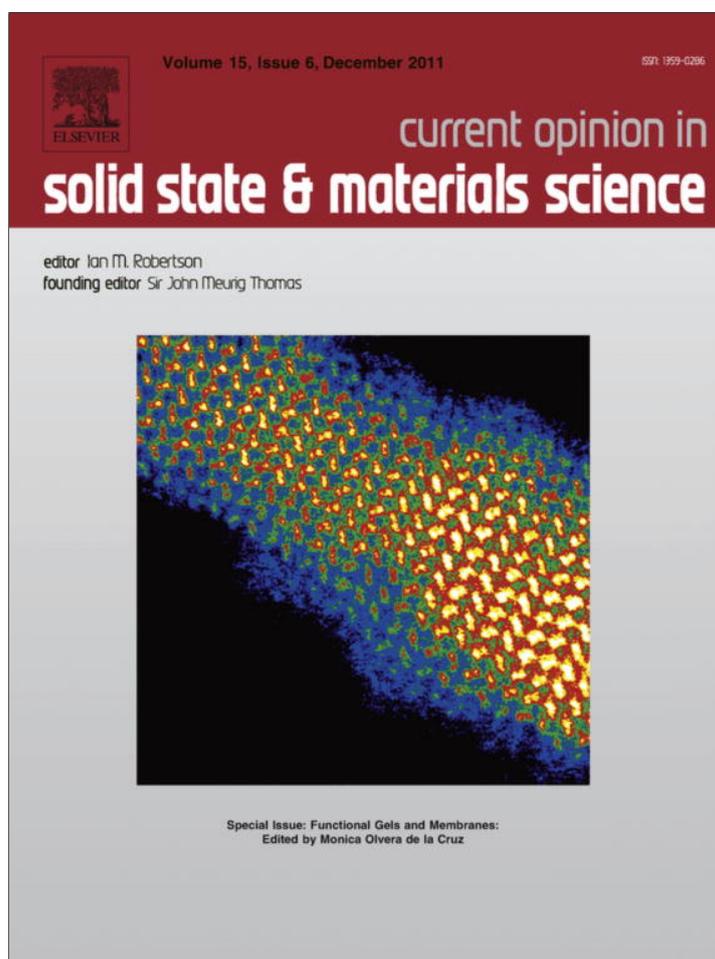


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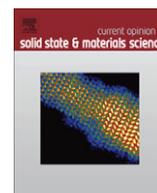
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Hydrogel-actuated integrated responsive systems (HAIRS): Moving towards adaptive materials

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ABSTRACT

The move toward sustainability and efficiency in nearly every field calls for dynamic materials that can harvest energy from and adapt to a changing environment. Here we review our recently developed, widely applicable strategy for adaptive surface design that integrates two rarely associated categories of materials – nanostructured surfaces and hydrogels – into a hybrid architecture. The nanostructure arrays provide unique topographic patterns that confer wetting, optical, and many other functions but on their own are generally static; by embedding them in a layer of responsive hydrogel, we channel the mechanical forces generated within the swelling/contracting gel to reversibly reconfigure the nanostructures in response to stimuli. Since the sensing and responding components are structurally distinct, they can each be programmed independently to match potentially almost any type of environmental change with almost any type of output. Several of our recent advances in nanofabrication make it possible to choose from an entire spectrum of nanostructured materials, stiffnesses, shapes, symmetries, orientations, and large-scale surface gradients, enabling a given stimulus to be translated into a vast assortment of complex multiscale patterns and adaptive responses. The gel chemistry and nanostructure flexibility can be further optimized for incorporating the surfaces into a variety of structures and environments. We envision using this platform to create a generation of sustainable, self-adapting, and self-reporting materials.

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1. Introduction

Designing for a sustainable future requires dynamic materials that respond, adapt, and harvest energy from the constantly changing environment. Currently, most building surfaces barricade against the outer elements and leave the interior conditions to be regulated independently, at often staggering energy costs. Light- and heat-sensitive surface materials that instead use the energy from ambient changes to intrinsically adapt their thermal transport and reflective properties would make a substantial dent in energy consumption. Stress-responsive coatings on buildings, planes, or bridges that change color and self-heal in response to microscopic, otherwise undetectable mechanical defects would further optimize energy efficiency as well as safety. Surfaces that adjust their wettability depending on humidity, pH, or solute content of water could autonomously modulate absorption and runoff, optimize water use, and potentially mitigate toxic exposure or bacterial growth anywhere from rooftops to purification plants to

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clothing. The same principles apply to the internal environment of our own bodies: dynamic materials that sense chemical or temperature cues would not only deliver therapies to appropriate destinations and spare others, but could enable diagnostic sensors to swim through the body driven by information and energy from local gradients. In each case, engineering adaptiveness at the nano-scale is essential for interconverting small- and large-scale signals and for designing integrated, hierarchical responsive systems. Environmental changes are inherently sources of energy but are often overlooked or considered counterproductive; maximizing their potential requires a design strategy versatile enough to incorporate dynamic adaptiveness into a wide range of materials and systems.

This vision precisely describes living organisms: each is built almost entirely from components that, together, continuously sense and adapt to all types of external and internal changes with an elaborate repertoire of integrated responses [1–3]. Flexible macromolecules that change shape in response to stimuli clearly play a key role and have inspired a growing field devoted to developing biomimetic responsive soft polymer materials [4–6]. Macroscale biomechanical strategies have similarly inspired a range of biomimetic approaches to dynamic systems [7]. However, the more

subtle ways in which nature acts as a matchmaker to create hybrid adaptive structures have been much less appreciated in this context. During bone formation, selective pairing between proteins and inorganic materials sets up a unique interplay that enables the composite to translate mechanical stress into changes in bone features. Integration of bones with muscles throughout the skeletonomuscular system then creates another hybrid system that responds to chemical input with specifically tailored movements. The interplay between the cell membrane and an embedded protein channel enables the cell to respond to changes in osmotic pressure by transporting solutes in or out; small protein changes that alter its interaction with the membrane tune the sensitivity of the response [8]. Hybrid pairings similarly underlie our hearing, squids' camouflage, bacterial navigation toward food, and countless other adaptive responses [9]. Each hybrid makes use of materials that complement each other – hard and soft, organic and inorganic, large- and small-scale organization – to intrinsically interconvert different scales and forms of energy and generate highly specific responses.

By shifting the focus of adaptation from a single material to the interplay between two, a hybrid approach to dynamic surface design offers tremendous combinatorial potential for mixing and matching a broad range of inputs and outputs. At the same time, it greatly expands the materials choices: rather than requiring synthesis of new materials from scratch, complementary pairing can generate adaptive responses from supposedly non-adaptive materials without sacrificing sensitivity. These opportunities led us to develop a versatile, tunable, and widely applicable strategy for adaptive surface design: by combining two well-developed but rarely associated categories of materials – nano/microstructured surfaces and hydrogels – we create a uniquely bioinspired class of hybrid materials in which adaptiveness arises from the interaction between two integrated but structurally distinct elements [10–14].

