Liquid Stratification and Diffusion-Induced Anisotropic Hydrogel Actuators with Excellent Thermosensitivity and Programmable Functionality

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Smart hydrogel actuators with programmable anisotropic structures present fascinating prospects considering their distinctive shape transformation and controllable environmental responsiveness under external stimuli. However, the design of anisotropic hydrogels with simple and universal fabrication and programmable functionality is challenging for their valuable applications in smart actuators and soft robots. Herein, a simple, green, and desirable strategy is proposed to construct a heterogeneous porous hydrogel system by the different liquid diffusion (such as amyl alcohol, water, and ethanol) into a monomeric precursor solution of thermosensitive hydrogels. The well-defined micro/nanoporous gradient and patterned structures related to selective liquid stratification and interfacial diffusion favor the fast response and accurate programmable deformation of hydrogels under temperature stimuli. Inspiringly, this simple diffusion-driven tactic can be perfectly applicable for different responsive hydrogels with programmable multifunctionality by adding functional nanomaterials into the diffusible liquid. This green, general, and facile diffusion-driven strategy provides significant guidance for fabricating environmentally responsive hydrogels with tailorability functionality for their multipurpose applications in drug delivery, bioengineering, smart actuators, and soft robots.

1. Introduction

Hydrogels have attracted significant attention due to their high water absorption, significant volume change in response to stimuli (such as temperature,[1] [Yao, 2015 #59; Zheng, 2015 #60] pH,[2] light,[3] electric field,[4] ions,[5] magnetic field[6]), programmable shape-change ability,[7] and similar physiochemical properties to biological soft tissues,[8] which favor them for potential use in the fields of medicine,[9] drug delivery,[10] bioengineering,[11] artificial muscles,[12] and soft robotics,[13] etc. The 3D deformation of a responsive hydrogel stems from the imbalance in volume change in the local network of heterogeneous structures upon the trigger of external stimuli, which causes internal stress within hydrogels. Therefore, considerable progress has been made in the designing and controlling of heterogeneous structures of hydrogels for further functionality and applicability.[14] Traditional strategies have been used to construct heterogeneous hydrogels by designing double-layer,[15] gradient,[16] and 3D fine structures.[17] For example, a bilayer structure with different types[15d] or diverse amounts of polymerized substance[18] was formed by stepwise polymerizing of a passive polymer hydrogel layer and active polymer hydrogel layer. The mismatched strain or asymmetrical change of volume within the two layers of gels with different properties induced a slow bending/unbending deformation, and possible delamination along a weak interface after a highly repetitive actuation. To overcome this limitation, some improvement approaches were attempted to construct individual hydrogels with laminated or porous structures[7] or with gradient component[19] and concentration differentiation by introducing ions,[20] functional nanoparticles,[21] or nanomaterials[13,22] in a hydrogel precursor, adding a heterobifunctional crosslinker,[23] and adopting special treatment (hydrothermal process, evaporation,[24] etc.) to improve their responsive characteristics under environmental stimuli. The major limitations of the existing preparation methods for heterogeneous hydrogels are their complicated process, complex operation, and difficult adjustment of functionality, which might limit the practical application of hydrogel actuators.
Therefore, the exploration of a simple, green, and universal preparation method for obtaining heterogeneous hydrogels with the capacity of fast actuation, recovering, diverse deformation, and easy functionalization is urgent and challenging.

When two liquids with different densities and properties come into contact, an interface is formed, and diffusion occurs under the action of thermal motion. Just like in a cocktail colorful and stratified structures are observed by mixing different wines, juices, and beverages. Inspired by this phenomenon, we propose a simple, fast, and broadly applicable method for preparing heterogeneous porous hydrogels based on the principle of liquid stratification and interfacial diffusion. We select different solutions, such as water, alcohol, amyl alcohol (AC), glycerol, and aqueous solution with functional materials. Driven by the diffusion of aqueous solution into the precursor solution of a responsive hydrogel, the heterogeneous porous structure can be directly generated and permanently preserved with subsequent gelation under UV light irradiation (Figure 1a). Furthermore, the patterned heterogeneous structure can be programmed by covering the hydrogel precursor with a striated mask. The hydrogel actuators with the heterogeneous structure and patterned surfaces can achieve stable, rapid, and adjustable bending motion in water under temperature, light, or magnetism stimulation. Our strategy has provided a simple, green, and common approach for structuring and functionalization of responsive hydrogels, indicating their potential application for intelligent actuators, soft robots, micromanipulation, and intelligent human–machine interface.

