

3D Printable Active Hydrogels with Supramolecular Additive-Driven Adaptiveness

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Smart hydrogels are a promising candidate for the development of next-generation soft materials due to their stimuli-responsiveness, deformability, and biocompatibility. However, it remains challenging to enable hydrogels to actively adapt to various environmental conditions like living organisms. In this work, supramolecular additives are introduced to the hydrogel matrix to confer environmental adaptiveness. Specifically, their microstructures, swelling behaviors, mechanical properties, and transparency can adapt to external environmental conditions. Moreover, the presence of hydrogen bonding provides the hydrogel with applicable rheological properties for 3D extrusion printing, thus allowing for the facile preparation of thickness-dependent camouflage and multistimuli responsive complex. The environmentally adaptive hydrogel developed in this study offers new approaches for manipulating supramolecular interactions and broadens the capability of smart hydrogels in information security and multifunctional integrated actuation.

Stimuli-responsive hydrogels have emerged as a promising candidate for the development of advanced smart soft materials, owing to their capacity to actively respond to external stimuli such as temperature,^[5] light,^[6] pH,^[7] ultrasound,^[8] and so on.^[9] These hydrogels, while sharing common characteristics with conventional hydrogels such as large water retention and biocompatibility, distinguish themselves by their ability to dynamically adapt their structures, morphologies, and physical properties in response to various stimuli.^[5–9] Notably, most of the responsiveness in smart hydrogels originates from the adaptiveness of polymer chains or functional groups towards certain changes in the surrounding environment.^[9,10] For instance, poly(*N*-isopropylacrylamide) (PNIPAM) undergoes a characteristic phase transition from a hydrophilic coil to

1. Introduction

With the rapid integration of intelligence into daily life and industrial production, there has been significant attention on the development of next-generation smart soft materials. These materials are designed to exhibit stimuli-responsiveness, large deformation capabilities, and highly advanced programmability, making them suitable for a wide range of applications in smart sensors and actuators, wearable devices, and soft robots.^[1–4]

a hydrophobic globule state by expelling water upon heating to the temperature above its lower critical solution temperature (LCST), resulting in significant volume shrinkage and sharp decrement of optical transmittance to 10% from about 90%.^[11,12] Due to its temperature responsiveness, PNIPAM has been extensively employed in the fields of soft actuators, cell attachment and detachment, drug delivery, smart windows, and smart displays.^[12,13] Similarly, poly(carboxylic acid) (PCA) is a type of pH-responsive hydrogel with ionization in basic environments and deionization in acidic environments.^[14] Additionally, force-triggered responsiveness of hydrogels can be achieved through mechanochemical reactions of contained mechanophore (e.g., mechanically coupled [2+2] cycloreversion of the sodium salts of bicyclo [6.2.0] decane).^[15] Enhancing the adaptability of hydrogels is crucial for extending their applications across diverse domains, including controllable drug delivery, health monitoring sensors, agricultural soil improvement, and so forth.^[16–19] Notably, this imperative arises from the constraints inherent in many conventional smart hydrogels, which exhibit responsiveness to singular environmental stimulus. Consequently, it becomes important to explore mechanisms enabling hydrogels to perceive and adapt to various stimuli from the environment. Such endeavors hold the promise of catalyzing the development of intricate systems that approach the remarkable adaptability seen in living organisms, thus propelling the field of smart materials toward new frontiers.

Design and fabrication of composite hydrogels with rigid functional additives that can confer new responsiveness in addition to the intrinsic responsiveness of the hydrogel have been densely

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explored to develop multi-adaptive smart hydrogels. Typically, dispersion of various stimuli-responsive inorganic additives, such as the photothermal transition of gold nanoparticles (AuNPs) and graphene oxide (GO),^[20,21] the conductivity of carbon nanotubes (CNTs),^[22] and the magnetism of Fe_3O_4 ,^[23] into hydrogel matrices has proved effective methods for acquiring isotropic hydrogel composites. In addition, the multilayer structures assembled via active and passive layers were also studied to prepare anisotropic lamellar or gradient composite hydrogels.^[23–25] Utilizing such approaches, composite hydrogels can sense various environmental changes and provide physical feedback.^[26–28] Furthermore, when rigid additives are incorporated, the high stiffness of additives can enhance the load-bearing capacity of composite hydrogels, and the interaction between hydrogel matrices and rigid additives contributes to more effective load distribution and energy dissipation, thus inducing an increase in the mechanical performance.^[29,30] Previous studies on environmentally adaptive and mechanically reinforced hydrogels have predominantly focused on the incorporation of rigid particles or layers. However, such integration often entails potential trade-offs in properties such as swelling and stretchability and introduces inhomogeneities that lead to variations in mechanical, thermal, and other characteristics, thereby imposing limitations on the overall advancements of these material systems.^[29–32]

Supramolecular interactions, including host–guest recognition, metal-organic coordination, π – π donor–acceptor effects, cation– π interactions, electrostatic bonding, salt bridges, and hydrogen bonding,^[33–35] have been employed to prepare various supramolecular polymers with rheology-controllable,^[36] recyclable,^[37] self-healing,^[38] highly stretchable,^[38] or adhesive properties.^[35] Their dynamic and reversible non-covalent bonds can be particularly useful for designing adaptive materials. Among supramolecular functional groups, 2-ureido-4-pyrimidinone (UPy) is well known for its ability to dimerize through self-complementary quadruple hydrogen bonding.^[39–41] Specifically, UPy dimers tend to arrange and assemble themselves to 1D linear stacking in hydrophobic environments, since urea units in UPy dimers can generate stable lateral hydrogen bonding without the effect of H_2O molecules as competing hydrogen bond donors or acceptors.^[39–45] This 1D stacking leads to the formation of the linear aggregation, therefore UPy has been used to enhance the crosslinking density and mechanical strength of polymers.^[46,47] Despite the significant advantages offered by this supramolecular interaction, there has been limited exploration of the use of UPy as a molecular additive to impart the environmental adaptiveness of hydrogels.

Here, we develop an environmentally multi-adaptive hydrogel by incorporating UPy supramolecular additives into the poly(*N*-isopropylacrylamide-co-acrylamide) (PNIPAM-co-AAm) hydrogel matrix. The resulting poly(*N*-isopropylacrylamide-co-acrylamide)-UPy (PNAU) hydrogel exhibits remarkable responsiveness to a range of environmental stimuli. PNIPAM segments within the hydrogel not only undergo volumetric shrinkage but also control the internal transition from a hydrophilic to a hydrophobic microenvironment when the temperature exceeds LCST. In the swelling-deswelling-reswelling process of PNAU, the microenvironmental transition occurring through deswelling promotes the linear aggregation of UPy supramolecular additives within the hydrogel matrix, leading to significant differences in

the kinetics of swelling and reswelling, as well as the microstructures and mechanical properties of swelled and reswelled samples. In addition, PNAU hydrogels exhibit environmentally adaptive transparency due to the presence of UPy additives. The opacity of PNAU hydrogels in H_2O can be attributed to the microphase separation between hydrophobic saturated alkanes within UPy additives and hydrophilic backbone, whereas this phase separation-induced opacity gradually disappears in amphiphilic dimethyl sulfoxide (DMSO). Moreover, the presence of hydrogen bonding in PNAU imparts solid-like behavior, and the addition of nanoclay enhances viscosity and shear thinning behavior, thus making PNAU suitable for 3D extrusion printing.^[48] Such modified rheological properties allow 3D printing of complex structures with good shape retention thus high resolution.^[49] Notably, the printed structures and patterns can be camouflaged through responsive transparency via solvent switching. As a demonstration, we have designed and printed a smart quick-response (QR) code that can encrypt and decrypt information using a multi-material 3D extrusion printer, providing a novel approach to information security. In addition, we have fabricated a multifunctional hydrogel/elastomer actuator capable of information protection through shape deformation and transparency control in responding to solvents and ambient temperature. These results highlight the potential of PNAU hydrogels in the realms of information security, and multimodal actuation and sensing. This environmentally adaptive hydrogel not only expands the possibilities for creating advanced smart hydrogels but also broadens the potential for applications in the field of bionic hydrogels.

