

Smart Actuators and Adhesives for Reconfigurable Matter

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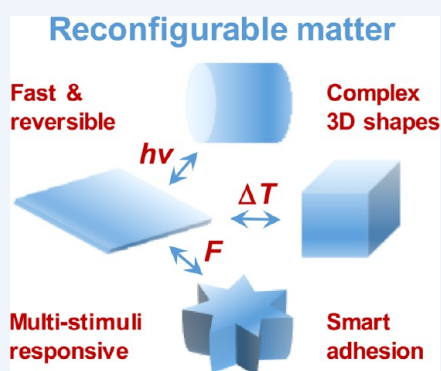
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CONSPECTUS: Biological systems found in nature provide excellent stimuli-responsive functions. The camouflage adaptation of cephalopods (octopus, cuttlefish), rapid stiffness change of sea cucumbers, opening of pine cones in response to humidity, and rapid closure of Venus flytraps upon insect touch are some examples of nature's smart systems. Although current technologies are still premature to mimic these sophisticated structures and functions in smart biological systems, recent work on stimuli-responsive programmable matter has shown great progress. Stimuli-responsive materials based on hydrogels, responsive nanocomposites, hybrid structures, shape memory polymers, and liquid crystal elastomers have demonstrated excellent responsiveness to various stimuli such as temperature, light, pH, and electric field. However, the technologies in these stimuli-responsive materials are still not sophisticated enough to demonstrate the ultimate attributes of an ideal programmable matter: fast and reversible reconfiguration of programmable matter into complex and robust shapes. Recently, reconfigurable (or programmable) matter that reversibly changes its structure/shape or physical/chemical properties in response to external stimuli has attracted great interest for applications in sensors, actuators, robotics, and smart systems. In particular, key attributes of programmable matter including fast and reversible reconfiguration into complex and robust 2D and 3D shapes have been demonstrated by various approaches.

In this Account, we review focused areas of smart materials with special emphasis on the material and device structure designs to enhance the response time, reversibility, multistimuli responsiveness, and smart adhesion for efficient shape transformation and functional actuations. First, the capability of fast reconfiguration of 2D and 3D structures in a reversible way is a critical requirement for programmable matter. For the fast and reversible reconfiguration, various approaches based on enhanced solvent diffusion rate through the porous or structured hydrogel materials, electrostatic repulsion between cofacial electrolyte nanosheets, and photothermal actuation are discussed. Second, the ability to reconfigure programmable matters into a variety of complex structures is beneficial for the use of reconfigurable matter in diverse applications. For the reconfiguration of planar 2D structures into complex 3D structures, asymmetric and multidirectional stress should be applied. In this regard, local hinges with stimuli-responsive stiffness, multilayer laminations with different responsiveness in individual layers, and origami and kirigami assembly approaches are reviewed. Third, multistimuli responsiveness will be required for the efficient reconfiguration of complex programmable matter in response to user-defined stimulus under different chemical and physical environments. In addition, with multistimuli responsiveness, the reconfigured shape can be temporarily affixed by one signal and disassembled by another signal at a user-defined location and time. Photoactuation depending on the chirality of carbon nanotubes and composite gels with different responsiveness will be discussed. Finally, the development of smart adhesives with on-demand adhesion strength is critically required to maintain the robust reconfigurable shapes and for the switching on/off of the binding between components or with target objects. Among various connectors and adhesives, thermoresponsive nanowire connectors, octopus-inspired smart adhesives, and elastomeric tiles with soft joints are described due to their potential applications in joints of deformable 3D structures and smart gripping systems.



1. INTRODUCTION

Reconfigurable matter is a stimuli-responsive material that reversibly changes its structure/shape or physical/chemical properties in response to external stimuli.^{1,2} Because of its tunable shape and properties, reconfigurable matter has attracted significant interest for applications in sensors, actuators, robotics, and smart systems.³ Amazing examples of reconfigurable matter

that simultaneously change shape and properties can be found in nature; for example, some cephalopods (octopus, cuttlefish) can adapt to various environmental changes and easily change their shape and skin color for camouflage purposes (Figure 1a,b).⁴

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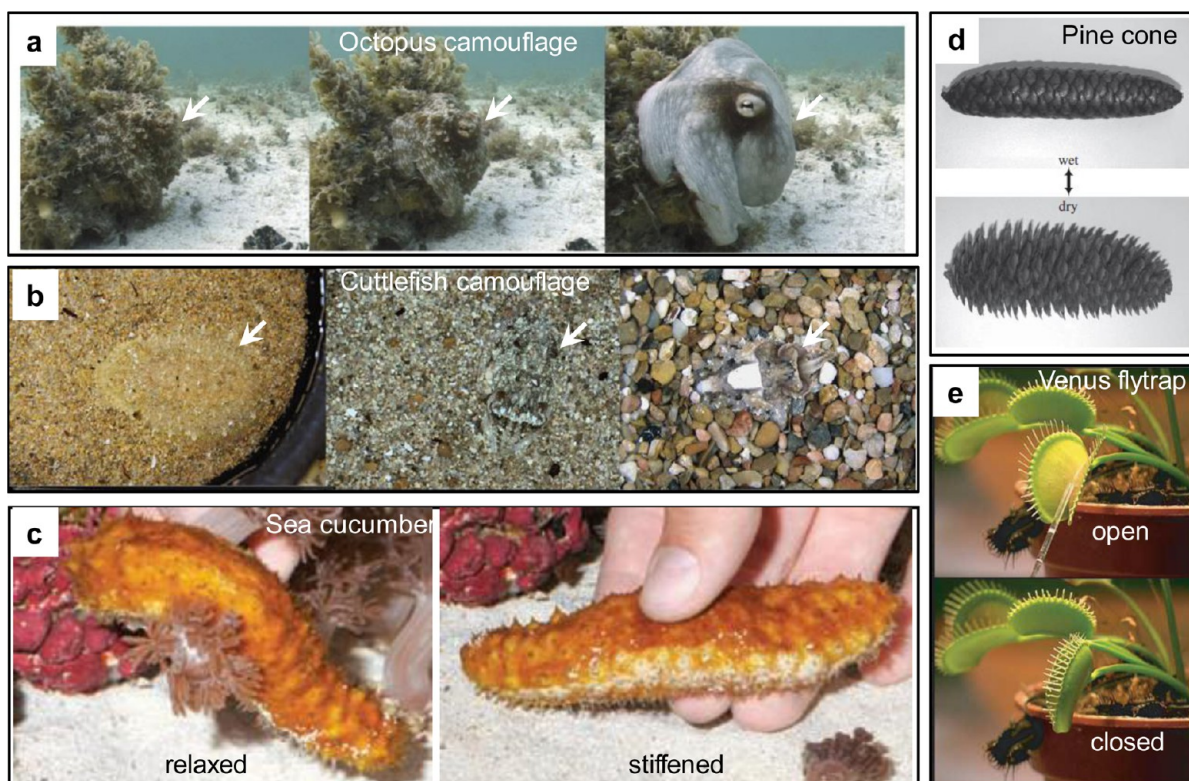


Figure 1. Reconfigurable matter in nature that changes shape and properties. (a) Octopus camouflage with change of both color and shape. (b) Cuttlefish changes its color and shape in response to an environment change. Copyright 2007; reprinted from ref 4 with permission from Elsevier. (c) Sea cucumbers rapidly and reversibly alter their stiffness as a defensive mechanism. Copyright 2008; reprinted from ref 5 with permission from AAAS. (d) Closed, tightly packed pine cone opens gradually in response to a change in humidity. Reproduced with permission from ref 6; copyright 2009 (Royal Society of Chemistry). (e) Venus flytrap snapping together in 0.1 s to capture insects. Reprinted by permission from Macmillan Publishers Ltd: *Nature* (ref 7), copyright 2005.