2. Results and Discussion

2.1. Design and Fabrication of Heterogeneous Poly(N-isopropylacrylamide) (PNIPAM) Hydrogels Induced by AC Diffusion

The “like dissolves like” principle states that substances that have the same polarity (either polar or nonpolar) dissolve into each other. The concept of solubility of chemical substances is related to their chemical structure. For example, the longer the carbon chain is in the alcohol solvent, the more insoluble it is in a polar solvent such as water. Based on this rule, the AC is less soluble in fairly polar solvents such as water when compared to ethyl alcohol and causes a stratification phenomenon at the interface of AC and water. The subsequent diffusion of AC in water induced by thermal motion might result in the homogeneous distribution of AC. This would be helpful for the synthesis of composite materials with heterogeneous structure. Here, we study the diffusion of AC in a hydrosoluble precursor solution including N-isopropylacrylamide (NIPAM) monomer, for example, and the typical preparation process of heterogeneous porous hydrogels induced by the principle of liquid stratification and interfacial diffusion is shown in Figure 1a. First, the uniform aqueous precursor solution containing NIPAM monomers, cross-linker, dyestuff, and photoinitiator was prepared and injected into a mold of plastic disks (Figure S1a, Supporting Information). Subsequently, a certain amount of AC was slowly dropped onto...

![Figure 1](image-url)

Figure 1. Fabrication and microstructure of heterogeneous PNIPAM–AC$_x$ hydrogels. a) Schematic illustration of the synthesis of the heterogeneous hydrogel induced by AC diffusion. b–g) Scanning electron microscopy (SEM) images of PNIPAM–AC$_x$ hydrogels with different magnifications: b) obverse surface of gel network, c) reverse surface of gel network, d) overall cross-section, and e–g) corresponding local pore structures.
the surface of the aforementioned aqueous solution. As AC is less dense than water and soluble in water slightly, the AC can spread out rapidly and evenly cover the surface of the precursor well, forming a clear interface and stratified structure[27] (Figure S1b and Movie S1, Supporting Information). The diffusion subsequently happens in a vertical direction at the interface of pentanol and the precursor solution (Figure S1c, Supporting Information). The diffusion of AC drops in the precursor solution was observed by a confocal laser scanning microscope, verifying the highly dispersed state of the microdroplets in the precursor solution (Figure S2, Supporting Information). Finally, the mixture in the mold was irradiated under UV light (365 nm) for 4 min in an ice-water bath, resulting in an anisotropic structure. It can be seen that after the AC diffusion and NIPAM polymerization under UV-light radiation, the obverse side of the obtained PNIPAM hydrogels induced by AC diffusion (PNIPAM–AC) is more rough and hallow, just like sandpaper when compared to the smooth reverse sides of PNIPAM–AC hydrogels (Figure S1d,e, Supporting Information). The scanning electron microscopy (SEM) images also show a heterogeneous structure of the hydrogel with the larger holes on the upper surface (rough obverse side) and the smaller ones on the lower surface (smooth reverse side) (Figure 1b,c). The SEM cross-section images confirm the hierarchical gel network that is loose above and dense below (Figure 1d–g). By contrast, the as-prepared pure PNIPAM hydrogels without AC-induced stratification and diffusion display almost similar pore structure on both sides of the hydrogels, indicating an isotropic characteristic in the vertical direction (Figure S3a and S4a, Supporting Information). Presuming from the aforementioned phenomena, we believe that the reason for the formation of this heterogeneous structure of PNIPAM–AC hydrogels is that the molecular thermal motion occurs at the interfaces of AC and the precursor solution. The diffused microspheres of AC, which is a poor solvent, occupy the position of the precursor solution including NIPAM monomers with the NIPAM chains coiling up and collapsing to reduce the Gibbs free energy of the system.[28] Therefore, a corresponding heterogeneous porous structure is obtained after the crosslinking and polymerization of NIPAM monomers under UV-light irradiation. In contrast, the Fourier transform infrared (FTIR) spectra (Figure S5, Supporting Information) show the absorption peak at 1640.3 and 1540.1 cm\(^{-1}\), corresponding to the stretching vibration of –C=O of the amide I band and II band in PNIAPM, indicating that AC does not contribute to the hydrogel polymerization but just influences its microstructure. This heterogeneous microstructure can be well controlled by changing the diffusion time of AC into the precursor solution. When the diffusion time increases from 0.5, 1, 3, to 5 min, the upper side (the diffusion region) of the obtained hydrogels, which are defined as PNIPAM–AC\(_x\) (\(x = 0.5, 1, 3, \) and 5, respectively), becomes loose and heterogeneous with an increase in the aperture, whereas the bottom side (the nondiffusion region) keeps the dense and homogeneous honeycomb structure (Figure 1 and Figure S3 and S4, Supporting Information). The thickness of the diffusion layer gradually increases from about 220 to 300\(\mu\)m with the increasing of diffusion time from 10 to 30 min until it reaches a relatively stable value about 350\(\mu\)m after 60 min diffusion (Figure S6, Supporting Information). As time further goes on, the thickness of the diffusion layer does not change much due to the low density and microsolubility of AC. The diffusion and nondiffusion regions with discrepant aperture structure contain the same PNIPAM matrix, without any interfacial delamination at microscopic level.