2. Results and Discussion

2.1. Environmentally Adaptive Swelling and Mechanical Behaviors of PNAU Hydrogels

The environmentally adaptive PNAU hydrogel was synthesized by a three-step method (Figure S1, Supporting Information), which includes: 1) the synthesis of supramolecular UPy additives that are known for their quadruple hydrogen bonding through the nucleophilic addition of isocyanate and amino; 2) the preparation of the thermal-responsive P(NIPAM-co-AAm) hydrogel matrix via free radical polymerization; and 3) the incorporation of supramolecular UPy additives into the P(NIPAM-co-AAm) hydrogel matrix. Within PNAU hydrogels, the PAAm segments contribute to both intramolecular and intermolecular hydrogen bonding, thereby improving the mechanical strength of the hydrogel and entrapping the supramolecular additives.^[50] Fourier Transform Infrared (FTIR) spectroscopy provides the evidence of hydrogen bonding interactions between UPy additives and polymeric matrix (Figure S2, Supporting Information). Specifically, the N–H stretching peak of P(NIPAM-co-AAm) was observed to split into two distinct peaks: one peak at 3412 cm^{-1} corresponds to free N–H groups, and another peak at 3280 cm^{-1} corresponds to hydrogen-bonded N–H groups.^[11] This splitting is the result of the redshift aroused by intramolecular and intermolecular hydrogen bonding of –CONH– in PNIPAM segments and –CONH₂– in PAAm segments.^[51,52] In other words, the free N–H groups and hydrogen-bonded N–H groups coexist in the pristine hydrogel matrix. In contrast, the N–H stretching peak of PNAU hydrogels is merged at 3280 cm^{-1} , indicating

that the N–H groups in PNAU hydrogels exist predominantly in the form of hydrogen-bonded species. Regarding PNIPAM segments, they undergo volumetric shrinkage while hydrophilic-to-hydrophobic microenvironment switch through coil-to-globule conformational changes when the environmental temperature reaches LCST.^[12] Since UPy dimers tend to self-assemble and form linear aggregation in hydrophobic environments,^[39–44] PNIPAM segments in PNAU hydrogels can further enhance the physical aggregation of UPy additives in the thermally induced deswelling process. It also leads to significant impacts on the microstructures, size, diffusion of solvents, and mechanical properties of PNAU hydrogels in the reswelling state. Furthermore, the swelling behavior of PNAU hydrogels is explored in various solvents (Figure S3, Supporting Information). The linear swelling, deswelling, or reswelling ratio in this work is calculated by $\lambda = \frac{d_t}{d_0}$, where d_t is either the diameter of PNAU hydrogel discs at a specific time t in swelling, deswelling, and reswelling or the diameter in swelling, deswelling, and reswelling equilibrium states at temperature t , and d_0 is the diameter of as-prepared PNAU hydrogel discs. Among these solvents, considering the relatively larger linear swelling ratios of PNAU hydrogels in H₂O (1.40) and DMSO (1.35), and their transparency is distinct in hydrophilic H₂O and amphiphilic DMSO environments, H₂O and DMSO were chosen as solvent conditions for subsequent experiments. To elucidate the environmental adaptiveness of PNAU hydrogels, the swelling, deswelling, and reswelling states of PNAU hydrogels in H₂O and DMSO were investigated (Figure 1a,b). According to optical photographs of PNAU discs in different environmental conditions, the as-prepared PNAU hydrogel disc with a d_0 of 9.5 mm exhibits the linear swelling ratios of 1.41 and 1.31 in H₂O and DMSO at 23 °C, respectively, and their transparency manifests opaque in H₂O but transparent in DMSO (Figure 1b-i,ii). Generally, the swelling behavior of hydrogels is determined by balancing the swelling force created by the solvation of polymer chains and the restraining force transmitted by elastic crosslinking points.^[53,54] When hydrogels are immersed in a solvent, coiled polymer chains gradually straighten due to the swelling force with an increase in entropy. Once the polymer chains are tensioned, the restraining force will increase until it is eventually balanced by the swelling force, reaching the swelling equilibrium. The final swelling ratio of hydrogels is heavily dependent on the degree of solvation of polymer chains in a specific solvent environment. In comparison to the solvation of PNAU hydrogels in H₂O, the solvation is weaker in DMSO since it is a weaker H-bond donor, resulting in a lower swelling force (Figure 1a-i,ii).^[55] However, after experiencing heating-induced deswelling in H₂O at 70 °C, the temperature greatly above LCST that can create a sufficient hydrophobic environment, the linear deswelling ratio of 0.89 is obtained due to coil-to-globule transition of PNIPAM segments (Figure 1b-iii), and their accompanied hydrophilic-to-hydrophobic microenvironment transition facilitates UPy dimers to form linear aggregation (Figure 1a-iii).^[39–44] In contrast to the swelling behavior of the as-prepared PNAU hydrogels, the reswelling behavior of the deswelled PNAU exhibited significant differences in H₂O and DMSO at 23 °C (Figure 1a-iv,v). Specifically, the reswelling ratio of deswelled PNAU hydrogels increased to 1.35 and its transparency retains opaque in H₂O (Figure 1b-iv), whereas the sam-