Nanostructured surfaces on their own generate a spectrum of tunable properties and functions unmatched by any other class of material [15–21]. In particular, surfaces bearing ordered arrays of high-aspect-ratio nanostructures can be designed to confer a wide range of optical [14], wetting [10,18,22], adhesive, anti-fouling [23,24], motility [25], and other behaviors, as exemplified by those used by lotus leaves to shed water [26], geckos to stick to surfaces [27], echinoderms to keep their skin clean [23], and microorganisms to swim [28]. Since many of the properties arise from

surface topography, they can readily be switched on and off or fine-tuned simply by reorienting or reconfiguring the structures to alter the patterns. Nanostructure arrays are therefore a potentially ideal platform for designing multifunctional, easily adaptable surfaces, and they do in fact responsively reconfigure in biological systems to allow, for example, beetles to modulate their foot adhesion [29] and fish to sense and respond to flow [30]. In practice, however, synthetic nanoarrays are almost completely static; altering a pattern and adjusting a property require making a new structure. A few responsive examples have been synthesized in an effort to mimic beating cilia [20,31,32], but these are severely limited in the stimuli they can sense and in the motions they can undergo. Stacks of magnetic nanoparticles [31] or magnetic PDMS structures [32] can move in a magnetic field but have no way of responding to other conditions, and for these structures as well as for hydrogel pillars [33], the balancing act between preventing breakage or collapse and ensuring flexibility leaves little room for programming shapes, movement patterns, or even reversibility. Synthetic nanoarrays are therefore rarely designed to be responsive.

In contrast, hydrogels specialize in responding to their environment [4–6,34]. As networks of soft polymers, their chemical composition can be adjusted to provide a large assortment of sensitivities as diverse as humidity, temperature, light, mechanical stress, magnetic or electric field, pH, glucose and other molecular species, and more. The sensitivity profile for each stimulus can be fine-tuned by varying polymer composition or crosslinking and, in parallel with the multifunctional potential of nanostructured surfaces, multiple sensitivities can be incorporated into one hydrogel. All stimuli are translated into polymer reconfigurations and water influx or efflux that swells or shrinks the gel. These volume and conformational changes have been used to alter surface properties by incorporating, for example, optically or biologically active components into the gel such that rearrangements expose or hide them, but in general, the output repertoire is limited in scope and tunability by the requirement for compatibility with the polymer chemistry and conformation. However, a more fundamental and potentially much more versatile feature of the gel response is the basic fact that it translates the energy associated with any type of environmental change into mechanical energy. The mechanical energy of bulk size change has been used in limited cases such as artificial muscles [35], but the responses also produce an entire 3D network of multiscale, multidirectional mechanical forces within the gel, particularly when attached to a

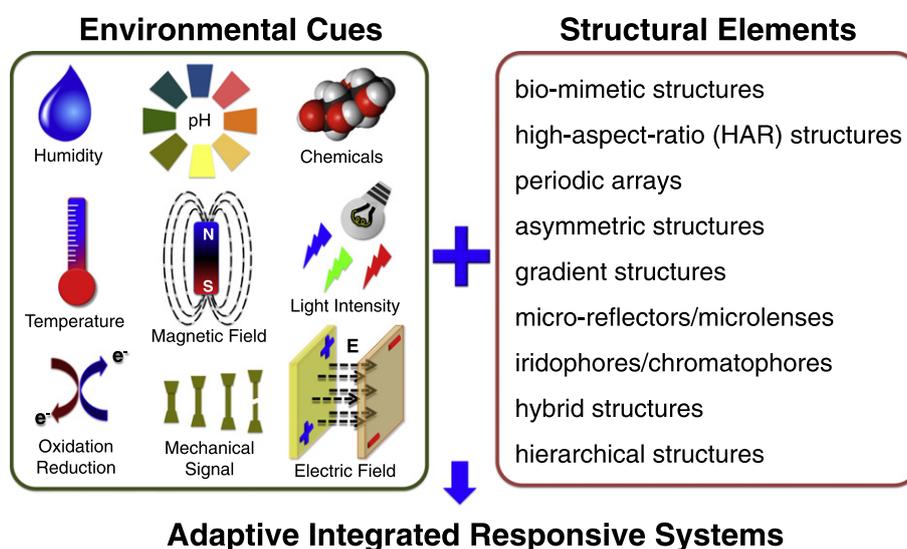


Fig. 1. The concept of adaptive integrated responsive systems.

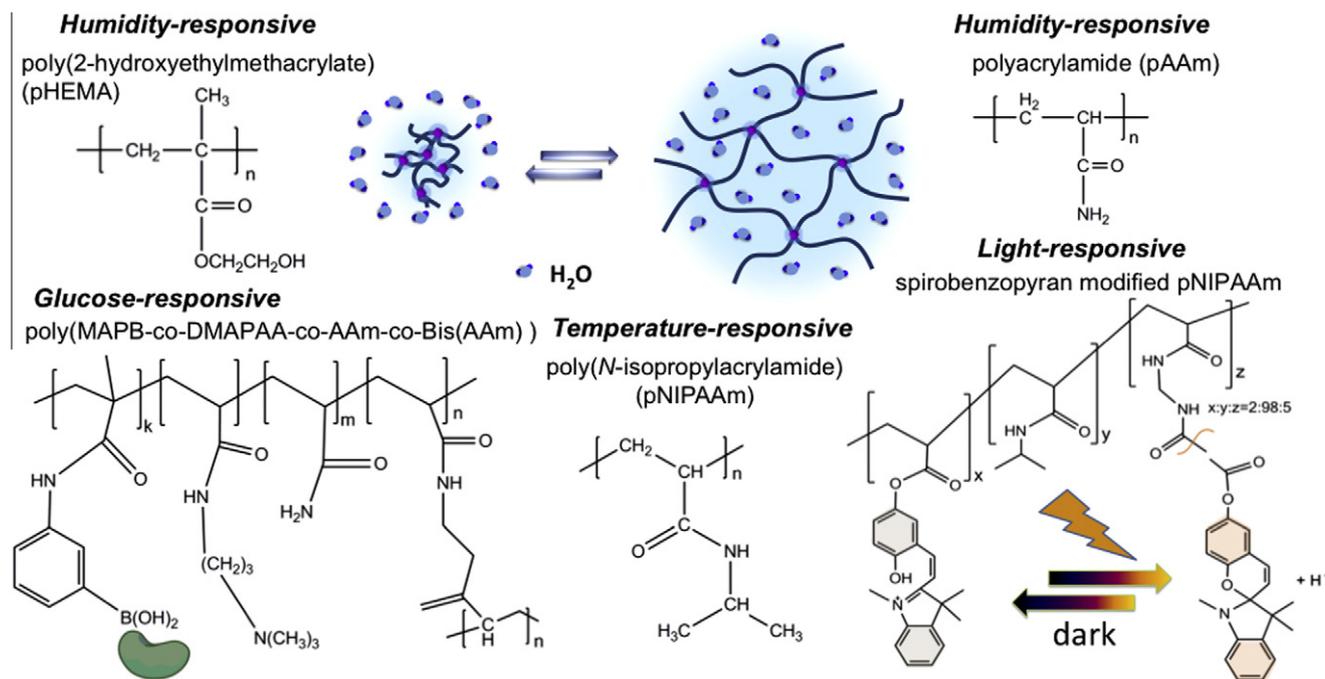


Fig. 2. Synthetic 'muscles' – a variety of hydrogels responsive to different stimuli.

substrate, that are only beginning to be appreciated and are largely untapped as a driving force for changing output properties [36–40].