### 2.2. Temperature-Responsive Driving Behavior of PNIPAM–AC Hydrogel as Soft Actuators

The heterogeneous microstructure greatly affects the temperature-responsive driving behavior of the PNIPAM hydrogel as the soft actuator. Usually, the volume of the temperature-sensitive PNIPAM will shrink by extruding water in hot environment with the temperature higher than the lower critical solution temperature (LCST), and expand by absorbing water at temperatures lower than the LCST.[15a] The addition of AC not only induces the heterogeneous structure of the hydrogel, but also decreases the LCST to 27°C for the obverse side of PNIPAM–AC\(_3\) with loose big pores, whereas the LCST on the reverse side of the hydrogel with dense small pores remains substantially unchanged just like that of the pure PNIPAM hydrogel (Figure S7a, Supporting Information). This might be attributed to the slight residuum of sparingly soluble AC in the diffusion region, which could affect entropy change of the whole system.[5a,29] The direction of bending deformation of the PNIPAM–AC\(_x\) hydrogel is related to the difference of volume shrinkage of the diffusion region and nondiffusion region, which results in internal stress within hydrogels and provides the impetus for deforming and recovering of the hydrogel. The pure PNIPAM hydrogel with isotropous structure only displays volume shrinkage due to water loss without bending behavior in 50°C water. The temperature-responsive bending characteristics of PNIPAM–AC\(_x\) hydrogels with the size of 30 mm × 10 mm × 1 mm (length × width × thickness) are realized by the design of the asymmetric heterogeneous structure. As shown in Figure 2a and Movie S2, Supporting Information, when the PNIPAM–AC\(_{0.5}\) hydrogel (the smooth reverse side toward the left and the rough obverse side toward the right) is immersed into hot water (50°C), it bends toward the reverse side and reaches to the maximum bending curvature of 1.28 cm\(^{-1}\) within 38 s. The detailed calculation method of bending curvature is shown in Figure S8, Supporting Information. This could be ascribed to the bigger volume shrinkage ratio (the ratio of the hydrogel volume at a certain time after water loss to its original volume) of the nondiffusion region than that of the diffusion region of hydrogel in the hot water (Figure S7b and S9a, Supporting Information), providing an impetus for the PNIPAM–AC\(_{0.5}\) hydrogel to bend toward the reverse side (Figure 2e). When the PNIPAM–AC\(_{0.5}\) hydrogel is put back in cold water (25°C), it recovers to its original state within 35 s (Movie S2, Supporting Information). With the further increase of diffusion time of AC to 3 min, the thickness of the diffusion region and the aperture will increase (Figure S9c, Supporting Information). The obviously decreased volume shrinkage ratio of the diffusion region for the PNIPAM–AC\(_3\) hydrogel makes the asymmetrical volume change between the nondiffusion region and diffusion region more outstanding (Figure S9a, Supporting Information), which would generate more motivation for hydrogel deformation. The PNIPAM–AC\(_3\) hydrogel presents a higher response rate toward temperature.
change from 25 to 50 °C, showing a maximum bending curvature of about 2.5 cm⁻¹ within 10 s (Figure 2c,f and Movie S4, Supporting Information). It needs about 3 min to return to its original shape due to the time-consuming recovery induced by the larger bending angle (Figure 2c and Figure S9b, Supporting Information). When the diffusion time of AC rises to 5 min, the deformation of the PNIPAM–AC₅ hydrogel slows down in hot water (Movie S5, Supporting Information). This could be attributed to the reduced impetus in the direction of deformation with the further increased diffusion layer thickness and reduced imbalance in volume change (Figure S9a, Supporting Information). Additionally, the volume of added AC and the thickness of PNIPAM–AC₃ hydrogels also affect the structure, volume shrinkage, and bending deformation of the anisotropic hydrogel in different degrees. When different volumes of AC (0.5, 1, 1.5, and 2 mL, respectively) are added onto the surface of mixture precursors, the