ple exhibited a limited reswelling ratio of 0.98 and its transparency gradually changes to transparent in DMSO (Figure 1b-v). This phenomenon is presumably caused by the aggregation of UPy dimers during the deswelling process at 70 °C, which could enhance the physical interaction between chains and result in an increased restraining force. Hence, as PNAU hydrogels reswell in H₂O, the heightened swelling force can counterbalance the increased restraining force, and the presence of competitive H₂O molecules can partially mitigate UPy aggregation.^[43] Consequently, the reswelling of the PNAU hydrogel in H₂O closely resembles its initial swelling state. However, the non-reswelling behavior of PNAU hydrogels in DMSO is significantly different from the initial corresponding fully swollen state, we hypothesize that the relatively lower swelling force in DMSO presumably cannot match the elevated restraining force. The corresponding cross-sectional Scanning Electron Microscope (SEM) images of PNAU hydrogels reveal changes in microstructures due to their environmental adaptiveness (Figure 1c). Initially, the as-prepared PNAU hydrogel shows non-porous internal structures (Figure 1c-i). Once PNAU hydrogels are swelled, they form porous structures with average pore sizes of $4.2 \pm 10.2 \mu\text{m}$ and $73.4 \pm 15.3 \mu\text{m}$ in H₂O and DMSO, respectively (Figure 1c-ii,iii). The significantly smaller but denser pores observed in DMSO are possibly formed due to the weaker solvation and the lower swelling force. After experiencing deswelling at 70 °C, the porous structure collapses and forms a closed-packing state (Figure 1c-iv). Remarkably, similar to the results shown in Figure 1b-iv,v, the significant difference in the recovered porous structures of PNAU hydrogels is observed upon reswelling in H₂O and DMSO (Figure 1c-v,vi, respectively). In the case of reswelling in H₂O, the porous structure recovers and pore size is re-expanded to $7.1 \pm 2.4 \mu\text{m}$ (Figure 1c-v). Compared to the larger pores formed during the initial swelling in H₂O (Figure 1c-iii), the smaller size of these recovered pores is caused by increased restraining force through deswelling-induced aggregation of UPy additives. On the other hand, the microstructure of the reswelled PNAU hydrogel in DMSO maintains a closed-packing state (Figure 1c-vi). This result implies that DMSO cannot provide enough swelling force to overcome the enhanced restraining force provided by the UPy aggregation and re-extend polymer networks. In addition, we also investigated the adaptive behavior of PNAU hydrogels in DMSO at 70 °C (Figure S4, Supporting Information). Interestingly, we did not observe clear deswelling behavior in warm DMSO. Moreover, the diameter of PNAU hydrogel discs slightly increased and the appearance of hydrogels became more transparent after immersing samples in DMSO at 70 °C for 2 h. Subsequently, we reswelled these highly transparent samples in H₂O at 23 °C, their appearance cannot recover to the high opacity observed in the initially swelled PNAU, and their linear reswelling ratio is further increased. We hypothesized that the UPy additives tend to diffuse into the surrounding warm DMSO solvent since the hydrogen bonding dissociation easily occurs in a good solvent of UPy additives at high temperatures.^[56,57] Simultaneously, the departure of UPy additives contributes to lowering the constrain force from hydrogel networks, thus causing the further increment of their linear swelling ratios when immersing them back in H₂O (Figure S4, Supporting Information).

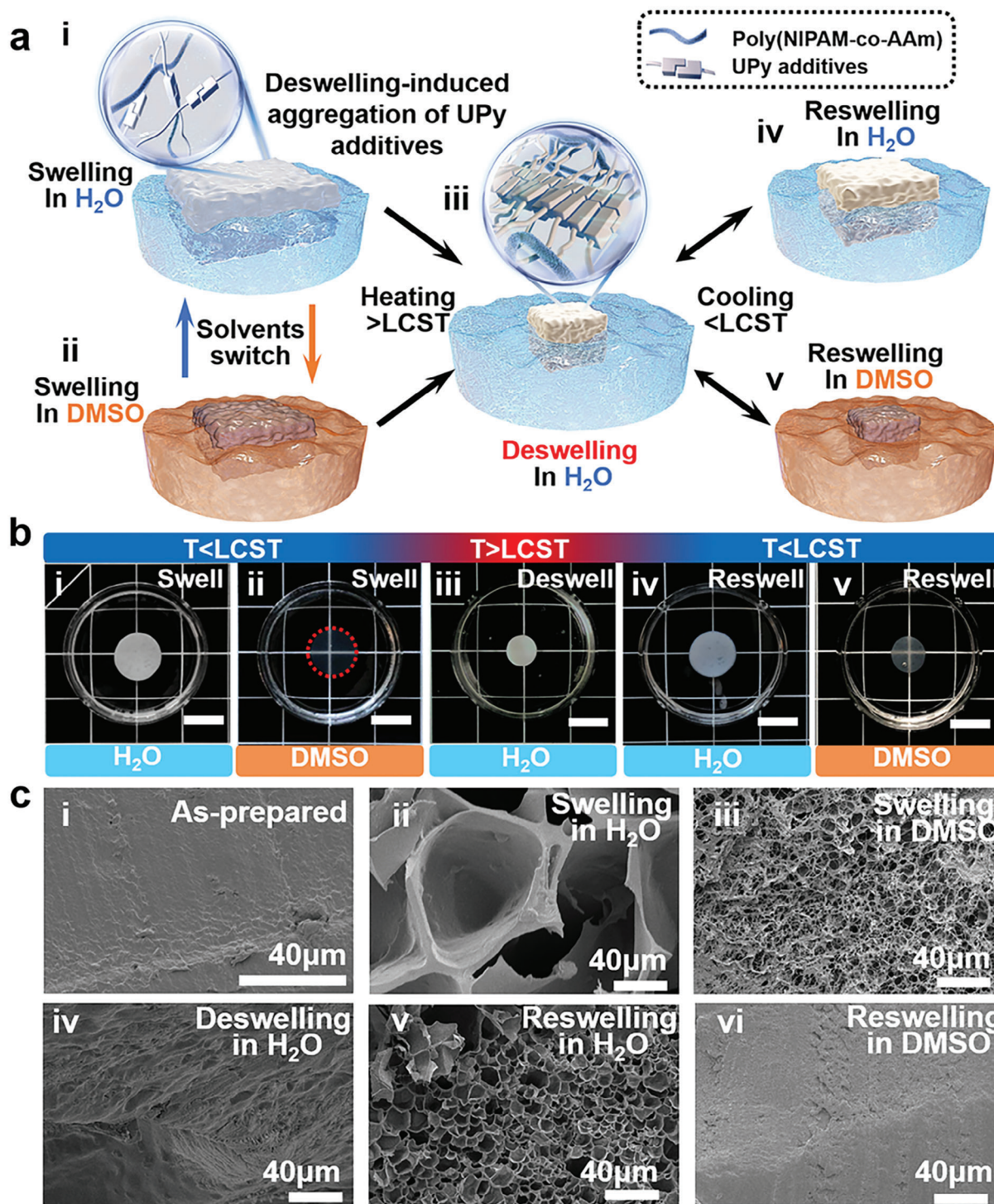


Figure 1. Environmentally adaptive behaviors of PNAU hydrogels and corresponding microstructures in different conditions. a) Schematics of the environmentally adaptive swelling and transparency of PNAU hydrogels: the equilibrium swelled states in i) H_2O and ii) DMSO at 23 °C, iii) the equilibrium deswelled state in H_2O at 70 °C, the equilibrium reswelled states in iv) H_2O and v) DMSO at 23 °C. The zoom-in schematic in i) presents the random distribution of UPy additives in the swelled state, and the zoom-in schematic in iii) presents the formation of the linear aggregation of UPy additives in the hydrophobic microenvironment aroused by deswelling. b) Optical photographs of the environmentally adaptive swelling and transparency of PNAU hydrogels: the equilibrium swelled states in i) H_2O and ii) DMSO at 23 °C, iii) the equilibrium deswelled state in H_2O at 70 °C, the equilibrium reswelled states in iv) H_2O and v) DMSO at 23 °C. Scale bars in the optical photographs are 10 mm. c) Cross-sectional SEM images of PNAU hydrogels in different conditions: i) the as-prepared state, the equilibrium swelled states in ii) H_2O and iii) DMSO at 23 °C, iv) the equilibrium deswelled state in H_2O at 70 °C, the equilibrium reswelled states in v) H_2O and vi) DMSO at 23 °C.