Together, then, nanostructure arrays and hydrogels are a tremendously potent combination: nanostructures can be used to program, switch, and control a wide range of surface properties by mechanical movement, and hydrogels produce highly tunable mechanical force networks that can be used to drive such motions in response to one or more chosen stimuli. Our hybrid design therefore comprises a surface bearing arrays of nanostructures embedded in a layer of hydrogel. The premise is simple: hydrogel swelling or contraction reconfigures the structures to bend/tilt or restore the initial configuration upon application or removal of the stimulus, with mechanical force serving as a switchboard for translating almost any type of environmental change into almost any type of output. Since the sensing and responding components are structurally distinct, stimulus and response can be programmed independently of each other (Fig. 1). The versatility of this strategy goes much further than even the combinatorial potential, however: any given stimulus–response pair can be put together in a variety of configurations to program how forces are transferred between them, producing responses that vary over a wide range of patterns, scales, and many other features. As we describe here, this simple strategy, combined with a number of fabrication techniques we have recently developed [41,42], has shown and continues to show immense potential as a generalizable design for adaptive materials.

2. Hydrogels: adaptive, responsive molecular motor to transform environmental signal into mechanical response

Hydrogels are an elastic network of hydrophilic polymer chains that are either physically or chemically crosslinked. Hydrogels swell or deswell by retaining or expelling a large quantity of water in the network without dissolution resulting in as large as 500-fold volume changes [43–46]. The thermodynamic interactions between the polymer chains and between the water molecules and the polymer chains govern this signature volume change, which

depends on various external stimuli such as pH, temperature, ionic strength, electric field, light, and solvent. This lends 'smart' or 'responsive' properties to the hydrogel, as one can design the polymer to be responsive to one or more specific stimuli. Fig. 2 summarizes exemplary structures of smart hydrogels that are sensitive to various external cues [47–49].

Acrylate-based hydrogels are simple and widely studied synthetic polymers typically prepared by photo- or thermo-initiated radical polymerization of monomers bearing different side groups that impart a variety of responsivities (e.g., pH, temperature, light) to the hydrogels. Anionically modified polyacrylamide (PAAm) such as poly(acrylamide-co-acrylic acid), poly(AAm-co-AAc) has ionizable functional groups which allow the gel to respond to changes in pH; for example, when the environmental pH is above the pK_a of the acrylic acid (4.25), a high ionic concentration is created in the polymer network putting the hydrogel network under a high negative osmotic pressure which brings in water molecules from outside to inside the network and induces swelling. When the pH is reduced below the pK_a of the acrylic acid, the polymer chain loses its negative charge, the water molecules leave the network, and the hydrogel collapses. This process is reversible, making it possible to use this type of polyionic hydrogel as a sensor and an actuator operating in response to pH change. The operating pH can be tuned by replacing the acrylic acid with other types of weak acid or base, such as carboxyethyl acrylate, 2-vinylpyridine, and dimethylaminoethyl methacrylate. Poly(*N*-isopropylacrylamide), poly(NIPAAm), has been extensively studied as a thermoresponsive hydrogel which shows negative temperature responsive behavior [50–52]. At lower temperatures below the lower critical solution temperature (LCST, typically 32 °C for poly(NIPAAm)), the increased hydrophilicity of the polymer chain favors the interaction with water molecules via hydrogen bonding, thus retaining a large volume of water, and the polymer is in its swollen state. When the temperature is above the LCST, the hydrophilic interaction is disfavored and the hydrophobic interactions between the isopropyl side groups are favored, the water molecules are expelled, and the hydrogel collapses to its deswollen state. This procedure is also reversible and the temperature of transition is tunable over a wide range.

Various potential applications have been demonstrated based on these adaptive, dynamic, and responsive hydrogels: microfluidic devices that sense pH, temperature, or light and adaptively control the flow [47,52–55], responsive scaffolds for tissue engineering [56], photonic crystals and responsive optics changing color in response to environment [51,57–60], sensors [46,61], artificial muscles [25,62–64], shape-shifting materials [65], and other intelligent materials [4,6,43].

3. Array of high-aspect-ratio nanostructures: bio-inspired synthetic approaches to design of versatile “hairy” surfaces

The synthetic design of next generation dynamic systems requires strategies to produce diverse surface topographies with customized mechanical, chemical, optical, and other properties in order to fine-tune their behavior. A commonly used approach to producing biomimetic arrays of structures with high-aspect-ratios (HAR) up to 100 is based on lithographically defining the arrays on a Si wafer followed by deep reactive ion etching, which is also colloquially known as the Bosch etching process [66,67]. Typical arrays of Si HAR structures are shown in Fig. 3a. These rigid arrays of HAR Si structures produced with precisely controlled geometry exhibit unique surface properties such as superhydrophobicity and anti-ice formation [18,68,69]. While we have recently demonstrated bio-inspired examples of hydrogel-actuated Si nanostructures that undergo reversible and dynamic reconfiguration at a time scale of 60 ms [11], these rigid structures have several limitations for dynamic applications such as requiring high forces for actuation, limited deflection due to the high degree of stiffness, and no control over the material stiffness. Therefore, the level of actuation was controlled only by varying the geometry of Si nanoarrays (e.g., aspect ratio) which required laborious and expensive fabrication for each Si nanoarray.

Soft lithography is a powerful, low-cost alternative fabrication technique to conventional lithography and typically utilizes an elastomeric polymer, polydimethylsiloxane (PDMS) for high-resolution replication of microfabricated structures [70,71]. In order to broaden the materials choice for making nanostructured arrays, an approach based on the use of PDMS as a secondary elastomeric mold for casting the replica in the material of choice was introduced [33,41]. This approach provides the ability to regulate the mechanical and chemical properties of the resultant nanostructures without any change in geometry. As outlined in Fig. 3b, this one-to-one replication method allows fine tuning of stiffness from a few megapascal to hundreds of gigapascal, when the replicas are made of polymers and metals/ceramics, respectively. A composite material can also be used for continuous tuning of the stiffness of the array over a wide range to modulate the sensing/actuation capability of the nanostructures.

An important issue for designing functional nanostructured materials for sensing and actuation applications is to understand the mechanics of the movement of the structures. For posts, there is a critical force for the onset of bending (buckling) for a post under stress parallel to the initial orientation of the unbent post. When the force F acts along the entire post length l , perpendicular to the posts, the deflection Y_{lz} , at a given point l_z from the base, is given by $Y_{lz} = Fl_z^3/8EI$, where E is the bending modulus and I is the moment of inertia [41]. Therefore, both the geometry and the material stiffness play an important role in determining the force required to actuate the posts. A more generalized parameter, “effective stiffness”, S_{eff} , can be defined as $S_{eff} = F/Y_{lz}$ to compare two different structures. For posts with circular cross-section of radius r , the moment of inertia is $I = \pi r^4/4$; therefore, the ratio of the effective stiffness can be expressed as:

$$\frac{S_{1,eff}}{S_{2,eff}} = \left(\frac{E_1}{E_2}\right) \left(\frac{l_2}{l_1}\right)^3 \left(\frac{r_1}{r_2}\right)^4$$