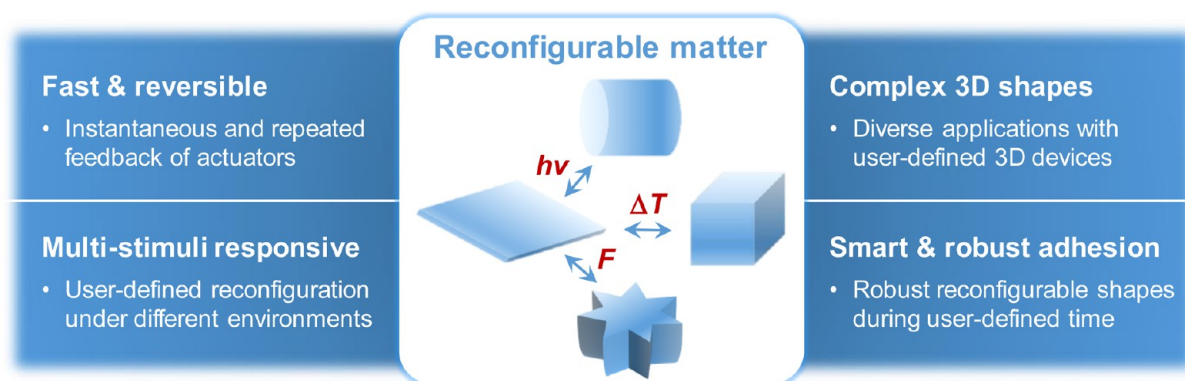


Figure 2. Key attributes of programmable matter that change their 2D shape into a 3D shape in response to external stimuli.

Other examples of biological reconfigurable matter include the rapid stiffness change of sea cucumbers as a defense mechanism (Figure 1c),⁵ opening of pine cones in response to humidity (Figure 1d),⁶ and rapid closure of Venus flytraps upon insect touch (Figure 1e).⁷ Artificial alternatives to these biological reconfigurable matters are still in their infancy compared to biological systems but have shown great recent progress. Bioinspired design of responsive polymer pillar arrays has shown stimuli-responsive functionalities including tunable wetting, adhesion, and actuation.⁸ Stimuli-responsive materials based on hydrogels, responsive nanocomposites, hybrid structures, shape memory polymers, and liquid crystal elastomers

have demonstrated excellent responsivities to various stimuli such as temperature, light, pH, and electric field.²

Among various stimuli-responsive materials, hydrogels and their hybrid structures have been predominantly investigated due to their significant change in physical/chemical properties in response to a large variety of stimuli such as temperature, pH, light, electric field, and so forth.³ Poly(*N*-isopropylacrylamide) (pNIPAM) hydrogels are a representative example exhibiting a dramatic change in physical/chemical properties in response to temperature.⁹ The pNIPAM hydrogel absorbs water and swells at a temperature below the lower critical solution temperature (LCST). Conversely, when the temperature is above the LCST, the water expels from the hydrogel network and the hydrogel