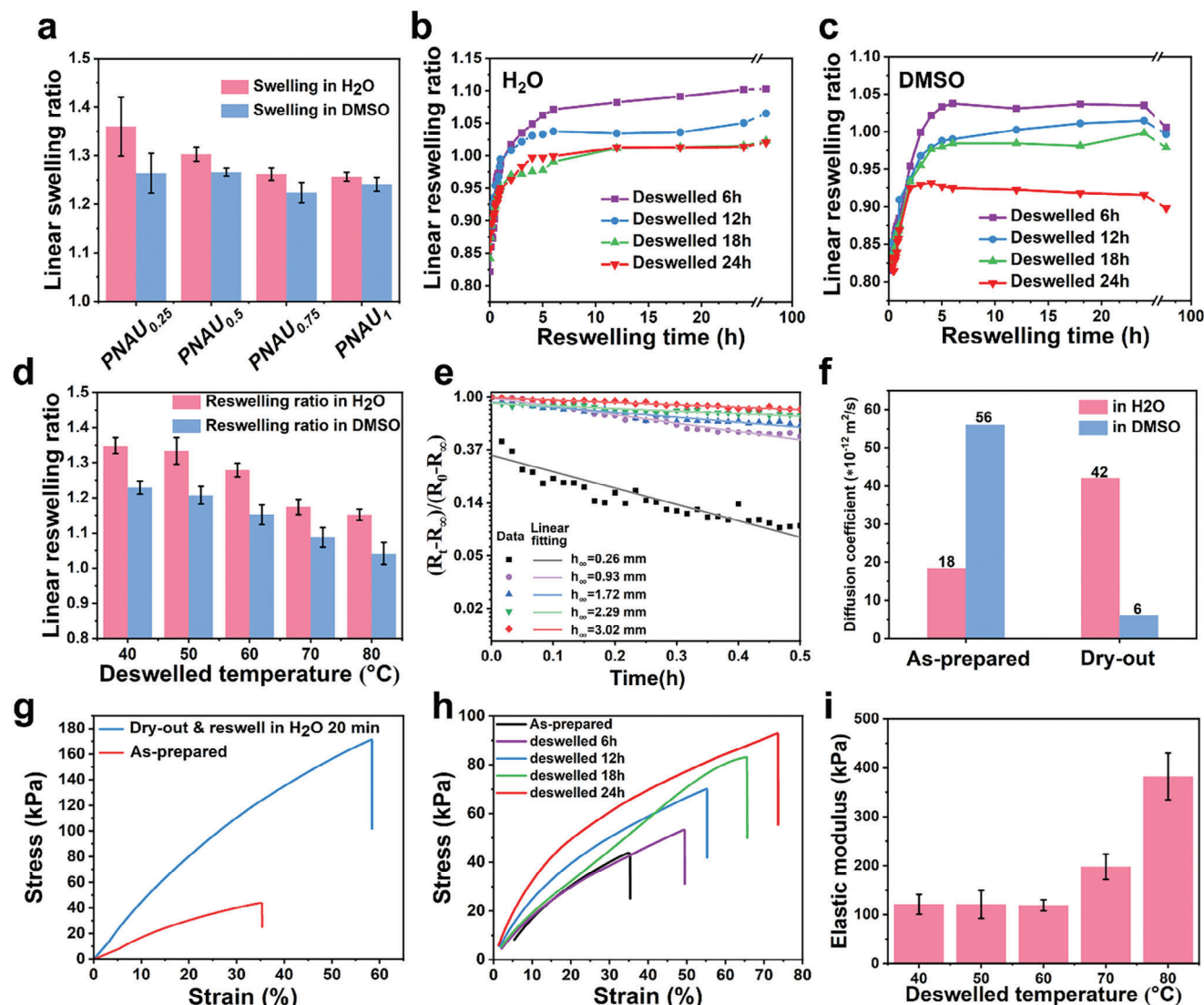


Figure 2. Environmentally tunable swelling and mechanical properties of PNAU hydrogels. a) Linear swelling ratios of PNAU_x hydrogels ($x = 0.25, 0.5, 0.75, \text{ and } 1$) in H₂O and DMSO, respectively. Time-dependent linear reswelling curves in b) H₂O and c) DMSO of PNAU hydrogels after experiencing deswelling at 70 °C for 6, 12, 18, and 24 h, respectively. d) Linear reswelling ratios in H₂O and DMSO of PNAU hydrogels after experiencing deswelling at different temperatures (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C for 6 h). e) Swelling kinetics of as-prepared PNAU hydrogels in H₂O at 23 °C: relative change of radius $(\frac{R_t - R_{\infty}}{R_0 - R_{\infty}})$ of PNAU hydrogels with different equilibrium thickness h_{∞} (0.56, 0.93, 1.72, 2.29, and 3.02 mm) as a function of the time t . The fitted lines are depicted as solid lines. f) Calculated diffusion coefficients of as-prepared PNAU hydrogels for swelling and dry-out samples for reswelling in H₂O and DMSO, respectively. The drying-out refers to the condition after completely removing the solvent in an oven at 60 °C overnight. g) Stress–strain curves of as-prepared and drying-reswelling treated PNAU hydrogels. The reswelling treatment was immersing the dry-out sample in H₂O for 20 min to guarantee its dimensions are comparable with that of the as-prepared state. h) Stress–strain curves of reswelled PNAU hydrogels after experiencing deswelling at different temperatures (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C for 6 h). i) Elastic moduli of reswelled PNAU hydrogels after experiencing deswelling at different temperatures (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C for 6 h). Data in Figure 2a,d,i were expressed as mean $\pm$ standard deviation (SD), where the sample number $N = 5$.

To quantitatively characterize environmentally adaptive swelling behaviors of PNAU hydrogels, we first unveiled the impact of UPy contents on swelling behaviors of PNAU_x in H₂O and DMSO, where x is the molar fraction of UPy additives to AAm (Figure 2a). As UPy content in PNAU hydrogels increases, linear swelling ratios exhibit a downward trend in both H₂O and DMSO. Specifically, linear swelling ratios of PNAU_{0.25}, PNAU_{0.5}, PNAU_{0.75}, and PNAU₁ in H₂O are 1.36 ± 0.06 , 1.30 ± 0.01 , 1.26 ± 0.01 , and 1.25 ± 0.01 , respectively.

Linear swelling ratios of PNAU_{0.25}, PNAU_{0.5}, PNAU_{0.75}, and PNAU₁ in DMSO are 1.27 ± 0.04 , 1.26 ± 0.01 , 1.22 ± 0.02 , and 1.24 ± 0.01 , respectively. The overall decreasing trend of swelling ratios is attributed to the enhanced restraining force of the polymer network with an increasing amount of hydrogen bonding. As the deswelling process of PNAU contributes to the linear aggregation of UPy additives, we tracked linear reswelling ratios of the PNAU hydrogels, which pre-deswelled in H₂O, as a function of the deswelled time (Figure 2b,c) and temperatures