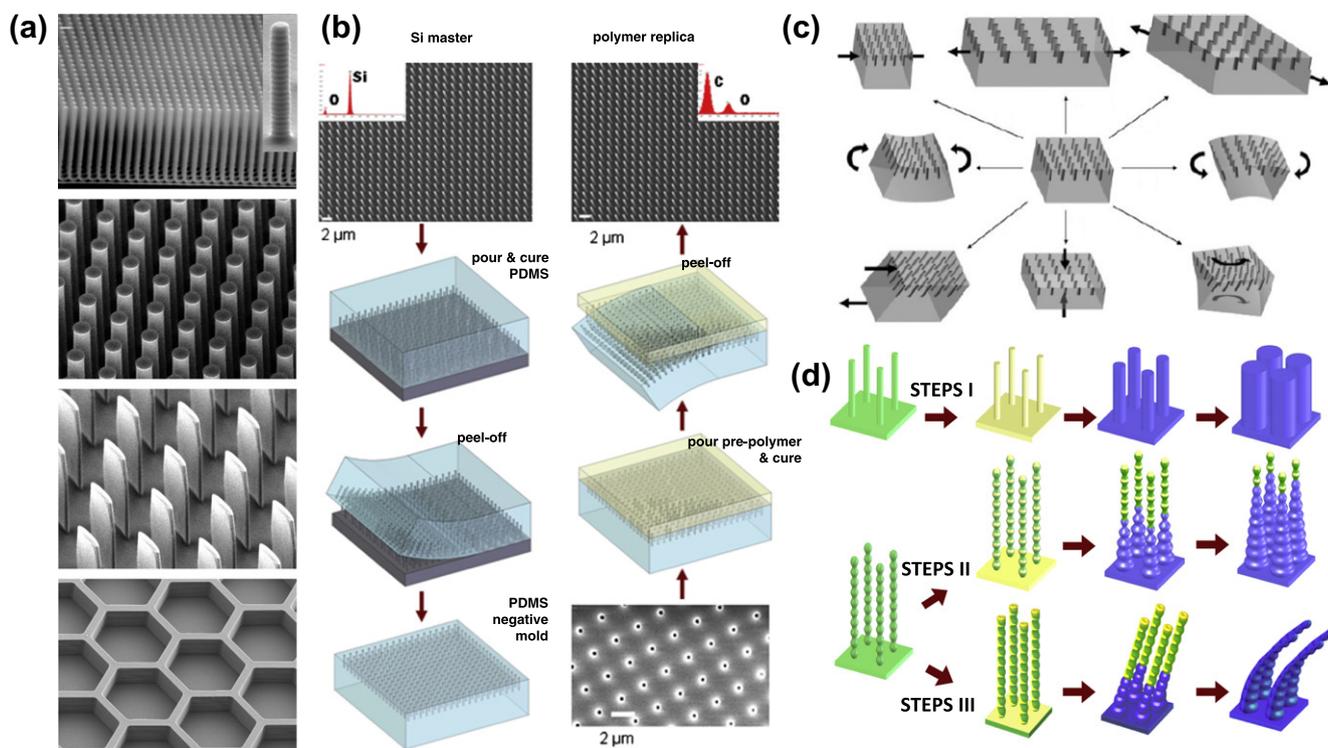


Fig. 3. (a) Representative silicon HAR structures. (b) Schematic showing how silicon HAR structures can be replicated into identical polymer structures via soft lithography. (c) PDMS molds of the silicon HAR structures can be systematically deformed to yield asymmetric or tilted replica structures. (d) Schematics of STEPS processes allowing for further structural modification of HAR arrays.

This dimensionless parameter allows direct comparison of the extent of actuation of the nanostructures that have different sizes and mechanical properties under a given force. For example, an epoxy micropost ($r = 0.75 \mu\text{m}$, $l = 10 \mu\text{m}$, $E = 1 \text{ GPa}$, aspect ratio = 6.7) would have an effective stiffness similar to that of a Si nanopost ($r = 0.15 \mu\text{m}$, $l = 8 \mu\text{m}$, $E = 200 \text{ GPa}$, aspect ratio = 26.7). Therefore, soft polymeric nanostructures produced by soft lithography will allow the bending actuation of a wider range of feature sizes and geometrically stiffer microstructures, for example, low aspect ratio structures that are easier to produce [12].

Another aspect of soft lithographic fabrication methods is that, by utilizing the elastic property of PDMS, the secondary mold can be subjected to various mechanical deformations, including compression, elongation, shear, bending, twist, and the combinations thereof, while the material is cast in the mold to allow arbitrary geometrical modifications from the original Si master structures (Fig. 3c) [41]. Particularly, this method allows for a high degree of tunability to change the symmetry of the projected 2D arrangement of the nanostructure array, to change the cross-section of the HAR arrays, for example, from circular to elliptical shape, and to fabricate non-vertically aligned and anisotropically shaped structures such as tilted or twisted nanopost arrays. In addition, two or more fundamental deformations (compression/stretching, rotation) can be applied either simultaneously or sequentially to allow compound deformations to prepare complicated nanostructured arrays.

Although replication in a mechanically deformed PDMS mold allows broad structural tunability at the nanoscale, the approach

is restricted to proportional modification of the original geometry and this method provides no means for creating modified structures with 3D shape or gradient patterns. Continuous or stepwise gradients of feature sizes and shape are particularly useful for systematic studies of structure–property relations and for fast screening of multiple geometric parameters affecting the surface properties. To address this issue, we have developed a complementary structural modification method in which a parent HAR structure array is reshaped with nanoscale precision by controlled electrodeposition of conductive polymers [42]. This method, termed Structural Transformation by Electrodeposition on Patterned Substrates (STEPS), is a high-precision, high-throughput, and low-cost benchtop method offering proportional change of the size of HAR nano/microstructures, production of 3D transformed tapered, bent, overhanging, and other anisotropic features, with the ability to produce either stepwise or continuous gradients of feature sizes and shapes from a single parent substrate. All of these patterns are very challenging to fabricate using conventional techniques. The schematics of three distinct STEPS methods are illustrated in Fig. 3d. Electrodeposition of conductive materials such as polypyrrole on these patterned electrodes transforms the original structures into a wide range of modified structures. As mentioned above, a great advantage of STEPS is its ability to create gradient nanoarrays. For example, a substrate with 250 different nanostructures within only 3 cm^2 can be prepared [42]. Such gradient substrates are useful for quick screening of substrate topography and for systematic combinatorial studies of the morphological effect on the dynamics of the nano/microstructures. These recently