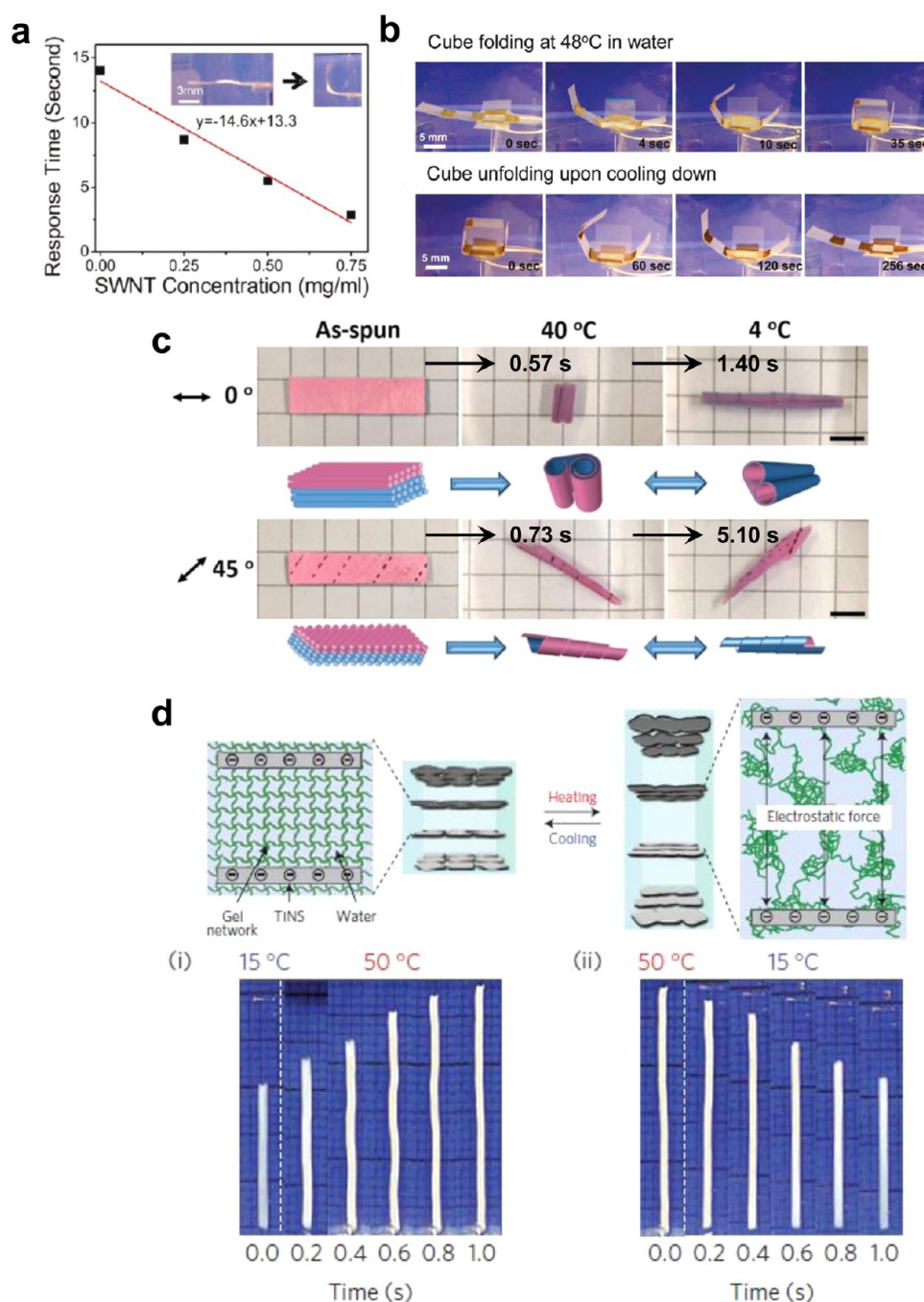


Figure 3. Fast and reversible hydrogel structures. (a, b) Thermoresponsive SWNT-pNIPAM hydrogel actuators. (a) Response time of actuator for 90° folding. (b) Programmable folding cube based on thermoresponsive hydrogel actuator. Copyright 2011; reproduced from ref 17 with permission from the American Chemical Society. (c) Rapid actuation of the bilayer TPU/P(NIPAM-ABP) fibrous membrane with different orientations of fibers at 0° and 45° with respect to the long axis of the sample in water at 40 and 4 °C, respectively. Copyright 2016; reproduced from ref 20 with permission from John Wiley and Sons. (d) Rapid thermoresponsive deformation of a PNIPAA/TiNS hydrogel rod in a glass capillary. Reprinted by permission from Macmillan Publishers Ltd.: *Nat. Med.* (ref 23), copyright 2015.

shrinks. This volume phase transition is similarly observed when the other stimuli including solution pH, solvent mixture, ionic strength, and electric field are applied on the pNIPAM hydrogel.^{3,9} As will be discussed later, this phase transition behavior of hydrogel significantly affects the response time, deformability, mechanical strength, responsiveness, and surface adhesion properties, all of which can be tuned by employing microstructures, hybrid materials, and functional nanomaterials within the hydrogels.

Recent research of stimuli-responsive materials has been driven primarily by the requirement of fast, reversible, complex, and robust reconfiguration in response to various physical and chemical stimuli. Figure 2 illustrates key attributes of programmable matter that change their 2D shape into 3D structures in response to external stimuli. For this reconfiguration process to be enabled, there are several critical functions (fast and reversible, complex shapes, multistimuli responsive, and robust adhesion) that are necessary for the reconfigurable matter. In this article, we review focused areas of smart materials with special emphasis on

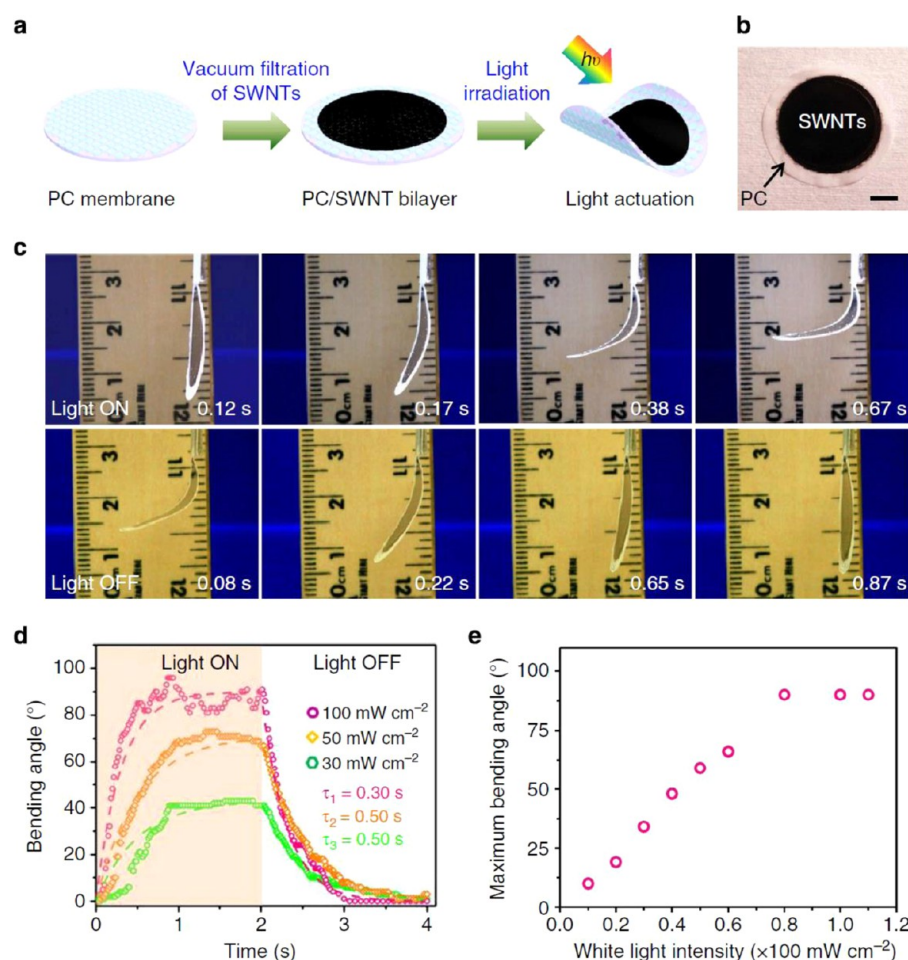


Figure 4. Photothermal actuation of the PC/SWNT bilayer film. (a, b) Fabrication of the bilayer actuator by vacuum filtration. (c) Photoactuation of the bilayer film. (d) Bending angle variation of the bilayer actuator for switching light on/off at different intensities. (e) Variation of maximum bending angle as a function of light intensity. Reprinted by permission from Macmillan Publishers Ltd.: *Nat. Commun.* (ref 27), copyright 2014.

the material and device structure designs to enhance the response time, reversibility, multistimuli responsiveness, and smart adhesion for efficient shape transformation and functional actuations.

2. FAST AND REVERSIBLE PROGRAMMABLE STRUCTURES

Among various stimuli-responsive materials, hydrogels have been dominantly investigated for shape-programmable matter due to the dramatic change of their shapes between 2D and 3D structures through swelling, shrinking, and distortions.^{2,9} For applications of shape-programmable matter in areas of artificial muscles, robotics, and smart actuation systems, the capability of fast reconfiguration of 2D and 3D structures in a reversible way is a critical requirement. Hydrogel-based programmable matters have shown excellent reversibility in diverse applications, but most hydrogel actuators suffer from weak mechanical strength and slow reconfiguration processes. The hydrogel is mechanically weak due to the existence of a large amount of fluid and the inhomogeneous polymer network.¹⁰ For the mechanical strength of the hydrogel to be enhanced, several approaches have been reported, such as reinforced composites by adding carbon nanotubes¹¹ or graphene¹² and modification of polymer network structures through interpenetrating networks and grafting approaches.¹⁰ The slow response time is attributed to limited water diffusion through the bulk network of hydrogel polymers

during the swelling/shrinking process. It is known that the characteristic time of swelling and shrinking of the hydrogel is proportional to the square of the smallest dimension of the hydrogel and inversely proportional to the diffusion coefficient of the hydrogel.¹³ Therefore, at least one dimension of the hydrogel should be sufficiently scaled down for the enhanced swelling/shrinking response time.