(Figure 2d), respectively. For PNAU hydrogels deswelled for 6, 12, 18, and 24 h, their equilibrium linear reswelling ratios in H₂O are 1.10, 1.05, 1.02, and 1.01, respectively (Figure 2b). In DMSO, their equilibrium linear reswelling ratios are 1.04, 1.01, 0.99, and 0.92, respectively (Figure 2c). Regarding their reswelling kinetics in H₂O and DMSO, the PNAU that experienced longer deswelling time spends less time to reach the reswelling equilibrium, and reswelling equilibrium in DMSO is slightly easier to obtain compare to that in H₂O. This is because longer deswelling leads to a more stable UPy aggregation of during deswelling, strengthening the polymer network and the resistance against reswelling, thus decreasing the expandable volume (i.e., linear reswelling ratios) and shortening the time to reach reswelling equilibrium.^[58] Notably, linear reswelling ratios of PNAU hydrogels after deswelling for 18 and 24 h are similar in H₂O but significantly different in DMSO. We hypothesize that reswelling in the protic solvent (i.e., H₂O), which contains hydrogen atoms that can compete with the formation of hydrogen bonds, preventing the growth of UPy aggregates and eventually reaching the UPy aggregation equilibrium.^[43] Especially for the reswelling of the 24 h deswelled PNAU hydrogel, the linear reswelling ratio of 0.92 in DMSO implies that the enhanced restraining force is only slightly offset by the solvation of DMSO, and the polymer network cannot be re-extended as much as that in H₂O. A similar result is also observed in the case of linear reswelling ratios of PNAU hydrogels after deswelling at different temperatures ranging from 40 °C to 80 °C (Figure 2d). Linear reswelling ratios of samples deswelled in H₂O at 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C are 1.35 ± 0.02 , 1.33 ± 0.04 , 1.28 ± 0.02 , 1.17 ± 0.02 , and 1.15 ± 0.01 , respectively. Regarding the reswelling of these deswelled samples in DMSO, the reswelling ratios are 1.23 ± 0.02 , 1.21 ± 0.03 , 1.15 ± 0.03 , 1.09 ± 0.03 , and 1.04 ± 0.03 , respectively. Since PNIPAM segments at a higher temperature undergo more significant phase transitions as the isopropyl groups are desolvated by heat,^[11] a more hydrophobic microenvironment can be created. Simultaneously, the severe shrinkage of PNAU hydrogels results in the compression of the free volume between polymer chains, thereby increasing the opportunity to form larger aggregations. As a result, reswelling ratios of PNAU hydrogels significantly decrease with increasing deswelling temperature (Figure 2d). To further support the above results, we characterized the swelling and reswelling kinetics of PNAU hydrogels by measuring the diffusion coefficients of PNAU hydrogels for swelling and reswelling in H₂O and DMSO. Generally, the relative radius change of hydrogels during solvent diffusion (i.e., swelling, deswelling, and reswelling) can be tracked by the equation $|\frac{R_t - R_\infty}{R_0 - R_\infty}| \cong A \cdot \exp(-\frac{t}{\tau})$, where R_∞ , R_t and R_0 are the radii of hydrogel discs at the equilibrium, time t , and initial state, respectively; τ stands for the final relaxation (i.e., equilibrium) time and A is a constant.^[42,59] After transforming, the linear relationship between the logarithm of $|\frac{R_t - R_\infty}{R_0 - R_\infty}|$ and t can be presented as $\ln |\frac{R_t - R_\infty}{R_0 - R_\infty}| \cong (-\frac{1}{\tau})t + \ln A$, where $-\frac{1}{\tau}$ is the slope and $\ln A$ is the intercept. We tracked the relative radius change of five samples with different initial thickness h_0 (i.e., 0.1, 0.5, 1, 1.5, and 2 mm) during swelling in H₂O, the equilibrium thickness h_∞ of five samples after swelling are 0.56, 0.93, 1.72, 2.29, and 3.02 mm, respectively. Linear fitting of five

samples is therefore determined with different slopes (S) and intercepts (Figure 2e). It is worth noting that S gradually increases (−3.08, −1.59, −0.93, −0.49, and −0.45) with increasing thickness of the hydrogel samples, which interprets the rise in the calculated τ (0.32, 0.63, 1.07, 2.06, and 2.23 h) (Figure S5, Supporting Information). As a result, thicker PNAU hydrogels exhibit less radius change in unit time and require longer time to reach swelling equilibrium in H₂O.^[42,59] Similarly, S values of five samples swelling in DMSO increase with the increasing thickness, and the calculated τ are 0.04, 0.18, 0.41, 0.73, and 0.58 h (Figure S6, Supporting Information). With similar initial thickness, samples swelled in DMSO demand a shorter time to reach swelling equilibrium than samples swelled in H₂O. Furthermore, the deswelling of PNAU in H₂O is proved to be faster than its swelling process with calculated τ of 0.01, 0.02, 0.12, 0.28, and 0.23 h (Figure S7, Supporting Information). Notably, although the discrepancy between initial swelling in H₂O and DMSO is not significant, relative radius changes of PNAU hydrogels exhibit considerable variation when reswelling in H₂O and DMSO. The S values of PNAU samples reswelling in H₂O overall present a similar trend to that of initial swelling in H₂O (Figure S8, Supporting Information), whereas all S values are close to 0 in PNAU samples reswelling in DMSO (Figure S9, Supporting Information), which signifies there is nearly no radius change in unit time and thus the reswelling of PNAU hydrogels in DMSO is neglectable. Additionally, after obtaining τ from the slope of fitted lines, the diffusion coefficient D can be calculated by $D = \frac{h_\infty^2}{\tau^2}$, where h_∞ is the equilibrium thickness of hydrogels; τ is the final relaxation time; k is the exponent.^[59,60] As shown in Figure 2f, the diffusion coefficient of PNAU hydrogels slightly increases from $1.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ during swelling in H₂O to $4.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ during reswelling in H₂O. In DMSO, however, the diffusion coefficient significantly decreases from $5.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ during swelling to $6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ during reswelling. This one order of magnitude decrease indicates that dehydration indeed enhances network strength by promoting the aggregation of UPy dimers, such that the weaker solvation in DMSO is hard to afford re-extension of polymer, causing negligible solvent diffusion during the reswelling process.

Considering the relationship that the higher crosslinking density typically causes a lower swelling ratio but higher mechanical strength,^[61–63] the environmentally adaptive mechanical property of PNAU hydrogels was probed by the tensile tests. The comparison of stress–strain curves of the as-prepared and the drying-reswelling treated PNAU hydrogels reflects the enhancement of strength and toughness, where drying aims to maximize the linear aggregation of UPy and reswelling is to make the dimension of samples similar to that of as-prepared hydrogels (Figure 2g). The tensile strength and break elongation of as-prepared PNAU hydrogels reach 43 kPa and 35%, respectively. After being treated by the drying-reswelling process, the tensile strength of the treated PNAU hydrogel was improved to 175 kPa, while the break elongation extended to 60%. Furthermore, the tensile strength and break elongation of the reswelled PNAU hydrogel are also affected by experienced deswelling time and temperature (Figure 2h,i). Specifically, for PNAU hydrogels after experiencing deswelling at 70 °C for 6, 12, 18, and 24 h, their tensile strength after reswelling 20 min in H₂O are 53, 70, 83, and

92 kPa, respectively, and their break elongation are 49%, 55%, 66%, and 74%, respectively. This indicates that longer deswelling time leads to the enhancement of the tensile strength and break elongation of reswelled PNAU hydrogels (Figure 2h). Similarly, when the deswelling temperature varies from 40 °C, 50 °C, 60 °C, 70 °C, to 80 °C, the elastic modulus of PNAU hydrogels after reswelling 20 min in H₂O are 121 ± 20, 120 ± 28, 119 ± 11, 197 ± 26, and 382 ± 48 kPa, respectively (Figure 2i). While similar elastic modulus of PNAU hydrogels when deswelling temperatures are 40 °C, 50 °C, and 60 °C, great enhancement can be observed when deswelling temperature increases up to 70 °C. We hypothesize that this is because sufficient UPy aggregation cannot be provided by deswelling at 40 °C, 50 °C, and 60 °C in only 6 h, high deswelling temperature like 70 °C and 80 °C is required to create considerable hydrophobic environment. These findings prove that deswelling and dehydration enable the aggregation of UPy additives and enhance the crosslinking strength, which is consistent with the results from swelling and reswelling kinetics measurements.