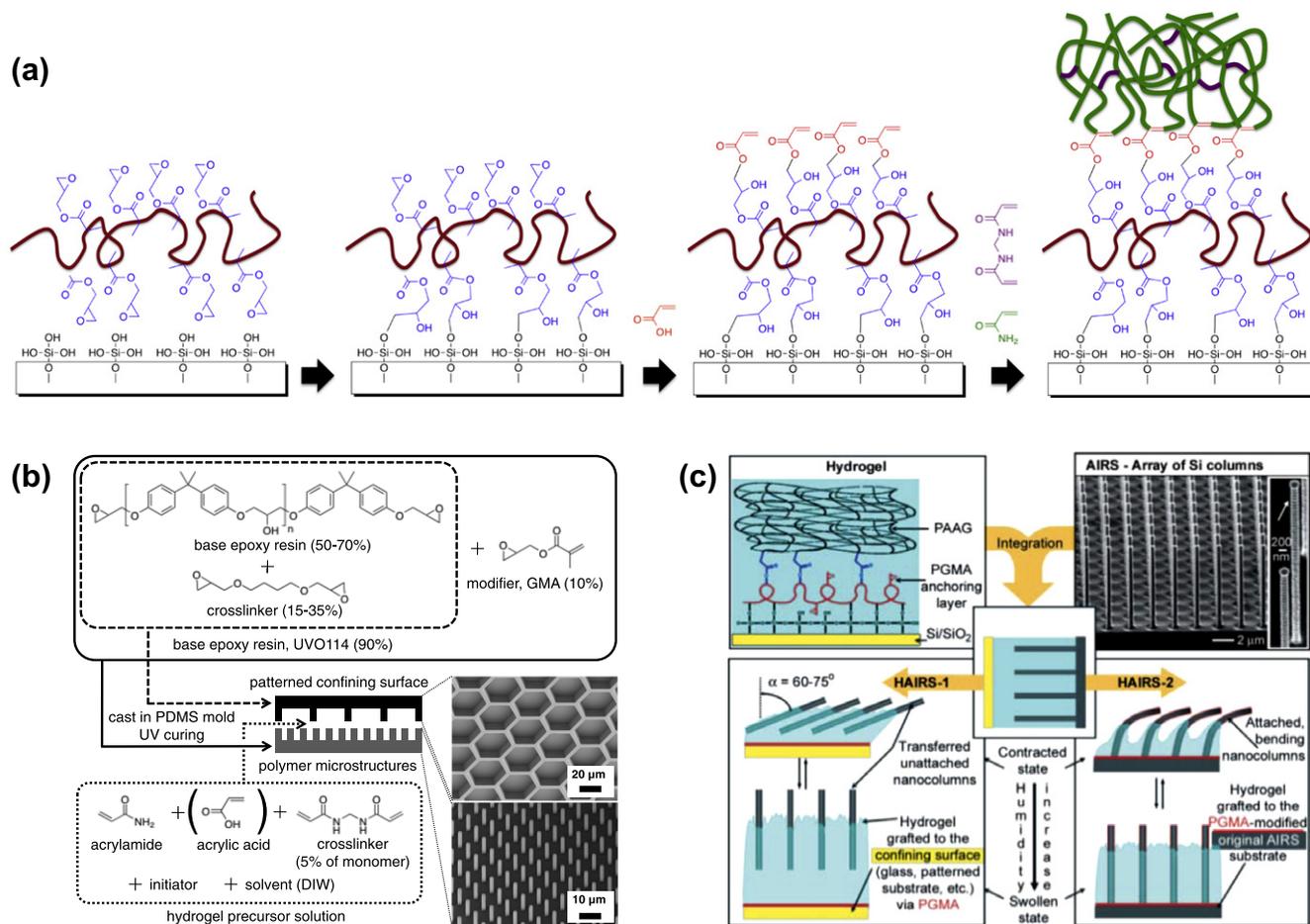


Fig. 4. (a) Schematic showing how silicon surfaces are chemically modified to allow for covalent attachment of hydrogel. (b) Schematic showing how epoxy structures are chemically modified to allow for covalent attachment of hydrogel on the surface. (c) HAR structures can either be suspended in hydrogel (not attached to the substrate, bottom left) or attached to the substrate (bottom right) allowing for two different actuation systems (HAIRS-1 and HAIRS-2).

developed fabrication techniques provide easy access to fabricate a wide variety of HAR nano/microstructure arrays inexpensively and conveniently.

4. Putting it all together: HAIRS (Hydrogel Actuated Integrated Responsive Systems)

Combining different classes of materials into an integrated system is not a trivial task. Carefully designed surface chemistry and the design ideas for integrating the skeletal elements (HAR structures) with hydrogel muscles are necessary breakthroughs for realizing true adaptive and dynamic surfaces. We have recently developed such techniques that have allowed us to open new avenues for hydrogel-actuated integrated responsive systems (HAIRS) [10–13]. However, it is noteworthy that these exemplary hybrid approaches represent only an entry into the expansive opportunity to create novel adaptive materials.

The first step to integrate hydrogel onto arrays of Si nanostructures is to chemically couple the two materials. This procedure is illustrated in Fig. 4a. The hydroxyl groups on the surface of Si react with poly(glycidyl methacrylate) (PGMA) to create a high density of glycidyl groups on the surface. The remaining surface glycidyl groups are then coupled with a nucleophile bearing a reactive double bond such as acrylic acid. This step effectively converts the surface glycidyl groups into vinyl groups that can act as a grafting site ('grafting-through' polymerization) on the substrate when the hydrogel is formed on the surface by photo- or thermo-initiated in situ radical polymerization of acrylamide and *N,N'*-methylene-bisacrylamide as a crosslinking agent. Polymeric HAR arrays produced by soft lithography are typically made from a UV-curable epoxy. In order to covalently attach the hydrogel layer to the surface of these arrays, a small portion (typically 10% or less) of bifunctional monomer, glycidyl methacrylate (GMA), bearing polymerizable groups for both the UV-curable epoxy and the hydrogel, is added to the UV-curable epoxy as shown in Fig. 4b.

Two hybrid architectures of HAIRS have been developed, as depicted in Fig. 4c, in which the HAR elements are either free-standing (HAIRS-1) or attached to the bottom substrate (HAIRS-2). In order to fabricate the HAIRS-1 architecture, the hydrogel-embedded HAR arrays are detached from the original substrate by breaking the structures off the substrate by shear force and transferring them to a secondary substrate which has been treated with an anchoring layer of chemisorbed PGMA and acrylic acid. In the case of the HAIRS-2 architecture, the surface of the HAR array is chemically modified to provide anchoring groups for the hydrogel layer. In both cases, a secondary substrate can be used to confine the hydrogel precursor solution by sandwiching the substrate with the original substrate with HAR arrays. Both architectures show reversible actuation of the hydrogel-embedded nanostructures as schematically shown in Fig. 4c. In HAIRS-1, the nanoposts are tilted when the hydrogel contracts and restore their original upright geometry when the hydrogel swells and releases stress. The nanoposts in HAIRS-2 are bent by the contracting hydrogel and return to upright configuration when the hydrogel swells. For highly symmetric nanoarrays such as nanoposts with circular cross-sections, the direction of actuation is unidirectional over a small area and these unidirectional regions form domains over a larger area.

The deformation mechanisms for HAIRS-1 and HAIRS-2 are fundamentally different from a mechanical point of view. The nanostructures in HAIRS-1 systems correspond to stiff elements under a compressive load while the shrinking hydrogel exerts tensile forces, forming a microscopic analog to tensegrity structures used for macroscopic architectural construction. At the molecular scale, a mechanical model for the cytoskeleton of cells has been proposed based on the same concept [72]. The nanostructures in HAIRS-1

redirect the tensile forces of the contracting gel into a lateral actuation. In a recent modeling study, this behavior was shown to correspond to a bifurcation at a critical humidity for a humidity-responsive hydrogel, analogous to a phase transition, through which the structure adapts to the drying environment in two ways: above the critical humidity, the HAR structures stand vertical, enabling the hydrogel to develop tension and retain water; below the critical humidity, the HAR structures tilt, enabling the hydrogel to reduce thickness and release water [73].