Because the water diffusion is the rate-limiting factor in the swelling/shrinking kinetics, one way to increase the response time of hydrogel actuators is to scale down the bulk hydrogel to microscale structures (microvalve, microlens), which can shorten the water diffusion path and thus improve the response time (below 10–20 s).^{14,15} The diffusion rate in submicrometer-scale porous structures is known to be enhanced by 3 orders of magnitude compared with that of nonporous materials.¹⁶ One recent approach to increase the response time of a hydrogel actuator is the addition of carbon nanotubes in the hydrogel for the formation of enhanced water diffusion channels within the hydrogel composites.¹⁷ Panels a and b in Figure 3 show the thermoresponsive actuation of a thin-layer of a single-walled carbon nanotube (SWNT)-pNIPAM hydrogel film deposited on the low density polyethylene (LDPE) film with anchor hole arrays. In this 2D bilayer architecture, when the temperature is above the LCST of pNIPAM, water loss in the SWNT-pNIPAM layer results in a contraction-induced mechanical strain, actuation of the 2D bilayer at predefined sites (hinge area with

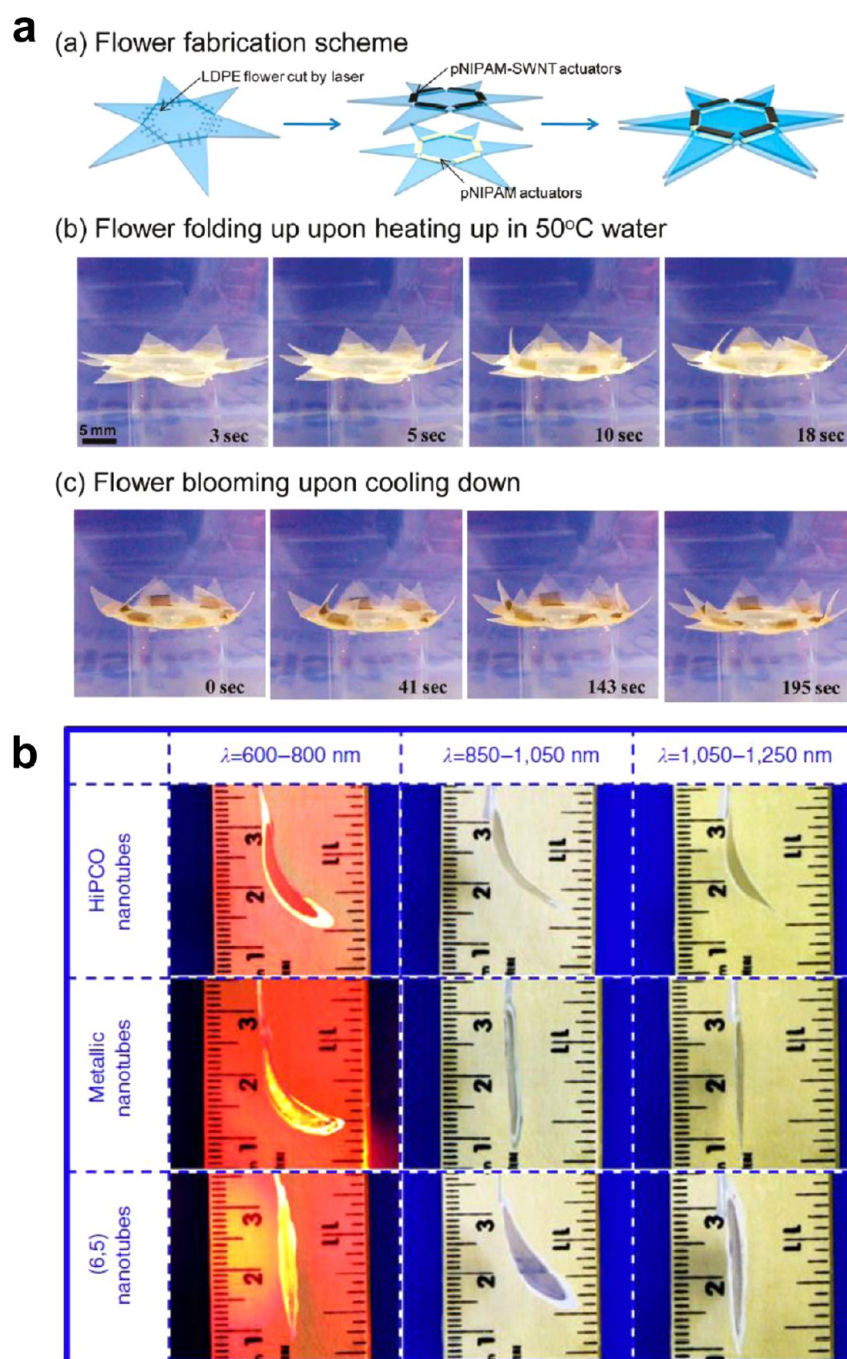


Figure 5. Multistimuli reconfigurable complex structures. (a) Programmable flower-shape actuator based on the multilayer integration of the pNIPAM and SWNT-pNIPAM bilayer. Copyright 2011; reproduced from ref 17 with permission from the American Chemical Society. (b) Photoactuation of the SWNT/PC bilayer film with wavelength-selective response depending on the type of SWNTs. Reprinted by permission from Macmillan Publishers Ltd.: *Nat. Commun.* (ref 27), copyright 2014.

anchored holes), and thus folding of the bilayer structure. The response time linearly decreases with the increase of SWNT content (Figure 3a). In particular, the response time of a hydrogel with 0.75 mg/mL of SWNTs is ~ 2.7 s, which is 5-times faster as compared to that of the hydrogel without SWNTs (~ 14 s). This greatly enhanced response time can be attributed to the enhanced water diffusion rate via the formation of fluidic channels between pNIPAM and SWNTs.¹⁸

The SWNT-pNIPAM hydrogel actuators with fast response time can be employed in the development of shape-reconfigurable systems with programmable shapes and response

times. Figure 3b shows a programmable folding cube based on SWNT-pNIPAM hydrogel actuators on a laser-patterned LDPE film. The self-folding cube can fold by itself when heated in warm water (48 °C) and unfold when cooled in cold water (24 °C). Contrary to the irreversible self-folding structures based on etching of sacrificial polymer and predefined residual stress release,¹⁹ the self-folding cube based on SWNT-pNIPAM hydrogel actuators can be reversibly reconfigured in response to a repeated heating/cooling process, which is a prerequisite for practical application of self-folding actuators.