2.2. Environmentally Adaptive Transparency of PNAU Hydrogels

The environment affects not only the swelling behavior but also the transparency of PNAU hydrogels (Figure 3a). The PNAU hydrogel sheets appear opaque in the as-prepared state and after swelling in H₂O (Figure 3a-i,ii). By exchanging solvents from H₂O to DMSO or dehydrating, the previously opaque PNAU hydrogel sheets gradually became transparent (Figure 3a-iii,iv). Note that the drying-out sample in Figure 3a-iv refers to the condition after completely removing the solvent in an oven at 60 °C overnight. Such environmentally adaptive transparency observed in PNAU hydrogels is ascribed to the in-situ microphase separation of hydrophilic and hydrophobic segments, thus the existence of H₂O molecules is critical to generating an opaque appearance.^[41,44] To further characterize the adaptive transparency of PNAU hydrogels, the effect of UPy contents and solvent compositions on the transmittance of PNAU hydrogels are investigated (Figure 3b). Notably, in the case of DMSO/H₂O = 0, the incorporation of only 0.13 molar fraction of UPy is sufficient to reduce the transmittance below 10%. As the UPy content increases, the lowest molar fraction of DMSO/H₂O that the transmittance attains to 45%, indicated by the region shaded in orange in Figure 3b, improves from 0.7 for PNAU_{0.25} to 1 for PNAU₁. Moreover, to track the time-dependent solvent adaptive transparency, the transmittance of PNAU hydrogels was measured as a function of time during the solvent-switching process (Figure 3c). For PNAU hydrogels with a thickness of 1 mm, the equilibrium period for their transmittance changing to 70% from 2% is approximately 60 min after switching solvents from H₂O to DMSO. In DMSO, PNAU hydrogels cannot be completely transparent because the micro-aggregates of the hydrophobic alkyl chains formed in H₂O are hard to dissociate in DMSO due to the strong hydrogen bonding of UPy.^[64–66] The presence of these microaggregates of the hydrophobic alkyl chains within PNAU hydrogels in DMSO can lead to light scattering, resulting in the slight opacity of PNAU hydrogels in DMSO. Additionally, the relationship between the transmittance of PNAU hydrogels and their thickness was quantitatively characterized (Figure 3d).

When the thickness of hydrogels increases from 0.5 to 3 mm, the transmittance of PNAU hydrogels exhibits a nearly linear decline to 19% from 78% in DMSO. This result arises from more microaggregates in the thicker PNAU hydrogels, which leads to more light scattering and thus higher opacity. In brief, the environmental adaptive transparency of PNAU hydrogels can be a consequence of the hydrophilicity of the copolymer backbone and the hydrophobicity of saturated alkyl chains in UPy additives (Figure 3e). Upon immersion of PNAU hydrogels in H₂O, hydrophobic interaction of saturated alkyl chains in UPy additives induces the formation of hydrophobic micro-aggregates. These micro-aggregates are surrounded by hydrophilic polymer chains, leading to micro-phase separation and a consequent reduction in transmittance (Figure 3e-i and Figure S10a in Supporting Information). However, the amphiphilic environment provided by DMSO eliminates the microphase separation between hydrophilic and hydrophobic phases, thus the transmittance of PNAU hydrogels increases as exchanging solvents (Figure 3e-ii and Figure S10b in Supporting Information).

2.3. 3D Extrusion Printing of PNAU Hydrogels and Environmentally Adaptive Camouflage Actuation

Since the printability of inks for 3D extrusion printing (Figure 4a,b) highly relies on their rheological properties with a requirement for shear-thinning and solid-like behaviors,^[67–69] the rheological measurements of PNAU hydrogels were conducted to confirm their printability. Due to the unique “house-of-cards” structure formed by nanoclay and the extensive hydrogen bonding introduced by UPy additives, the spread of PNAU precursor is hindered (Figure S11a, Supporting Information). By increasing the shear rate from 0 to 300 s^{−1}, the viscosity of PNAU_x hydrogels ($x = 0.25, 0.5, 0.75$, and 1) decreases significantly. For example, the viscosity of PNAU_{0.5} dramatically decreases from 2000 Pa s to around 10 Pa s (Figure S11b, Supporting Information). The shear-thinning behavior is presumably due to the shear force induced disruption of the “house-of-cards” structure and hydrogen bonding, leading to increased precursor mobility.^[68] Additionally, we investigated the comparison of the storage moduli (G') and loss moduli (G'') of PNAU_x hydrogels to unveil their self-supporting behaviors (Figure 4c). For PNAU_x samples, their G' are significantly higher than G'' , indicating that PNAU_x hydrogels are capable of maintaining their extruded shape without collapse or spreading out.^[67–69] Notably, the PNAU_{0.5} hydrogel possesses the highest G' (around 5000 Pa), making it an optimal candidate for following 3D printing. The 3D printing of PNAU hydrogels was performed by a multi-material 3D extrusion printer (Figure 4a), which integrates printing substrates, nozzles, ink syringes, printing holders, gas adaptors, and air pumps to enable the precise and rapid manufacture of complex structures. This printer fabricates 3D structures in the way of line-by-line stacking of extruded filaments (Figure 4b), and the printing resolution mainly depends on the diameter of the nozzle and printing parameters (e.g., extrusion pressure, the speed of moving nozzle, infill pattern, and infill density).^[67] To evaluate the printing resolution and quality of PNAU hydrogels, a mesh structure (10 mm × 10 mm × 2 mm) was printed out (Figure 4d and Movie S1 in Supporting Information). The photo-

