneous pH conditions in which structures are programmed to stand upright in the contracted gel state (Fig. 3c top), upon homogeneous swelling the gel deforms vertically and increases in thickness; the gel is surface-attached and cannot expand laterally (Fig. 3c bottom) and as a result structures do not actuate. However, under conditions of a sharp pH gradient (Fig. 3c middle) we observed that the hydrogel was additionally able to deform horizontally, and this displacement was always in the direction of the acidic region causing structures to be sheared toward the contracted gel. The calculated result is shown in Fig. 3c, middle, where the gel color indicates the magnitude of horizontal displacement leftward. Our model suggests that the largest

thickness; as the gel thickness increases, the width of the region in which structures bend (indicated by brackets above the micrographs) also increases given the same pH interface.

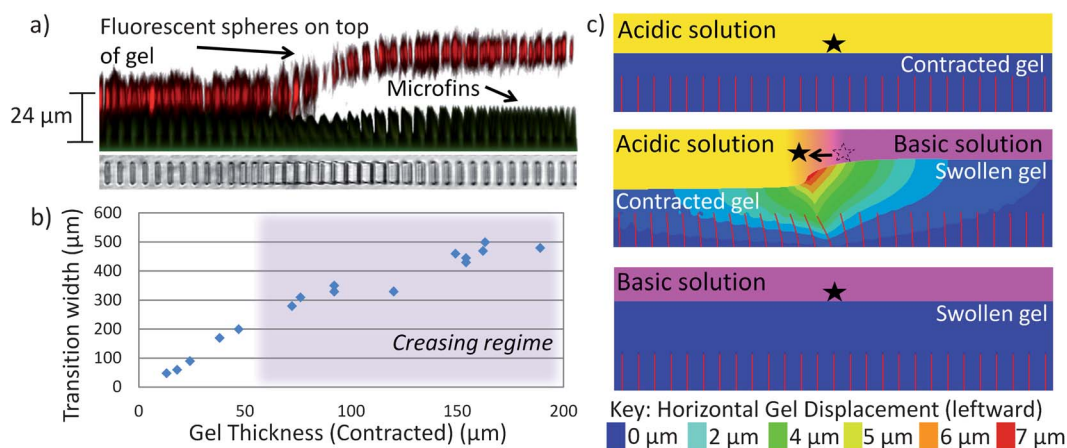


Fig. 3 Quantitative investigation of the mechanism of actuation and effect of the pH gradient on hydrogel thickness and profile shape. (a) Exemplary confocal Z-stack cross-section of the microstructure/hydrogel surface while in a microfluidic channel under acid/base laminar flow. Red corresponds to 1 μm red fluorescent particles adhered to the hydrogel surface and green corresponds to the microfins. Top-view optical image of the same area is aligned underneath to better visualize structure bending. (b) Correlation of the transition width with hydrogel thickness (measured in contracted state) indicates a linear relationship for gels < 50 μm thick before creasing in the gel occurs and the linear relationship ceases to hold. (c) Finite element method (FEM) simulation of the hydrogel and embedded structures in contracted gel (top), across a sharp acid/base interface (middle) and in swollen gel (bottom). The star marks the center of the gel to emphasize the lateral shifting of the hydrogel in the pH gradient case (middle), which is the underlying mechanism for actuation. Gel color indicates the magnitude of leftward displacement. Background color indicates pH (yellow is acidic and purple is basic, correlating with the colors of the pH indicator used in Fig. 1 and 2).

horizontal displacement should take place near the acid/base interface and the hydrogel should gradually revert to zero horizontal displacement farther from the interface. This prediction correlates well with the experimental observation of structural bending within a transition zone of finite width. Furthermore, if influence from the embedded structures is neglected, the width of this transition zone should be proportional to the thickness of the gel, which is the only relevant length scale in the system. The experimentally determined correlation between the thickness of the gel and the width of the transition zone appeared to initially follow this predicted linear behavior (Fig. 3b). At larger gel thicknesses (> 50 μm), however, we began to observe that the gel formed creases both along and perpendicular to the interface, and the linear relationship was no longer valid.

In summary, we have presented here a novel mechanism for gradient-responsive, hydrogel-driven actuation of microstructures. First, we effectively removed the homogeneous pH response of the hybrid systems made of pH-responsive hydrogel, allowing us to explore the use of gradient pH stimuli to affect tunable actuation *via* locally generated asymmetries in the hydrogel. We have demonstrated that by using pH gradient stimuli we can achieve a higher level of control over the actuation location, degree of structure reconfiguration, actuation direction, and general customizability and adaptiveness of the responsive hybrid surfaces. Furthermore, such surfaces now have a built-in actuation response to humidity, providing extended combinatorial sensitivity to multiple stimuli, each with its characteristic actuation pattern. In particular, microstructures embedded in a thick layer of pH-responsive gel similar to the ones in Fig. 1c would show either uniform actuation of all microstructures upon dehydration, or a highly localized stripe of actuated microstructures in response to a pH gradient, or no actuation in response to the bulk pH change.

Through modeling and simulations we have been able to explain the fundamental mechanism of this new method of hydrogel-driven

actuation; lateral displacement of hydrogel occurring at the acid/base interface shears structures always in the direction of this displacement (towards contracted gel) providing the system with highly localized and directional chemical sensitivity. We expect that this new actuation mechanism may prove useful for precise reconfiguration of surface structures, especially for tunable optical systems, or as visual sensors which provide insight into gel dynamics and creasing studies. Furthermore, the mechanism of actuation which we describe here is highly general and not only pH-specific, meaning that this method could be applicable for a range of environmentally responsive hydrogels. Broadly, the multifunctional dynamic systems developed in this study, in particular the use of non-uniform chemical stimuli within environmentally sensitive gels to induce structural asymmetry and highly localized reconfiguration (in this case, the use of a pH gradient), coupled with the ability to induce uniform bulk actuation upon application of a different stimulus (in this case, the use of hydration/dehydration), may have far reaching impact on the growing field of "smart", adaptive and multi-responsive systems.

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