HAIRS-2 systems are even more complicated than tensegrity structures as the tensile stress is largely transferred to elastic deformation of the nanopillars, leading to bending actuation of nanopillars. The stored elastic energy is released when the tensile stress is removed upon swelling of the hydrogel, restoring the original straight geometry of the nanopillars. In contrast to the HAIRS-1 system in which the net force exerted by the contracting gel has no direct influence on the shape of the embedded nanopillars, there is a direct correlation between the extent of the bending of the nanopillars and the force developed by the gel in HAIRS-2. Estimation of the force required to bend a nanopillar using simple beam theory indicates that the force depends strongly on the aspect ratio of the nanopillars and this force should not exceed the fracture strength of the basal part of the nanopillars for reversible actuation [11]. As a consequence, Si nanopillars with a small aspect ratio (<20) cannot be fully bent before they break, whereas Si nanopillars with an aspect ratio of 80 can be fully and reversibly bent to touch the substrate without breaking. Soft polymeric pillars are typically at least two orders of magnitude less stiff than Si pillars and therefore low aspect ratio structures (~6) and even up to 100 μm scale microstructures of similar aspect ratios can be reversibly bent without fracture by hydrogels in the HAIRS-2 type architecture [12]. These mechanical assessments provide insights into the dynamic actuation behavior of HAIRS and offer the basis for the rational design of dynamic surfaces.

5. Control of directional motion of embedded structural elements for patterned actuation

An important feature that HAIRS must exhibit for many applications is the ability to induce a desired *patterned* actuation. Directional or patterned actuation can be achieved by precisely controlling the direction of actuation for each structural element in the hybrid system. Ideally, if the hydrogel layer is uniformly thick, a symmetric HAR structure (e.g., pillars) would not show a preferred direction of actuation. However, symmetric HAR structure arrays tend to form domains of uni-directionally bending structures even without intentionally modulating the thickness of the hydrogel. This is due to local imperfections in the structure or in the hydrogel thickness which result in breaking of the local symmetry, leading to deterministic change in the direction of actuation. Once directional bending takes place at one site, the effect is propagated over a small area within which uni-directional actuation takes place [19]. These observations led to a main hypothesis for controlling the actuation direction: the oriented movement is governed by the local changes in the hydrogel thickness profile. To test this hypothesis, a numerical model was implemented in the finite element package, ABAQUS, to visualize the effect of hydrogel thickness gradient on the direction of the actuation as shown in Fig. 5a [36]. The polymer pillars embedded in a hydrogel layer bend toward the thicker region of the hydrogel upon contraction of the hydrogel and restore the upright geometry when the hydrogel is swollen. We can, therefore, expect that the direction of actuation in the HAIRS could be precisely controlled by appropriate patterning of the topography/thickness profile of the gel layer. Experimentally, the hydrogel thickness can be modified by

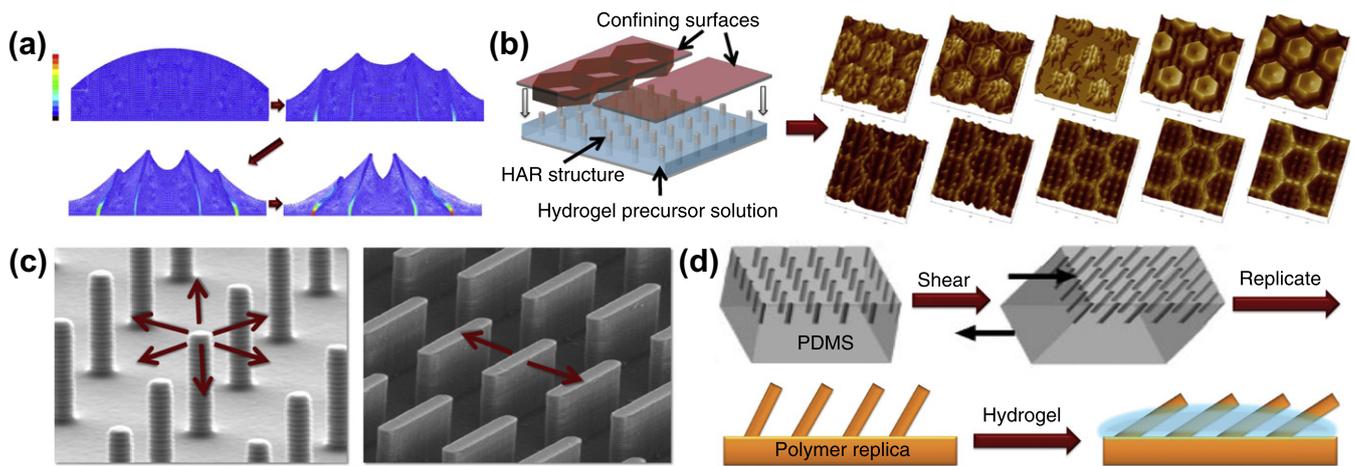


Fig. 5. (a) Finite-element simulation predicting how posts embedded in a dome-shaped hydrogel will bend in response to hydrogel contraction and expansion; the posts always bend toward the center of the dome, where the hydrogel muscle is thickest. (b) Experimentally, the surface topography of the hydrogel can be patterned using a confining surface with a relief structure. A honeycomb confining surface, for example, creates either opening or closing microflorets as shown by a series of AFM images (scan size = $80\ \mu\text{m} \times 80\ \mu\text{m}$, $z = 7.5\ \mu\text{m}$) with varying hydrogel thickness. (c) Cylindrically shaped posts have no preferred bending direction, but actuation direction can be highly controlled by the use of asymmetric microfin shapes which have a preferred bending orientation along a single axis. (d) Pre-tilted structures can be fabricated via replication from a sheared PDMS mold. Such pre-tilted structures show uni-directional bending in the same direction as the pre-tilting.

either photo-patterning the hydrogel or by using a patterned confining surface as shown schematically in Fig. 5b. Also shown in Fig. 5b is a series of AFM height images of the patterns generated from an array of polymer micropillars embedded in honeycomb-patterned hydrogel of gradually increasing thickness in its dry state (i.e., hydrogel is contracted). The overall thickness of the hydrogel layer within each confining pattern also influences the morphology of the surface of HAIRS.

Beyond what is achievable by topographically patterned hydrogel, additional control over the direction of the actuation is possible by utilizing principles of symmetry breaking found in nature: asymmetric distribution of growing actin filaments allow for unidi-

rectional cellular motion [74], and fish and amphibians can sense anisotropic flow fields due to the oval cross-sections of cilia on their bodies [9,75]. Therefore, HAIRS utilizing asymmetric embedded structures can show more predictable and controlled motion. We have demonstrated such bio-inspired asymmetric actuators using a fin-like microstructure array shown in Fig. 5c and by using pre-tilted pillars shown in Fig. 5d [13,14]. The resulting uni-directional beating of such structures may be useful for particle propulsion and switchable, directional wetting properties.