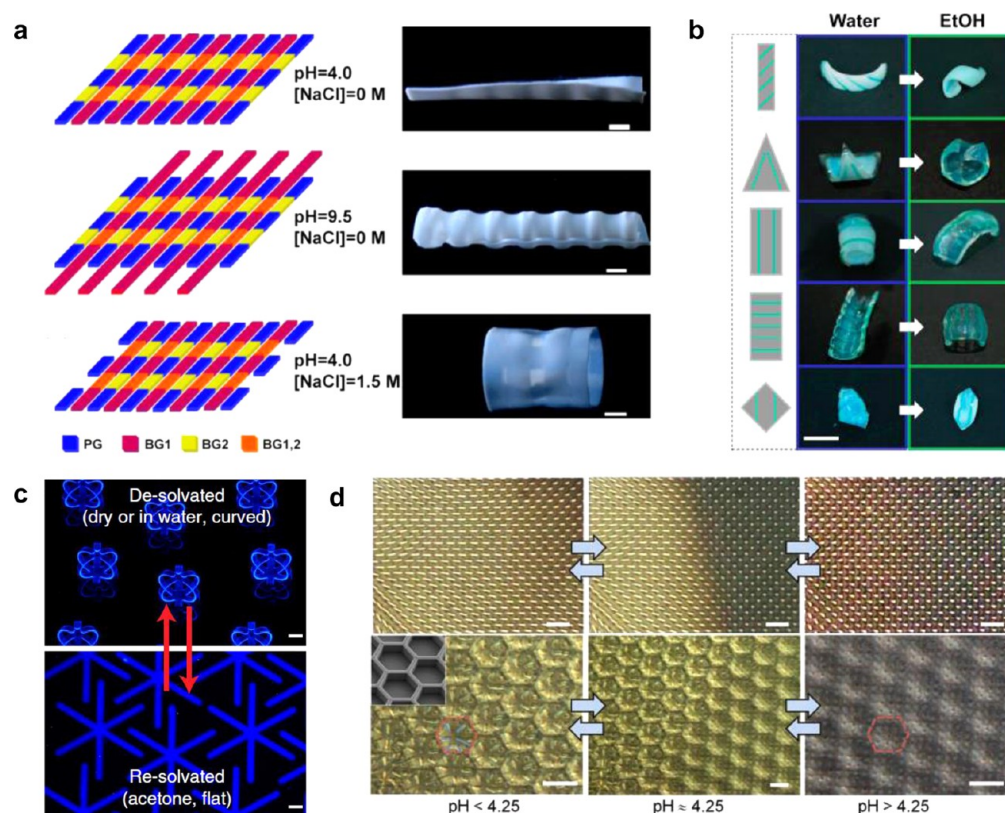


Figure 6. Multistimuli reconfigurable complex structures. (a) Shape transformations of the composite gel sheet patterned with perpendicularly oriented binary gel stripes in response to different pH levels. Copyright 2013; reproduced from ref 36 with permission from the American Chemical Society. (b) Multiresponsive bilayer hydrogel sheet actuators, whose directional bending response is tuned by modulating the solvent quality and locally cross-linked patterns induced by ionoprinting. Reproduced from ref 37. (c) Differentially cross-linked and conditioned SU-8 films: Fluorescence images of an array of flower-shaped structures that (top) reversibly curve upon desolvation and (bottom) flatten upon resolvation. Scale bars are 100 μm . Reprinted by permission from Macmillan Publishers Ltd.: *Nat. Commun.* (ref 38), copyright 2011. (d) pH-responsive surface actuation in response to pH gradients for (upper) flat confinement and (bottom) confinement using a honeycomb-patterned surface. Copyright 2011; reproduced from ref 39 with permission from John Wiley and Sons.

Electrospun hydrogel nanofiber mats are another approach to fabricate high-porosity hydrogel actuators with fast response times. In particular, when the nanofibers are unidirectionally oriented, directional actuation functionality can be obtained without sacrificing the response time. Figure 3c shows the actuation of a fibrous bilayer system with oriented polyurethane and PNIPAM fibers for directional actuation.²⁰ The actuation is fast with ~ 0.6 – 5.1 s for rolling and reverse rolling actuations at high and low temperatures. Of particular interest, depending on the fiber orientation with respect to the long axis of the film, directional rolling can be achieved. The strategy of decreasing water diffusion time in porous structures was also utilized in water-triggered shape memory polymers, where microfibrillar web structures greatly reduce the shape recovery time down to 1.3 s.²¹ Water is known to reversibly change its electrostatic permittivity, which decreases on the hydration and recovers on the dehydration of the hydrogel.²² This property has been utilized in the design of fast and directional thermoresponsive actuators enabled by permittivity switching in an electrostatically anisotropic hydrogel.²³ Figure 3d shows hydrogel composites containing cofacial electrolyte titanate nanosheets (TiNSs), which exhibit enhanced response time and directional actuation due to electrostatic repulsion between cofacial nanosheets.²³ The hydrogel shows 70% directional deformation per second upon the heating and cooling process. Temperature-responsive shape memory polymers that do not require water can be potentially

actuated fast because their response time is not limited by water diffusion like hydrogel systems.²⁴ However, heat transport and the subsequent phase transition is still a limiting factor for the fast response time. Strategies to increase the thermal conductivity of shape memory polymers such as adding carbon nanotubes²⁵ and graphenes²⁶ have been employed to increase the response time.

Photothermal actuation can be another way to provide reversible shape reconfigurations with enhanced response time of actuation. Panels a and b in Figure 4 show the bilayer photoactuator of an SWNT film on a polycarbonate (PC) film, which can be fabricated simply by the vacuum filtration of SWNT solution on a PC membrane.²⁷ In the SWNT/PC bilayer films, the photothermal effect of the SWNT layer induces the conversion of absorbed photon energy into heat and subsequent thermal expansion of the bilayer structure. The large difference of thermal expansion coefficients (PC is over 10-times larger than that of SWNT) induces the asymmetric thermal expansion of the bilayer, resulting in bending of the bilayer structure toward the SWNT layer. Figure 4c shows the photoresponsive behavior of the bilayer actuator under the exposure of a solar simulator with 1 sun intensity (100 mW cm^{-2}).²⁷ The actuator can be bent 90° in 0.67 s and unbent in 0.87 s when the light is turned on and off, respectively. The response time and bending angle can be tuned depending on the light intensity. As can be seen in Figure 4d and e, the response time and bending angle increase with the increase of light intensity.

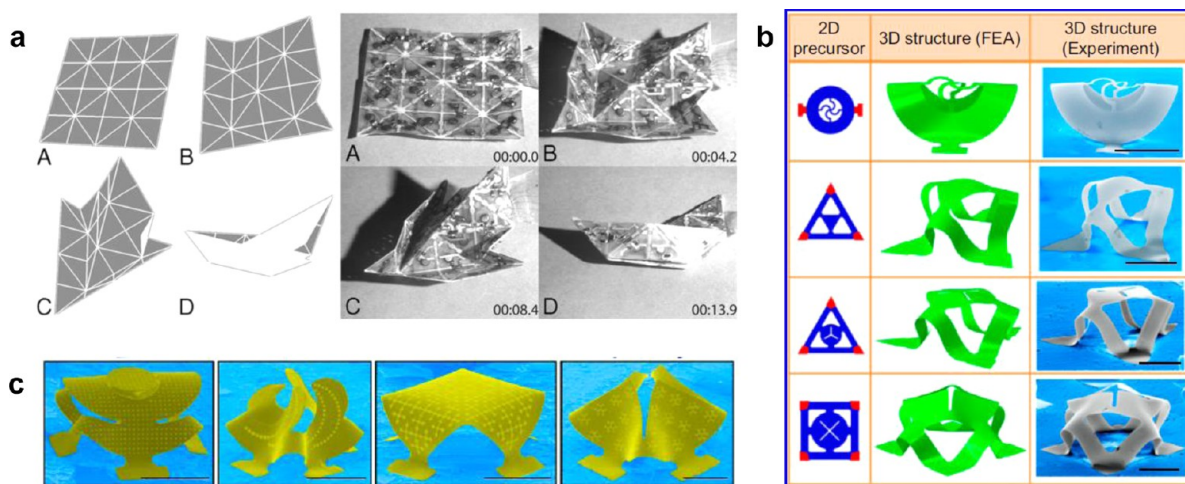


Figure 7. Complex structures by origami and kirigami principles. (a) Self-folding origami “boat” with crease patterns. All actuators receive current, self-fold, and engage magnetic closures. Reproduced from ref 1. (b, c) Kirigami assembly of 3D mesostructures from 2D micro/nanomembranes with strategically designed geometries and patterns of cuts. Reproduced from ref 30.