thickness of the diffusion layer would increase from 273.5 ± 6.3 to 436.2 ± 8.5 μm within 60 min. The increased thickness of the diffusion layer would result in a reduced impetus or an increased resistance in the direction of deformation, which makes the bending of the hydrogel slow down (Table S1, Supporting Information). Note that the bending curvature of the hydrogel with 0.5 mL AC addition is irregular (0.941 ± 0.064 cm⁻¹) because it is hard for AC to cover the whole Petri dish. When the thickness of the PNIPAM–AC₃ hydrogels increases from 0.5 to 3 mm, the thickness of the diffusion layer is almost about 162 μm after 3 min diffusion of AC; the driving speed is first increased and then decreased because of the continuous increment in its own gravity, with the optimal value obtained at the 1 mm thick PNIPAM–AC₃ hydrogel (Figure 2 and Figure S10, Supporting Information). The PNIPAM–AC₃ hydrogel also displays excellent reversibility and repeatability without obvious changes in the bending curvature, response time, and recovery time during the repeated thermoresponsive bending/unbending driving process (Figure 2g). The quick response, large bending deformation, and acceptable mechanical property of our prepared PNIPAM–ACₓ hydrogel are comparable to other hydrogel
actuators reported previously\(^{1b,2b,5a,6a,15a,18,20,23,30}\) (Figure 2h and Figure S9d, Supporting Information), indicating that the solution diffusion induced heterogeneous PNIPAM hydrogel obtained by the proposed simple, green, and facile method has a potential for soft actuators.

To realize some special and accurate deformation, we design a patterned structure with the heterogeneous PNIPAM–AC\(_3\) hydrogel for better use as a soft actuator in various environments. For this purpose, masks with a hollow stripe pattern were put on the surface of the hydrogel precursor, followed by AC dropping onto it and UV-induced polymerization. Here the stripes with the width of 1 mm and fringe spacing of 2 mm were oriented at different angles (90°, 60°, 45°, and 30°), and then the patterned hydrogel were cut into rectangular strips of 40 mm × 5 mm × 1 mm (length × width × thickness) (Figure 3a–d). As shown in Figure 3e–g, the hollow-out section (namely, the salient stripe “e” in Figure 3a) of the patterned PNIPAM–AC\(_3\) hydrogel with the orientation angle of 90° is the diffusion region and has larger holes on the obverse surface, whereas the sunk part “f” covered by the mask is the nondiffusion region on the obverse surface and has smaller holes due to the selective diffusion of AC in designated areas. These patterned hydrogel stripes quickly bend into a ring or different types of cylindrical helices in 50 °C water, which is related to the orientation angles of rectangular stripes (Figure 3a–d and Movie S6–S9, Supporting Information). All of this directional twisting started perpendicular to the orientation direction of the stripes, and formed a twisted figure with stripes along the axis of cylindrical helices and the patterned surface facing outside. It is noteworthy that these rectangular stripes will unwind themselves automatically to some degree in 50 °C water after the stripes reach maximum bending limit for a moment (Figure 3a–d). This phenomenon can be explained as follows. The nondiffusion region on the reverse side of the PNIPAM–AC\(_3\) hydrogel with uniform and dense small pores has a larger volume shrinkage than the obverse side with the staggered diffusion region and nondiffusion region; therefore, the PNIPAM–AC\(_3\) hydrogel presents a bending deformation toward the reverse side. When the water-loss rate of the reverse side reaches a balance, the obverse side with alternate streaks continues to shrink due to the water dissipation, leading to the despiralization of the hydrogel strip.\(^{31}\) The kinetics of twisting and untwisting movements of the 90° oriented PNIPAM–AC\(_3\) hydrogel is assessed by plotting the twisting angle of the formed helix against time, resulting in a bending angle of 700° in 7 s and subsequent recovering in 60 s (Figure 3h). The processes of twisting and untwisting can be controlled by changing the width of a