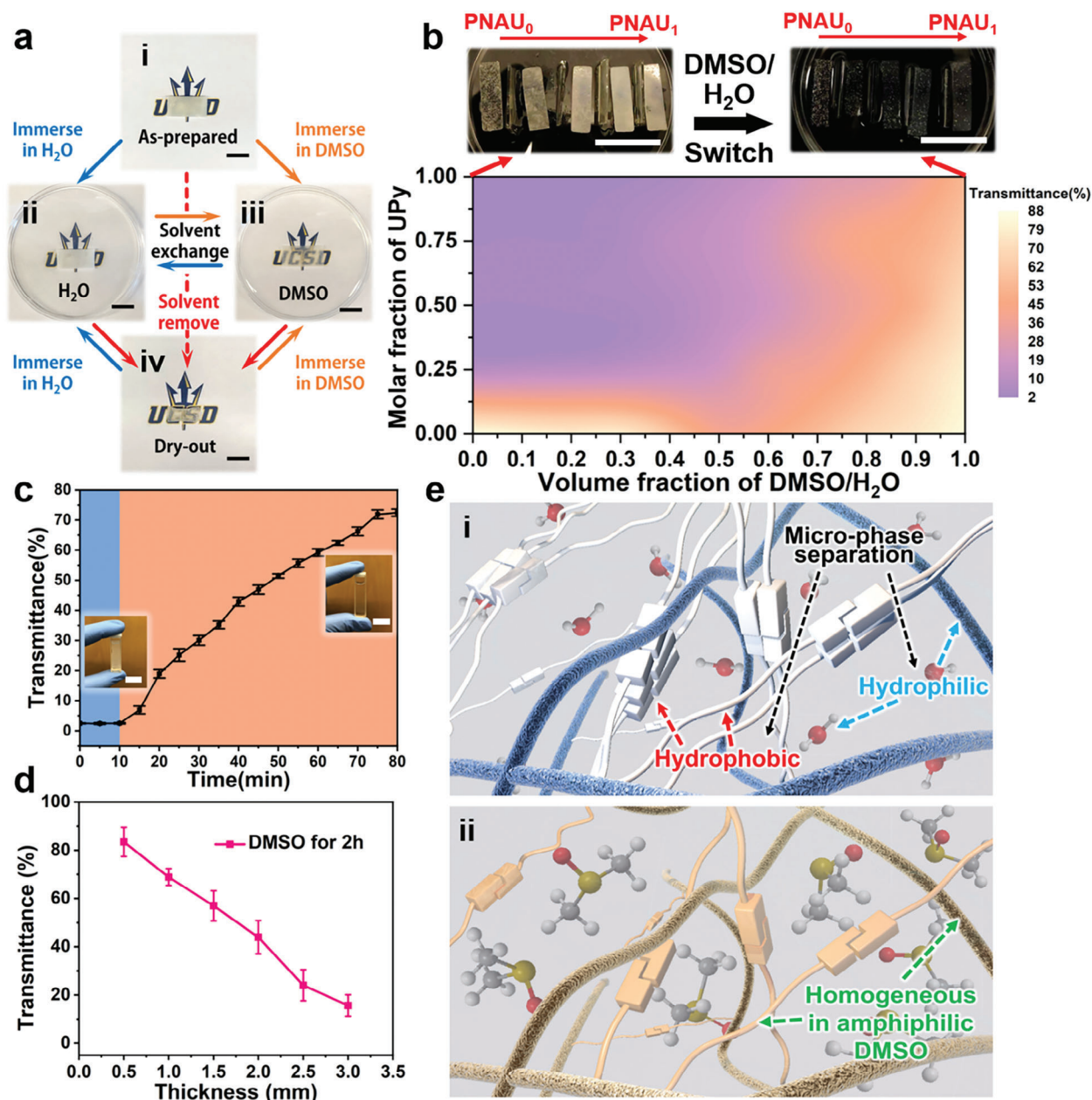


Figure 3. Environmentally adaptive transparency of PNAU hydrogels. a) Transparency change of PNAU hydrogels at i) the as-prepared state, ii) in H₂O, iii) in DMSO, and iv) at the dry-out state. The drying-out refers to the condition after completely removing the solvent in an oven at 60 °C overnight. Scale bars are 15 mm. b) Transmittance of PNAU_x hydrogels with different molar fractions of UPy in solvents consisting of various volume fractions of DMSO and H₂O. Optical photographs exhibit PNAU_x hydrogels (from left to right, $x = 0, 0.25, 0.5, 0.75$, and 1) in H₂O and DMSO, respectively (scale bar is 30 mm). The purple and yellow regions correspond to the lower and higher transmittance, respectively, in the 2D transmittance color map of PNAU_x hydrogels. All samples were immersed in the corresponding solvents for 2 h. c) The time-dependent transmittance of PNAU hydrogels by switching solvents. The blue and orange background indicates that hydrogels are immersed in H₂O and DMSO, respectively. The scale bar in the insert photographs is 20 mm. d) Relation between transmittance and thickness of PNAU hydrogels. All samples were immersed in DMSO for 2 h. e) Mechanism of the solvent adaptive transparency of PNAU hydrogels in i) H₂O and ii) DMSO. Data in Figure 3c,d were expressed as mean $\pm$ standard deviation (SD), where the sample number $N = 5$.

graph of the printed mesh structure depicts the successful line-by-line fabrication using the PNAU ink (Figure 4d-i). Extruded PNAU filaments are consistent and well-defined without spreading (Figure 4d-ii). The stacking of filaments in the vertical direction remained intact after printing, with no deformation or

collapse of the structure observed (Figure 4d-iii). Subsequently, to further verify the suitability of PNAU hydrogels for 3D printing of intricate structures with various shapes and dimensions, several custom designs were printed, including fishbone, octopus, airplane, grille, and letter “B” (Figure 4e-i). Digital