3. MULTISTIMULI RECONFIGURABLE COMPLEX STRUCTURES

For the use of reconfigurable matter in diverse applications including actuators, robotics, sensors, and smart systems, the ability to reconfigure programmable matters into a variety of complex structures is beneficial. To convert 2D structures into 3D structures, stimuli-triggered asymmetric stress may be applied for autonomous bending or folding.² This principle has been previously applied in the simple bending of curled structures or folding of cubic structures, but these simple structures are not sufficient to be used in various applications requiring specific and complex structures. For the complex 3D structures reconfigured from 2D structures, asymmetric and multidirectional stress needs to be applied. Previously, shape-programming technologies such as local hinges with stimuli-responsive stiffness, multilayer laminations with different responsiveness in individual layers,^{28,29} origami crease patterns,^{1,29} and kirigami cutting patterns^{30,31} have been employed to induce asymmetric and multidirectional stress on 2D structures, thus enabling reconfiguration of 2D structures into complex 3D shapes. However, many of these previous demonstrations are irreversible and thus cannot be reconfigured multiple times.

One approach to demonstrate reconfigurable complex structures is the integration of multiple heterogeneous actuators into a desired structure, where each individual actuator responds differently to the same stimulus, thus providing multilevel control of shape programming for the reconfiguration of complex structures. Figure 5a shows the programmable flower-shape actuator based on the multilayer structure of the pNIPAM and SWNT-pNIPAM bilayer, which mimics the closing or blossoming of a real flower.¹⁷ Here, the first layer is programmed to show a slow thermoresponsive actuation with a pure pNIPAM hydrogel, whereas the second layer is programmed to exhibit a fast response with a SWNT-pNIPAM hydrogel, thus allowing the multilayer actuator to exhibit multilevel response to a single thermal stimulus.

The other approach for enabling complex reconfiguration is the use of multistimuli-responsive actuators that respond to a combination of two or more external signals and reconfigure their complex shapes or functions in a more controlled way.

Photoactuation of the SWNT/PC bilayer film is advantageous for providing a wavelength-selective response of the actuator depending on the type of SWNTs. As the SWNTs show the chirality-dependence of optical absorption,³² the photothermal effects can be tuned depending on the type of SWNTs and the wavelength of incident light. Figure 5b shows the wavelength-dependent response of photoactuators containing SWNTs with different chirality distributions; that is, HiPCO nanotubes with mixed chiralities, metallic nanotubes with M_{11} absorption peak at 700 nm, and (6,5) single-chirality nanotubes with S_{22} and S_{11} absorption peaks at 560 and 970 nm, respectively.²⁷ When the photoactuators are exposed under three different illumination wavelength bands of 600–800, 850–1,050, and 1,050–1,250 nm at the same power, three different bilayers exhibit different light responses. One example of multistimuli-responsive multilevel photoactuation is the expansion and contraction of photo-responsive materials via dual wavelength of light: one for expansion and the other for contraction of photoactuators.³³

Multiple shape transformation of hydrogel composites has been demonstrated by the integration of multiple structural components with different compositions in the regularly structured composite gel, where each component was programmed to respond to a particular well-defined stimuli such as temperature, pH, and ionic strength.^{34–39} Figure 6a shows multiple shape transformations of a composite gel sheet into complex 3D shapes, where the composite gel sheet combines three different photopatterned components with different shrinkage/swelling behaviors in response to a particular pH and ionic strength.³⁶ Ionoprinting is another way to provide locally different cross-linking patterns in the hydrogel sheet actuators. Figure 6b shows various shape transformations of bilayer hydrogel sheets with locally different ionoprinted patterns in response to different solvent environments.³⁷ Figure 6c is another example of locally structured actuators with cross-link gradients along the thickness to provide stress gradients.³⁸ The actuator exhibits an array of flower-shaped structures that reversibly curved and flattened upon solvation switching. The programmable surface texture is attractive in camouflage actuators. In Figure 6d, programmable surface textures have been demonstrated by embedding polymer micropost arrays in the pH-responsive hydrogel film with and without physically confined patterns.³⁹ Here, the hydrogel contraction or swelling at