Fig. 6 shows examples of reconfigurable surface patterns created by using the confining surface method (a and b) and by using symmetry breaking (c). It should be noted that the wettability of

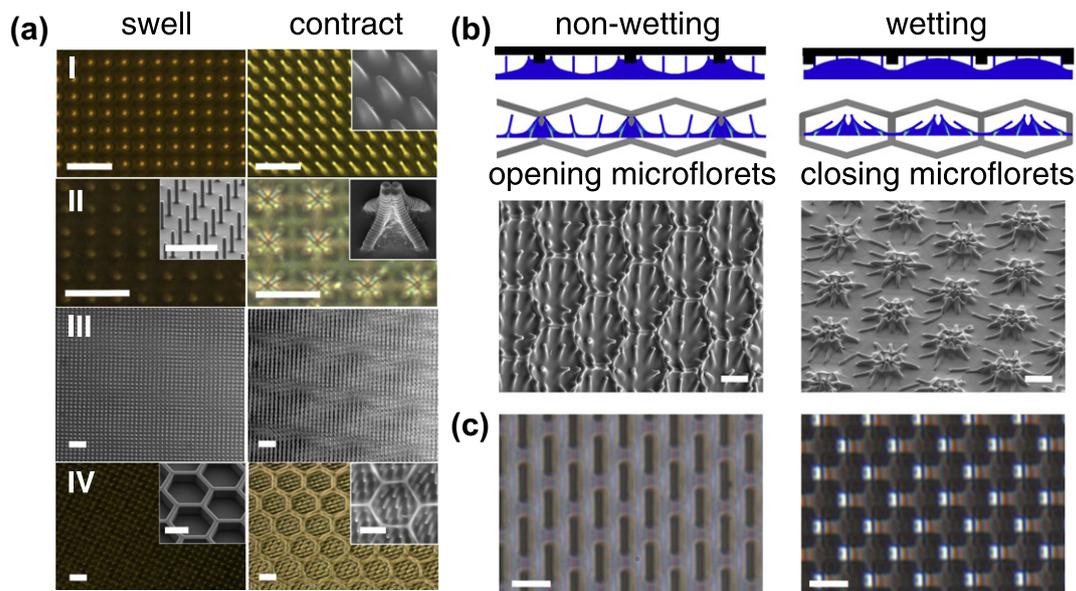


Fig. 6. (a) Optical microscope images comparing various reconfigurable HAIRS samples fabricated from an array of polymer microposts ($1.5\ \mu\text{m}$ diameter, $10\ \mu\text{m}$ height, $8\ \mu\text{m}$ pitch, square array pattern) and using confining surfaces with different patterns. I: flat confining surface resulting in unidirectional bending, II and III: the same HAR post as confining surface resulting in the formation of cross array from four adjacent posts or a Moiré pattern, and IV: honeycomb well (wall to wall distance = $30\ \mu\text{m}$) confining surface resulting in the formation of microfloret arrays. Scale bars are $20\ \mu\text{m}$ in all images. (b) Schematics comparing the effect of wettability of the confining surface on the resultant microfloret arrays as shown in the SEM images (scale bar = $20\ \mu\text{m}$). An opening microfloret array is formed from a non-wetting confining surface, while a closing microfloret array is formed from an oxygen plasma-treated, wetting confining surface. (c) Optical microscope images of HAIRS fabricated from a $15\ \mu\text{m}$ tall microfin array in its upright configuration when the hydrogel is swollen (left), and in reconfigured pattern of overlapping tiles by the bending actuation of each microfin along the preferred axis due to symmetry when hydrogel is contracted (right).

the confining surfaces to the hydrogel precursor solution also influences the patterns generated as shown in Fig. 6b. In particular, the florets formed using the honeycomb-patterned confining surface either open or close depending on the wettability of the confining surface. Therefore, one can create a variety of adaptively and dynamically reconfigurable patterns by (i) carefully designing the symmetry of the structural elements, (ii) combining them with appropriately patterned confining surfaces, and (iii) controlling their wetting properties.

6. HAIRS in liquid

Thus far, all HAIRS systems presented have used humidity responsive hydrogel. Humidity responsive systems could be useful for some purposes such as surfaces with switchable wettability (i.e., when it is humid the surface is hydrophobic and when it is dry the surface hydrophilic) [10]. However, many other proposed applications of microscale actuators, such as propulsion, particle trapping and release, mixing, or cargo transport, typically occur in fluidic environments [6,76]. Therefore, integration of HAIRS with hydrogels that function while completely submerged would be desirable, and a wide variety of hydrogels (pH responsive, temperature responsive, light responsive, etc.) can be utilized.

We have extensively explored HAIRS systems functioning in aqueous environments which respond to pH based on poly(acrylic acid-co-acrylamide), poly(AAm-co-AAc), hydrogel [13,14]. The volume phase transition of this hydrogel is fairly sharp and highly reversible. Similar to the HAIRS involving humidity responsive hydrogels working in the HAIRS-2 architecture, a pH-responsive system generates a bent (or strained) conformation of surface

structures in the contracted state and an upright (or unstrained) conformation in the hydrogel's swollen state.

pH-responsive gels exhibit anisotropic swelling/deswelling behavior, such that the process of swelling is always slower than deswelling [77]. This asymmetry in swelling rates is common among hydrogels which function in submerged environments due to differing rates of diffusion of water in and out of the gel; these diffusive properties lend more complexity in such HAIRS. The rates of diffusion are tunable and depend on a number of factors including gel thickness, crosslinking density, and ionic strength. Even though diffusion may be a relatively slow process, the hydrogels used in HAIRS are generally very thin (on the order of 10 μm or less), so the actuation is quite fast (fractions of a second) and it can be difficult to visualize such asymmetric behaviors without the aid of a high speed camera. One way to observe how this swelling/deswelling rate is transduced to the bending of the underlying structures is to slow down the rate of pH change significantly, and thus slow down the volume transition rate. Use of electrochemically generated pH gradients [78] allows for gradual, controllable, and reproducible rates of pH change across a sample, and this method allows us to observe in real time the phase transition of the hydrogel and how it correlates with the rates of actuation (Fig. 7a).

HAIRS which function in a submerged environment can also be integrated into microfluidic systems as shown in Fig. 7b. Not only does this bring the actuation system closer to applications (for example, in lab-on-a-chip devices) but phenomena occurring in microfluidic environments, such as laminar flow, allow for the control and localization of flow of acid and base over pH-responsive HAIRS. Acid and base in laminar flow across a sample can, for example, create a highly localized actuation response in which