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**Figure 3.** Controllable actuation of stripe-patterned heterogeneous PNIPAM–AC\(_3\) hydrogel actuators in response to temperature change. The stripe width was 1 mm with the fringe spacing of 2 mm. The stripes were oriented at different angles relative to the length direction of the hydrogel strip, showing directional bending and chiral twisting: a) \(\theta = 90°\), b) \(\theta = 60°\), c) \(\theta = 45°\), and d) \(\theta = 30°\). The scale bar is 1 cm. e–g) SEM images of different parts of the stripe-patterned PNIPAM–AC\(_3\) hydrogel strip with orientation angle of 90°. h) Plot of twisting angle against time for stripe-patterned hydrogel actuator with orientation angle of 90°. The error bars are the standard deviation calculated from eight data.
stripe (hollowed-out section) from 1 to 9 mm. The statistical results indicate that the wider the hollowed-out part on the mask is, the longer the helical shape remains, and therefore, the longer it takes to begin unwinding (Figure S11, Supporting Information).

Based on the enlightenment of the pattern effect on the bending behavior of the hydrogel, we designed some 2D or 3D special deformations. For example, a four-arm hydrogel manipulator without pattern design can pick up targeted objects with a weight of about 600 mg in the 50 °C water bath and transfer and release it in 25 °C water (Figure 4a and Movie S10, Supporting Information). The four-arm hydrogel manipulator with pattern design can realize the grab and release in the same vessel with 50 °C water (Figure 4b and Movie S11, Supporting Information). Moreover, by adjusting the diffusion surface (front or back) and diffusion position of AC on the hydrogel (Figure S12, Supporting Information), well-designed patterned hydrogels are constructed with controllable bending position, bending direction, and bending amplitude to realize the complex deformation of numbers 1–9 in the 50 °C water (Figure 4c,d and Movie S12, Supporting Information).

2.3. Universality of the Proposed Method

To prove the effectiveness of the general method in inducing anisotropic heterogeneous porous hydrogel, we replaced pentanol with equal amounts of water or ethanol, or replaced the thermosensitive hydrogel monomer of NIPAM with ion-sensitive acrylic acid (AAC) and acrylic amide (AAM) monomers. As shown in Figure S13, Supporting Information, when water or alcohol was added into the NIPAM-including precursor, an interface was formed and the water or alcohol diffused into the aqueous precursor solution, inducing a heterogeneous porous structure that is loose above and dense below (Figure S13a1–a2,b1–b2, Supporting Information), which favors the PNIPAM hydrogel’s quick response to temperature change (Figure 5a,b). Therefore, a regularity summary for the relationship between the added solution properties and the actuation ability of the hydrogel is proposed. In our experiment, we designed and selected three types of liquids with different densities when considering the density of the hydrogel precursor solution (ρ₀ = 1.05 g cm⁻³), namely, AC and ethanol (ρ_{ethanol} ≈ ρ_{AC} < ρ₀), water (ρ_{water} ≈ ρ₀), and glycerol (ρ_{glycerol} > ρ₀). We find that AC, ethanol, and water can float on the surface of the hydrogel precursor after addition, while glycerol will sink to the bottom of the hydrogel precursor due to its high density. No matter which liquid is added, liquid stratification would be produced and the added liquids would gradually diffuse with the increase of time, until the heterogeneous microstructure of hydrogels is formed with large pores on the contact surface and small pores on the other side after cross-linking under UV irradiation. The AC forms bigger microdroplets in the hydrogel precursor due to its slight density difference.