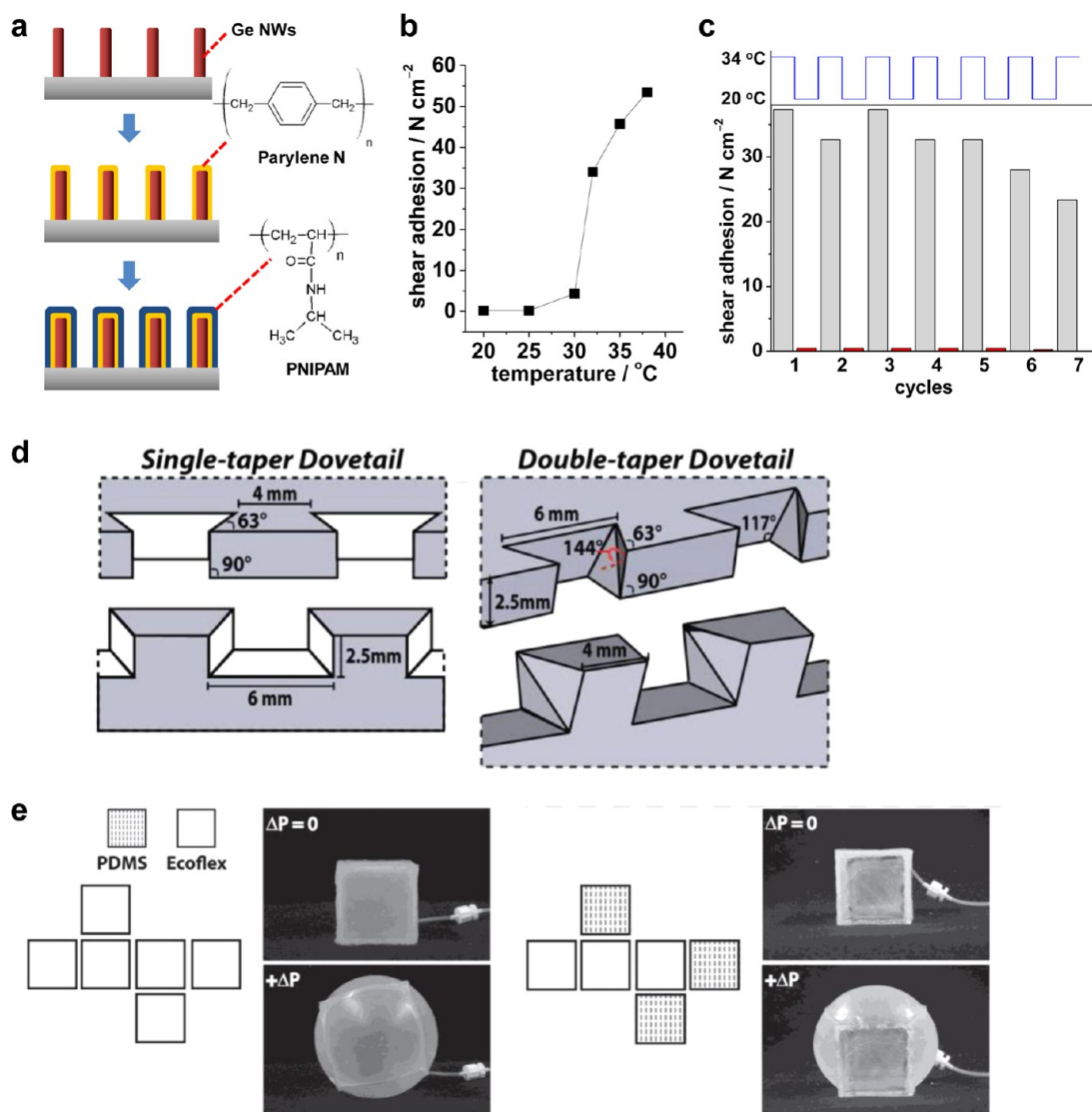


Figure 8. Smart connectors for robust programmable matter. (a–c) Thermoresponsive interlocked NW connectors. (a) NW connector based on Ge/parylene NW forests coated with a pNIPAM hydrogel layer. (b) Shear adhesion strength of NW connectors as a function of water temperature. (c) Switchable adhesion strength of the NW connector for temperatures below and above the LCST of pNIPAM. Copyright 2010; reproduced from ref 43 with permission from John Wiley and Sons. (d, e) Elastomeric tiles with soft joints for the inflatable structures. (d) Schematic of single and double-taper dovetails (top) and mating pins (bottom). (e) Shape-changing cubic structures fabricated from tiles of varying extensibilities. The “lock-and-key” joints resist component separation during the inflation process. Copyright 2014; reproduced from ref 46 with permission from John Wiley and Sons.

different pH levels induces the embedded microstructures under high strain, resulting in the deformation and bending of microposts.

Shape transformations from 2D planar sheets into various 3D complex structures have been challenging by traditional hydrogel actuators. Recently, origami^{1,29} and kirigami^{30,31} assembly approaches have been successfully employed for the reconfiguration of 2D planar sheets into various complex 3D shapes. Here, the origami crease and kirigami cutting patterns induce asymmetric and multidirectional stress on 2D structures, thus enabling transformation into complex 3D structures. The detailed principles of origami and kirigami approaches for diverse materials and shapes can be found in recent review articles.^{29,31} Figure 7a shows a programmable origami sheet that can autonomously fold into a 3D boat shape.¹ Here, the single origami sheet contains repeated triangular tiles connected by flexible creases, thereby decreasing the complexity of traditional approaches relying on many individual subunits. In addition, one

single origami sheet can be preprogrammed to adopt several 3D shapes. The kirigami approach involves cutting and folding of 2D planar sheets into pop-up 3D structures. Panels b and c in Figure 7 show that 2D planar sheets with various cutting patterns can be transformed into complex 3D structures.³⁰ Although these origami and kirigami approaches provide promising concepts of complex programmable matter, the reversible reconfiguration is a critical future challenge that can be addressed when combined with reversible actuators.

4. SMART ADHESIVES FOR ROBUST RECONFIGURABLE STRUCTURES

For the practical use of reconfigurable matter, robust adhesion and connection in the desired structure is crucial. Furthermore, the adhesion and connection strength should be easily controllable by the external signal for the facile reconfiguration of programmable matter. Smart connectors or adhesives have been used for the joining of two components (or surfaces)

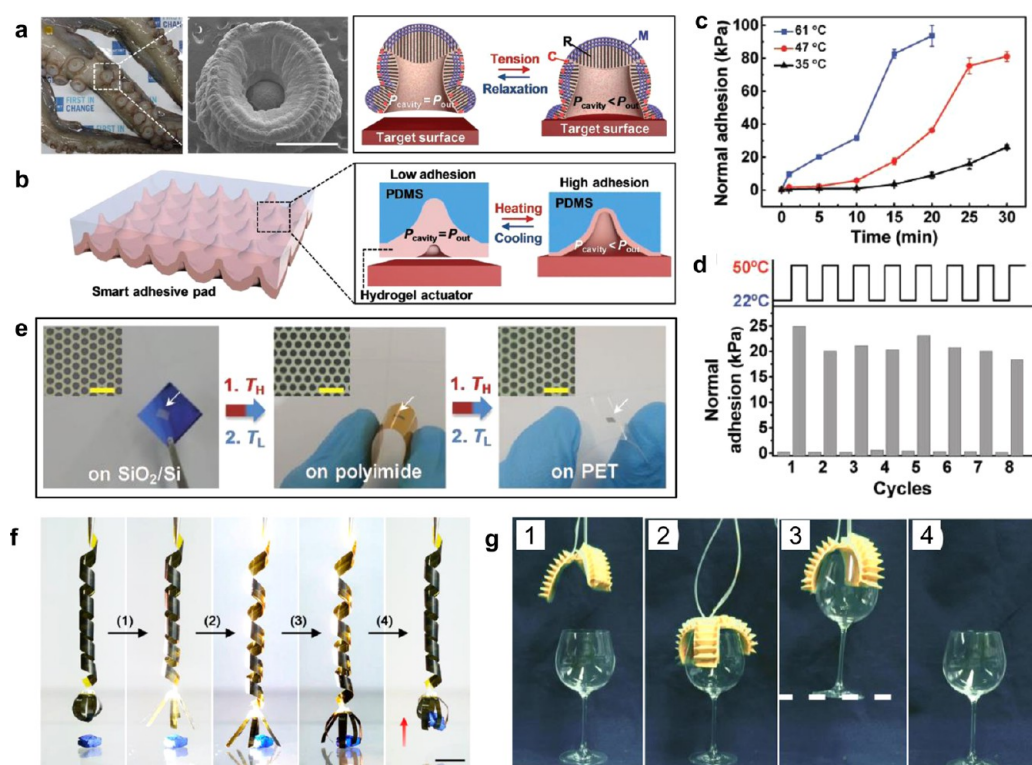


Figure 9. Smart adhesives for the programmable gripper. (a–e) Octopus-inspired smart adhesive. (a) Switchable wet adhesion of octopus suckers. (b) Schematic of octopus-inspired smart adhesive based on a nanohole-patterned PDMS film with a pNIPAM hydrogel coating that exhibits thermoresponsive swelling/shrinking of nanoholes. (c) Adhesion strength as a function of time at various temperatures. (d) Switchable adhesion at low and high temperatures. (e) Smart printing for the sequential transfer of the Si membrane on various substrates. Copyright 2016; reproduced from ref 49 with permission from John Wiley and Sons. (f) Aligned CNTs in paraffin wax on a polyimide substrate for the photoresponsive gripping and lifting of an object. Copyright 2016; reproduced from ref 54 with permission from the American Chemical Society. (g) Elastomeric pneumatic gripper picks up a wine glass by gripping the exterior surface gripper using positive pressure (~ 100 kPa): the convex curvature on the interior of the gripper surface conformed to the convex exterior of the smooth glass. Copyright 2013; reproduced from ref 55 with permission from John Wiley and Sons.