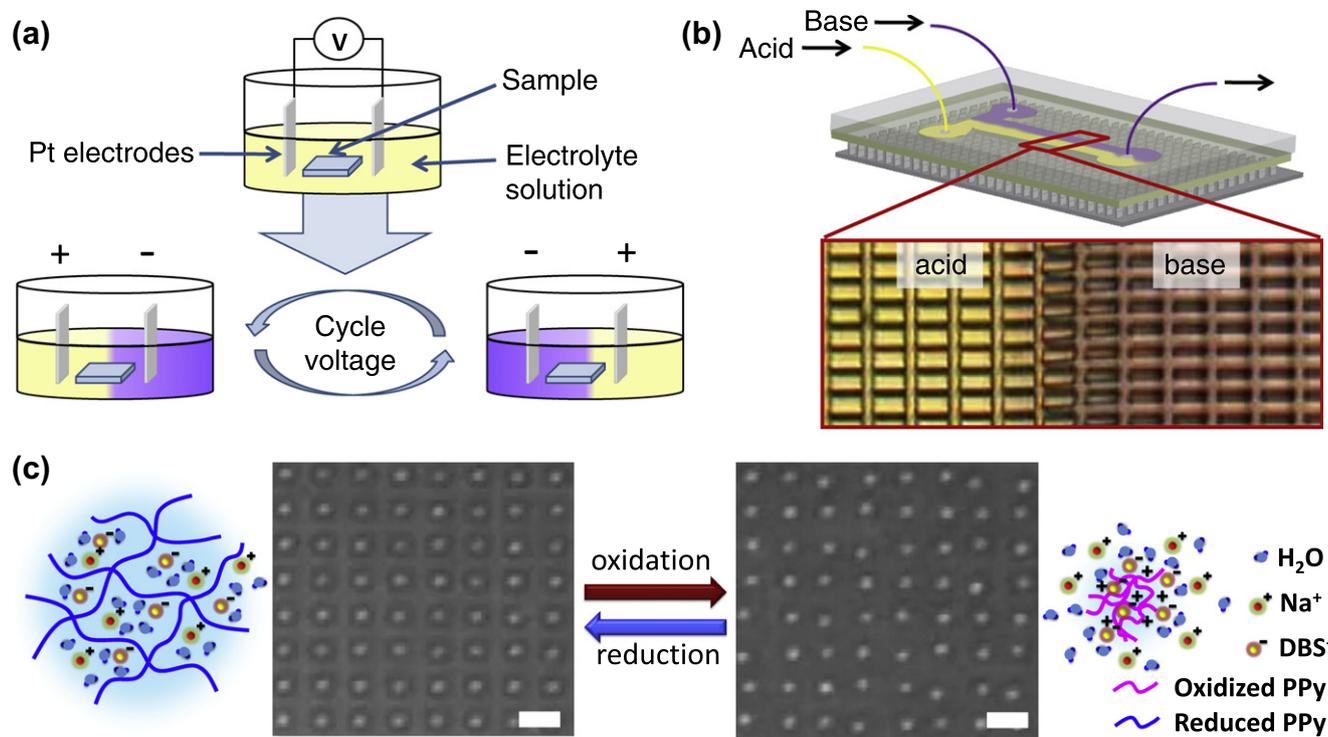


Fig. 7. (a) Schematics of pH-responsive HAIRS actuated by electrochemically generated pH gradients represented as yellow (acidic) and purple (basic) color. Electric fields of ca. ± 0.5 V/mm can induce the actuation of the microfin array shown in (b). Switching of the polarity of the applied electric field reverses the effect. (b) Schematics and optical microscope images of HAIRS fabricated using a microfin array (10 μm in length, 15 μm tall) embedded in pH-responsive hydrogel. HAIRS operating in a microfluidic channel demonstrates spatially controlled actuation of microfins using laminar flows of acid and base. Microfins are bent when the hydrogel contracts in acid and restore the original upright configuration when the hydrogel swells in base. The color arises from bromophenol blue indicator. Flow is from top to bottom of the images. (c) Schematics and optical microscope images of HAR structures actuated by conductive polymer muscle, polypyrrole (PPy), in 0.1 M sodium dodecylbenzenesulfonate (Na^+DBS^-) electrolyte solution. Reversible actuation of the HAR nanopillars is possible by cycling the applied DC voltage between -1.0 V (reduction) and 0.5 V (oxidation). Scale bar = 10 μm .

only the structures under the acid are bent while the structures under the base are upright (Fig. 7b).

HAR structures can also be actuated in liquid using electroactive polymers or composites of them with hydrogels [79–81]. Conductive polymers such as polypyrrole or polyaniline can be selectively deposited by electrochemical deposition on our HAR structures using the STEPS method [42]. Cycling of the voltage applied to these samples in an electrolyte solution gives rise to reversible changes of the oxidation states of the conductive polymer backbone, which in turn induces the movement of counter ions to restore electroneutrality. The associated reversible volume change of the conductive polymer muscle results in the actuation of nanopillars as shown in Fig. 7c. However, the extent of actuation is limited compared to HAIRS due to the relatively small strain (typically 30%) generated by the conductive polymer muscle [82].

7. Summary and outlook

By reducing adaptation to the simple problem of hydrogel-driven nanostructure movement, the HAIRS strategy provides unprecedented versatility in stimulus–response coupling, in tuning the sensitivity, pattern, complexity, and scale of the response, and in incorporating the surfaces into a variety of structures and environments. The fabrication techniques we have developed in conjunction with this platform enable us to take advantage of its many degrees of freedom. Nanostructure stiffness can span the range from hard to soft by varying the material composition, geometry, and/or mechanical reinforcement, enabling the surfaces to sense and generate a broad range of force magnitudes. Precise specification of the shapes, symmetries, orientations, and tilts of nanostructures makes it possible to translate isotropic forces into anisotropic motions to generate both directional actuation and complex patterns. Gradients of any of these features across the surface, or large-scale surface deformations such as twisting, can be used to build these motions into multiscale, hierarchical responses. Topographically patterning the gel itself complements nanostructure manipulation to orchestrate complex patterned motions such as opening and closing of microfingers, while varying the nanostructure materials and surface chemistry enables even further specification of the pre- and post-response surface properties. As demonstrated by our switchable wetting surfaces [10,11], the hybrid system allows components to be attached in multiple configurations, enabling a single stimulus to be translated into either of two opposite responses by only a small variation in design. The versatility in input–output scenarios is matched by the HAIRS system's potential to function just about anywhere; tailoring the gel enables functionality in liquid or air, and, as we have begun to explore, the surface materials and flexibilities can be optimized for microfluidic systems as well as a variety of curved or uneven surfaces.

Yet continuing research suggests we have only begun to mine the possibilities of this system. In addition to our simulations, other sophisticated modeling efforts [73,83] inspired by our work on HAIRS suggest that, while stimulus–response coupling is ultimately unidirectional on the scale of relevant properties, a complex interplay between the hybrid components underlies the response and offers another realm that can be manipulated to specify the sensitivity, amplification, and kinetic profile, and potentially to create dynamic feedback loops. In general, the ability to tune nanostructure stiffness along the whole spectrum, from hard to soft, enables HAIRS to unite at least two disparate lines of responsive materials research. At one end of the spectrum, as assumed in the latter models, an array of stiff structures constrains hydrogel swelling analogously to the rigid substrates that give rise to complex forces and surface patterning in elastomeric media

[38–40]. At the other end, soft structures approach the elasticity of the gel polymers and provide some advantages of more traditional hybrid hydrogels [84]. In both cases, however, HAIRS is unique: in the first, the rigid nanostructures can move; in the second, the soft array retains its own distinct structure rather than mixing as a gel ingredient. The HAIRS system therefore provides a platform for drawing on, integrating – and providing new insight into – theoretical and practical progress in the budding field of adaptive functional materials. Ultimately, the HAIRS strategy enables us to envision making dynamic responsiveness a widespread feature of our material environment, from roofs and clothing that reversibly switch their wetting properties, to walls, planes, and bridges that change color in response to mechanical stress, to windows that adapt reflectivity according to temperature, to pipes that actively regulate flow speed and direction based on liquid chemistry, and a vast array of additional possibilities yet to be imagined.

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