Figure 4. Controllable deformation of heterogeneous PNIPAM–ACₓ hydrogels in response to temperature change. a) Capture and transportation of a cuvette lid by a cross-shaped hydrogel as the gripper from 50 °C water to 25 °C water. b) Capture and transportation of a cuvette lid by a cross-shaped hydrogel with 90° orientated pattern in 50 °C water. c,d) Visual display of different numbers by using uniquely designed PNIPAM–ACₓ hydrogels with a specific pattern. The detailed design is shown in Figure S12, Supporting Information. The scale bar is 1 cm.
dissolution in the precursor solution. The higher-density glycerol sinks to the bottom of the hydrogel precursor and generates a heterogeneous microstructure from the bottom of hydrogels. In addition, as the hydrogel with glycerol addition could not be freeze dried due to the frost resistance, we did not obtain SEM images of this hydrogel. By comparing the aperture sizes of hydrogels induced by different liquid stratification and diffusion, we can speculate that the rule of aperture radius \( R \) at the contact surface is \( R_{\text{water}} < R_{\text{glycerol}} < R_{\text{ethanol}} < R_{\text{AC}} \); namely, the most obvious anisotropy of hydrogels is produced by dropping AC in the precursor solution. The difference of volume shrinkage between the diffusion region and the nondiffusion region also presents a similar tendency, namely, the driving force for bending deforming is the most prominent for the AC-diffusion-induced hydrogel under a temperature stimulus, which is consistent with the rule of actuation behavior (Figure 1, 2, and 5a,b, and Figure S14, Supporting Information).

Similar phenomena and rules are also observed for the water-diffusion-induced polyacrylic acid (PAAC) hydrogel and polyacrylamide (PAAM) hydrogel (Figure S13c1–c2,d1–d2, Supporting Information). These two hydrogels present excellent response to the buffer solutions with pH 11 and pH 4, respectively (Figure 5c,d). Furthermore, this simple diffusion-driven strategy can be perfectly applicable for programmable multifunctionality of hydrogels by adding functional nanomaterials into the diffusible liquid. Typically, when the carbon nanotube (CNT)-including solution was added and diffused into the precursor solution with NIPAM monomer, the gelatinized PNIPAM actuator displayed a distinct light-responsive characteristic, demonstrating controllable worm-like crawling and flexible gestures under light stimuli (Figure 6a1–a6,b1–b6 and Movie S13 and S14, Supporting Information). A magnetic-responsive robot “fish” was also constructed by adding the solution with Fe3O4 nanoparticles into the precursor solution with NIPAM monomer, and it happily swam in water with constant changing of magnet position and water temperature (Figure 6c1–c6 and Figure S15 and Movie S15, Supporting Information). The SEM images also confirm the successful addition of functional nanomaterials into the PNIPAM hydrogels (Figure S16, Supporting Information).
3. Conclusion

In summary, we proposed a simple, green, and fast strategy with one-step synthesis to prepare robust gradient porous hydrogel actuators. Driven by diffusing of AC into a NIPAM-including precursor solution, the anisotropic hydrogel with adjustable heterogeneous microstructure and well-designed pattern could be directly generated within a couple of minutes. The optimum anisotropic structure of the hydrogel produced by controlling the diffusion time between the two liquids presented fast response, accurately programmable deformation, and high cycle stability under temperature stimuli. The controllable responsive

Figure 6. a) Some CNT-including solution was added to the surface of the precursor solution to realize the photosensitive characteristic of the PNIPAM–AC, hydrogel actuator, which could realize worm-like crawling by adjusting the position of laser irradiation. b) Adding some CNT materials in the PNIPAM–AC, hydrogel, which could be actuated in different forms just like our hands by adjusting the position of laser irradiation. c) Adding some Fe3O4 nanoparticles in the PNIPAM–AC, hydrogel, we could control the “fish” to swim in water by changing the magnet position.
deformation and action of soft actuators could be intentionally designed by adjusting the type and pattern of the hydrogel, the category of diffused solution, diffusion time of the solution, and the functionality of added materials in the solution. This demonstrated the general applicability of the proposed diffusion-driven strategy for the preparation of different responsive hydrogels with programmable multifunctionality and their multipurpose applications in soft robots, artificial muscle micromanipulation, and intellective human–machine interfacing materials.