together or sticking of one component to another arbitrary component in response to external stimuli,^{8,42} which may find applications in robust reconfigurable matter. For reconfigurable matter, the adhesive functions such as high adhesion strength, high on/off adhesive strength ratio, and repeated switchability will be required.

Figure 8a shows the thermoresponsive connectors based on Ge/parylene core/shell nanowire (NW) forests coated with a pNIPAM hydrogel layer.⁴³ In this Ge/parylene/pNIPAM connector structure, the outermost PNIPAM shell serves as the thermoresponsive muscle for the modulation of the adhesion properties of the hybrid NW connector. Similar to the hook and loop interlocked geometry of Velcro fasteners, the NW connector system is established when the two hybrid NW connectors are combined together with the NW sides facing each other, resulting in an interlocking geometry.^{40,41,44,45} In this geometry, the van der Waals bonding between interlocked NW contacts is amplified by the geometric configuration of high aspect ratio NWs, which enables a strong binding of the components. As can be seen in Figure 8b, the shear adhesion strength of NW connectors increases with the water temperature and shows an adhesion strength above 34 N/cm^2 at temperatures above the LCST, which is over 170-times enhancement of minimal adhesion ($\sim 0.2 \text{ N/cm}^2$) at temperatures below LCST. Furthermore, the NW connector exhibits a reversible adhesion strength when the temperature of the connector is switched below and above the LCST of the pNIPAM shell (Figure 8c).

The smart connectors can be potentially employed in the integration and connection of individual components onto the target programmable matter. Although it is not autonomous, a good example of 3D programmable matter enabled by individual tiles and soft connectors is shown in Figure 8d and e.⁴⁶ Here, tapering soft dovetails are used to form interlocked joints between the elastomeric tiles (Figure 8d). When the elastomeric tiles are joined together by dovetail connectors, shape-changing cubic structures with hollow interiors can be fabricated. In particular, when positive pressure is applied on this pneumatic actuator, the dovetail joints withstand large mechanical deformations without failure, enabling robust inflatable cubes (Figure 8e).

For the hydrogel-based shape-programmable matter in a wet environment, a reversible wet adhesion with a high on/off switching ratio will be required. One of nature's example of excellent wet adhesion systems can be found in octopus suckers, which exhibit an excellent switchable wet adhesion to any foreign surface.⁴⁷ An octopus utilizes the muscle actuation of its sucker to control the cavity pressure and thus the pressure-induced adhesion on the contacting surface (Figure 9a).⁴⁸ Figure 9b shows a schematic illustration of octopus-inspired smart adhesive pads that mimic the muscle actuation of a sucker to control the cavity-pressure-induced adhesion.⁴⁹ The smart adhesive pad consists of a poly(dimethylsiloxane) (PDMS) film patterned with nanohole arrays to mimic the sucker hole arrays and a thermoresponsive hydrogel coating of pNIPAM within the PDMS cavity array for the formation of a thermoresponsive

actuator. When the pNIPAM layer within the PDMS cavity swells or shrinks in response to cooling or heating, the cavity volume decreases or increases, resulting in an increase or decrease of cavity pressure and thus the adhesion strength between the adhesive pad and target surface.

Figure 9c shows that the adhesion strength and response time of smart adhesive pads increase with temperature. Here, the on-state adhesion strength of 94 kPa at 61 °C results in the adhesion switching ratio of ~293 with respect to the off-state adhesion strength of 0.3 kPa at 22 °C. Furthermore, the smart adhesive pad maintains excellent switchable adhesion ability even after 100 repeated cycles of attachment/detachment, demonstrating the mechanical durability (Figure 9d). As an example application, this smart adhesive can be employed for the transfer printing of micro/nanostructured materials onto various substrates. As can be seen in Figure 9e, identical Si micromembranes can be reversibly detached at high temperature (T_H) and transferred at low temperature (T_L) onto various Si, polyimide, and poly(ethylene terephthalate) (PET) substrates without damage. This smart printing technique is advantageous over the previous transfer-printing techniques based on kinetically controlled adhesion of planar elastomeric stamps,⁵⁰ which cannot provide a high on/off adhesion ratio.^{51–53}

One potential application of smart adhesives is the grasping/releasing of objects, which have been previously demonstrated by mechanical arm actuators. Figure 9f shows the photothermal actuation of aligned CNT composite films, where an object is lifted up by a mechanical arm actuator.⁵⁴ Another example of a mechanical arm is shown in Figure 9g, where an elastomeric pneumatic actuator picks up and releases a wine glass.⁵⁵ One critical challenge for these mechanical arms is the gripping of heavy objects because most of current actuators do not provide enough force. In the future, actuator grippers combined with smart adhesives can be a viable solution to this issue.

5. SUMMARY AND FUTURE PERSPECTIVES

In this Account, we reviewed focused areas of smart materials with special emphasis on the materials design and fabrication to enhance the response time, reversibility, multistimuli responsiveness, and smart adhesion. However, current technologies of smart materials are still premature for demonstrating the ideal type of programmable matter as described above. Various challenges still remain to be addressed. First, there are trade-off properties in the ideal reconfigurable matter. Mostly, reversible and large deformability can be easily achieved with hydrogel materials, but these hydrogels suffer from slow response and low mechanical strength, which limit their practical application areas. For all of these properties to be achieved simultaneously, new architectures and mechanisms need to be developed. Second, for diverse applications under various physical and chemical environments, site-specific, selective, and multistimuli-responsive materials are needed. Although there have been several attempts to show multistimuli responsiveness in smart actuators, the selective response to a specific signal without disturbance from other signals has been rarely demonstrated. Finally, the previously demonstrated programmable shapes still lack sufficient complexity. In addition, the reconfiguration into dual or multiple shapes within a single device can further expand the utility of reconfigurable matter. For these challenges to be addressed, materials-based approaches to develop smart actuators may be combined with recent developments of shape-programming technologies such as self-folding origami with crease patterns and kirigami 3D structuring. For the

reconfigurable shapes to be maintained, further performance improvements in smart adhesives with on-demand adhesion strength is required for the switching on/off of the binding between components.

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Notes

The authors declare no competing financial interest.

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