4. Experimental Section

Materials: NIPAM monomer, purified by recrystallization, and 1-hydroxy-cyclohexyl-phenylketone (Irg.184) were purchased from Shanghai Aladdin Chemical Agent Co., Ltd (China). The synthetic hectorite “Laponite XLC” (IM65.L-40-66 SiO2(OH)4N2O6) was purchased from Rockwood Chemicals Co., Ltd (China) as the inorganic clay. The clay was dried at 125 °C for 2 h. Ethanol, amyl alcohol, CNT, Fe3O4 nanoparticles, methylene blue (MB), and rhodamine B (RB) N,N’-methylenebisacrylamide (MBAA), 2,2’-azobis(2-methylpropionamide) dihydrochloride (V-50), AAC, AAM, and 1-vinylimidazole (VI) were purchased from Shanghai Aladdin Chemical Agent Co., Ltd (China). All other reagents were of analytical grade and used without further purification. Deionized water (18.2 MΩ at 25 °C) was used throughout the experiments.

Synthesis of Anisotropic PNIPAM–AC Hydrogels: A uniform aqueous solution containing NIPAM monomers, cross-linker (Laponite XLC), dye-stuff (MB or RB), and photoinitiator (Irg.184) was first prepared. Specifically, the photoinitiator was made by Irg.184 (2.26 mg) and methanol solution (100 μL) with ice-water stirred. The dye-stuff was first dispersed in water and stirred for about 20 min with the given concentration of 0.2 g L–1. And then the clay (Laponite XLC) was added into the dye-stuff solution and stirred for 2.5 h until the solution became transparent. Subsequently, NIPAM monomers were added into the dye-stuff and clay solution, and then the suspension was stirred in an ice-water bath for 2 h. The concentrations of clay and NIPAM monomer were fixed at 5 × 10–2 and 1.0 mol L–1, respectively. Finally, the photoinitiator was added into the solution, and the concentration ratio of photoinitiator to NIPAM monomer was controlled to 0.2 wt%. The aqueous mixture was injected into a mold of plastic disks with a radius of 2.5 cm and the thickness of 1 mm. Subsequently, a certain amount of AC was dropped onto the surface of the aqueous mixture. Finally, the mixture in the mold was irradiated under UV light (365 nm) for 4 min in an ice-water bath. To investigate the effect of diffusion time on the microstructure, mechanical property, and intelligent responses of the hydrogels, the diffusion time of AC on the surface of the aqueous mixture was controlled to 0.5, 1, 3, 5, 10, 30, and 60 min, respectively, and the obtained hydrogels were then defined as PNIPAM–ACAC (x = 0.5, 1, 3, 5, 10, 30, and 60). The prepared PNIPAM–ACAC hydrogels were washed with excessive ethanol and water thoroughly to remove the unreacted substance. Additionally, different solutions such as water and alcohol were also used to replace AC and diffuse into the aqueous mixture to construct anisotropic hydrogels. The pure PNIPAM hydrogel was also prepared without extra solution (such as AC, water, alcohol, etc.) addition.

Synthesis of Patterned Anisotropic Hydrogels: To realize flexible and accurate deformation, patterned hydrogels were prepared by diverse dimension hollowed-out mask. The hollowed mask was put on the surface of the hydrogel precursor. After AC addition, the anisotropic structure was reserved by UV light irradiation with 4 min in an ice-water bath.

Functionalization of PNIPAM–AC Hydrogels: Different solutions with CNT or Fe3O4 nanoparticles were also used to replace AC and diffuse into the aqueous precursor solution for 1 min to construct anisotropic functional hydrogels. The volume ratio of CNT solution (5 mg mL–1) to precursor solution was 1:5 in the mixed solution. The volume ratio of Fe3O4 solution (10 mg mL–1) to precursor solution was 1:4 in the mixed solution.

Synthesis of PAAC–H2O Hydrogels: To explore the universality of our preparation method, we fabricated H2O-diffusion-induced PAAC (PAAC–H2O) hydrogel. The uniform aqueous solution containing AAC monomer (3.6 g), crosslinker MBAA (0.14 g), photoinitiator V-50 (0.18 g), and dye-stuff was first made with ice-water stirred. Subsequently, a certain amount of H2O was dropped onto the surface of the aqueous mixture. Finally, the mixture in the mold was irradiated under UV light (365 nm) for 15 min in an ice-water bath.

Synthesis of PAAM–H2O Hydrogels: The uniform aqueous solution containing AAM monomer (3.56 g), crosslinker MBAA (0.14 g), photoinitiator V-50 (0.18 g), and VI (0.332 g) was first made with ice-water stirred. Subsequently, a certain amount of H2O was dropped onto the surface of the aqueous mixture. Finally, the mixture in the mold was irradiated under UV light (365 nm) for 12 min in an ice-water bath to obtain H2O-diffusion-induced PAAM (PAAM–H2O) hydrogel.

Characterization: The hydrogel samples in deionized water were frozen in liquid nitrogen for 15 min, and then the samples were lyophilized by a freeze dryer (FD-1C-50, Beijing BoYiKang) at −35 °C for about 24 h. The morphologies of freeze-dried anisotropic hydrogels were observed by SEM (S-4800, Hitachi, Tokyo, Japan) at an acceleration voltage of 5 kV. The FTIR data were recorded in the wavenumber range from 500 to 4000 cm–1 on an infrared spectrometer (Thermo Scientific, Nicolet i550 Series). The microcosmic dynamic scenario of AC on the surface of liquid precursors was observed using a confocal laser scanning microscope (CLSM, IX83, OLYMPUS, Japan). Tensile tests of hydrogels with the size 30 mm × 10 mm × 1 mm (length × width × thickness) were recorded on a tensile testing instrument (INSTRON, LEGEND 2366, USA) at room temperature after the samples were washed in 25 °C water bath for 5 min. Two ends of the rectangular samples were clamped, and stretched at a certain velocity of 20 mm min–1. The tensile stress (σ) was calculated by σ = F/A, where F is the load and A is the cross-sectional area of the real-time specimen. The process of dynamic thermoresponsive bending performance was recorded by a digital camera (SONY FDR-AX4S) in the hot water (50 °C). The hydrogels were cut into rectangles of size 30 mm × 10 mm × 1 mm (length × width × thickness), and one end was caught in a clamp. The LCST of hydrogels was calculated on a differential scanning calorimeter (DSC, TA DSC Q200, USA) by heating the sample from 20 to 45 °C with the heating rate of 5 °C min–1. The PNIPAM–AC hydrogel sheets were cut to 1 cm × 1 cm and placed into the hot water. The thermoresponsive volume change of PNIPAM–AC hydrogels was recorded by a digital camera at different time intervals. The ambient temperature of the PNIPAM–AC hydrogels was controlled by a thermostatic stage system. The volume shrinkage of the hydrogels was calculated by area and bulk at different time intervals in optical pictures. The pore size of the samples was calculated by an area-counting method. Quantity of pores (N) was counted for a given area (S) and the average of multiple SEM samples was obtained. Supposing that the pores structure was perfectly piled-up rounds, the average pore diameter (r) could be calculated with S = Na2π. Then the aperture ratio could be obtained by calculating the specific value of r of PNIPAM–AC with different diffusion time and PNIPAM.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

Acknowledgements

P.D. and W.X. contributed equally to this work. This work was supported by the Zhejiang Outstanding Youth Fund (No. LR19E020004), the National Natural Science Foundation of China (No. 11672269 and 11972323), the Zhejiang Provincial Natural Science Foundation of China.
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
anisotropic hydrogels, interfacial diffusion, liquid stratification, programmable functionalities, smart actuators

Received: February 15, 2021
Revised: May 18, 2021
Published online: July 9, 2021

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