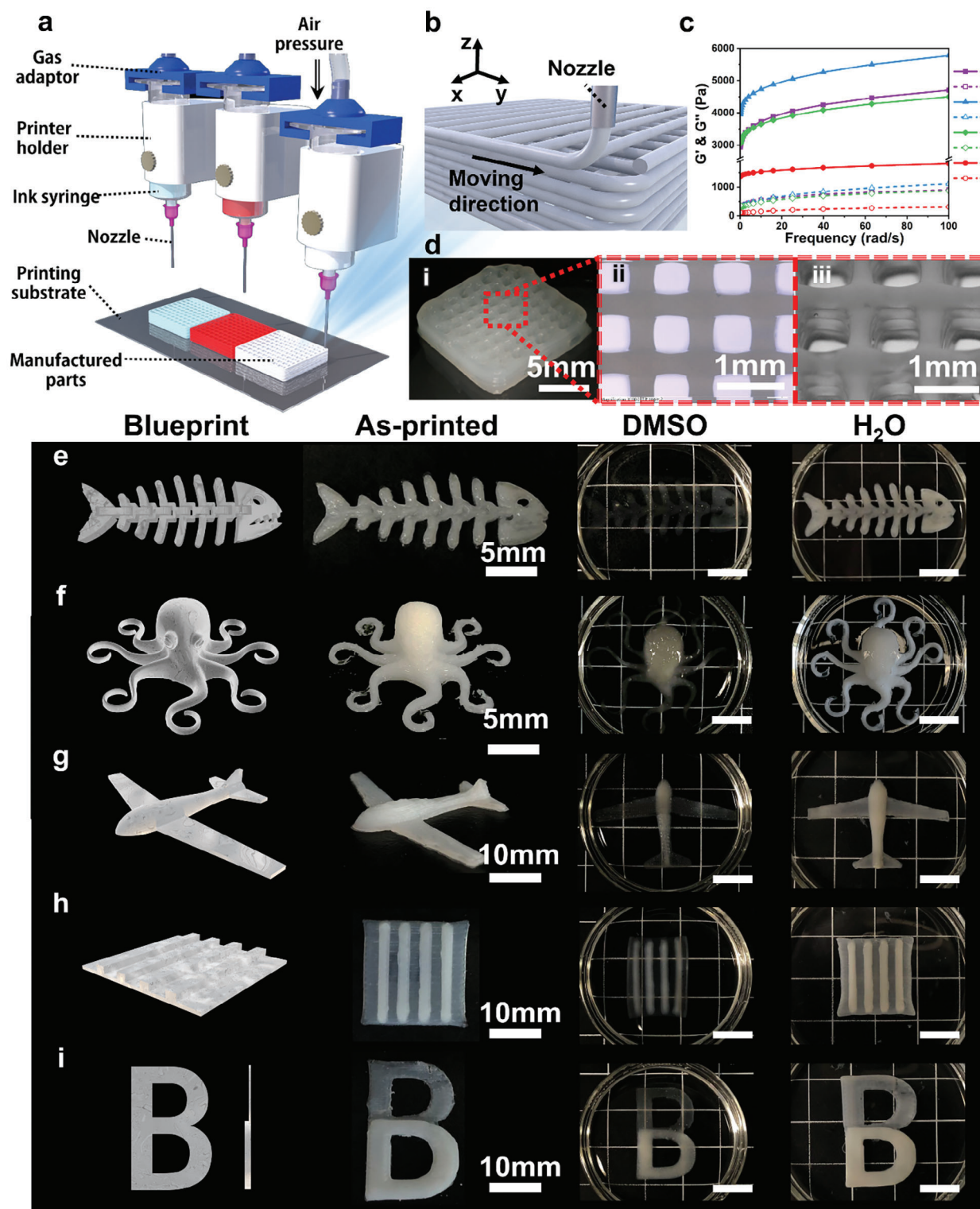


Figure 4. 3D extrusion printing of PNAU hydrogel inks. a) Schematic of the multi-material 3D extrusion printer. b) Schematic of stacking filaments within the 3D extrusion printing process. c) Plots of shear storage moduli (G') and shear loss moduli (G'') as a function of frequency (rad s^{-1}) for PNAU_x hydrogel inks ($x = 0.25, 0.5, 0.75$, and 1). d) Optical photographs of the printed simple mesh structure: i) the overall structure; ii) the top view and iii) 60°-tilted view of the overlapped region after zooming in. e–i) 3D printed complex environmental adaptive camouflage structures: e) fishbone, f) octopus, g) airplane, h) grille, and i) letter “B,” which includes the blueprints of corresponding structures, optical photographs of as-prepared structures, disguised structures in DMSO, and revealed structures in H₂O. Here, all photographs of PNAU hydrogels in Petri dishes were taken after UV-curing for 10 min and then swelling cured samples in H₂O and DMSO for 2 h. Scale bars are 10 mm.

photographs of these as-printed structures demonstrate high-resolution printing, closely aligning with the corresponding blueprints in CAD (Figure 4e–i). Furthermore, the transition interface between vertical and horizontal surfaces is well-controlled without any interlayer slipping or fracture (as-printed structures of Figure 4e–i). Inspired by the camouflage in nature (e.g., octopus, stick insects, and chameleons),^[70] we utilized thickness-dependent opacity of PNAU hydrogels (Figure 3d) to generate the camouflage patterns of printed structures in DMSO. Specifically, the structure with a uniform thickness, such as the fish-bone shape, becomes fully transparent and conceals its appearance in DMSO (Figure 4e). In contrast, 3D structures with varying thicknesses exhibit diverse camouflage patterns in DMSO, including sphere-like, cylinder-like, separated lines, and the letter “D” appearances (the DMSO adaptiveness of Figure 4f–i). Moreover, these disguises can be unmasked when printed structures are transferred into H₂O (the H₂O adaptiveness of Figure 4e–i). Simultaneously, the H₂O environment facilitates the swelling of printed complex PNAU hydrogels, the volumetric expansion does not cause delamination between printed lines, thus illustrating the printing of PNAU hydrogels has excellent structural integrity. Additionally, PNAU inks are applicable for bath-assisted 3D printing to fabricate highly complex structures. The supporting bath (mixing nanoclay (8 wt%) and H₂O) allows for the freedom fabrication of complex PNAU hydrogels like a frog and a vase (Figure S12, Supporting Information). Furthermore, PNAU hydrogels can be used for multi-material 4D printing. As shown in Figure S13 in Supporting Information, a bi-layer actuator consisting of NC-PNIPAM (lower LCST $\approx$ 32 °C) and PNAU (higher LCST $\approx$ 60 °C) was printed out, through regulating the thickness fraction of NC-PNIPAM/PNAU bi-layer and controlling temperature, the multi-shape transformation with different bending curvatures of this bi-layer can be obtained, which demonstrates their promising potential in the fields of 4D printing and smart actuation.^[71]

2.4. 3D Printed Smart Adaptive Devices for Information Security and Multifunctional Actuation

Utilizing the environmentally adaptive transparency and 3D printability of PNAU hydrogels, we demonstrated different concepts of adaptive smart devices to showcase their potential for information security and multi-functional actuation. To develop the information security system, an adaptive smart QR code was printed using a multi-material 3D extrusion printer. The QR code was composed of three sections: one PNAU spacing layer with a thickness of 3 mm and two 1 mm thick layers including split QR code patterns, which employ the thermochromic (red color changes to white when the temperature is higher than 31 °C) powder incorporated PNIPAM (TC-PNIPAM) ink (Figure 5a). These three layers assembled a sandwich-like structure, two QR code pattern layers were spaced apart via the PNAU hydrogel layer. Owing to the solvent adaptive transparency of PNAU hydrogels, the PNAU spacing layer is capable of reversibly controlling the overlap of the top and bottom code patterns. Simultaneously, the red color of code patterns will become white once the environmental temperature is above the color change temperature of thermochromic powders inside, resulting in QR code pat-

terns instantly concealing. Thus, activating or deactivating intact QR code patterns closely relates to its surrounding environmental conditions (i.e., solvent and temperature) (Figure S14, Supporting Information). In addition to the appearance of QR code patterns, the recognition of QR code patterns is another key factor in unveiling the hidden information. Considering the transmittance change of PNAU hydrogels is time-dependent in DMSO (Figure 3c), only immersing the QR code into DMSO longer than 3 h can overlapped patterns be successfully identified by scanning software on a cellphone. Based on the above mechanisms, the photographs in Figure 5b present the specific process of decoding and encoding the smart adaptive QR code. Initially, each side of the as-prepared QR code displays an incomplete red code pattern. The decoding process of the QR code starts when the entire structure is immersed in DMSO at 23 °C. Although the transparency change of the PNAU spacing layer and the overlap of two QR code patterns can be observed in the first 2 h, the overlapped QR code pattern is hard to recognize by scanning software, which is primarily due to the shallower red color of the bottom QR code pattern. Until waiting longer than 3 h, the transparency improvement of the PNAU spacing layer contributes to exhibiting the clearer bottom code pattern, thus realizing the QR code identification (Movie S2, Supporting Information). Contrarily, when the QR code is transferred into H₂O, the transparent-to-opaque transition of the PNAU layer returns to screen the bottom code pattern and encodes within 30 s. Moreover, increasing the temperature to 60 °C arouses the instant color change (from red to white) of code patterns, which deactivates QR code patterns in 10 s and provides secondary protection for encoded information. By leveraging a similar concept, a seven-segment display device was fabricated using a multi-material 3D printer (Figure S15, Supporting Information), the upper and bottom patterns of the device are comprised of PDMS inks integrated by three distinct thermochromic powders (TC-PDMS). The blue, red, and black printed lines become colorless above 31 °C, 45 °C, and 71 °C, respectively (Figure S15a, Supporting Information). Owing to the environmentally adaptive transparency of PNAU hydrogels as the middle layer, the number exhibited by the seven-segment display can be different in response to varying environmental conditions. For example, the device exhibits “3,” “7,” and “1” in H₂O at 23 °C, 40 °C, and 70 °C, respectively, while the number changes to “8” and “4” in DMSO at 23 °C and 70 °C, respectively. Through this environmental adaptiveness, the triple encryption of information can be achieved. Knowing the correct solvents, temperature, and sequence are required to unlock the password (Figure S15b, Supporting Information). For instance, the password “7184” corresponds to the specific sequence “H₂O at 40 °C, H₂O at 70 °C, DMSO at 23 °C, and DMSO at 70 °C”.

To further demonstrate the potential of the environmental adaptiveness of PNAU hydrogels for multi-functional integrated actuations, a bi-layer hydrogel/elastomer multi-functional actuator integrating the information protection is designed (Figure 5c,d). The same multi-material 3D extrusion printer was employed to fabricate this structure. Within the hydrogel/elastomer actuator, the active layer and passive layer are constructed by the PNAU hydrogel and porous PDMS, respectively. We printed “UCSD” letters using the porous PDMS ink between the PNAU hydrogel layer and the porous PDMS layer, which can serve as information that needs to be protected. Dimensions of

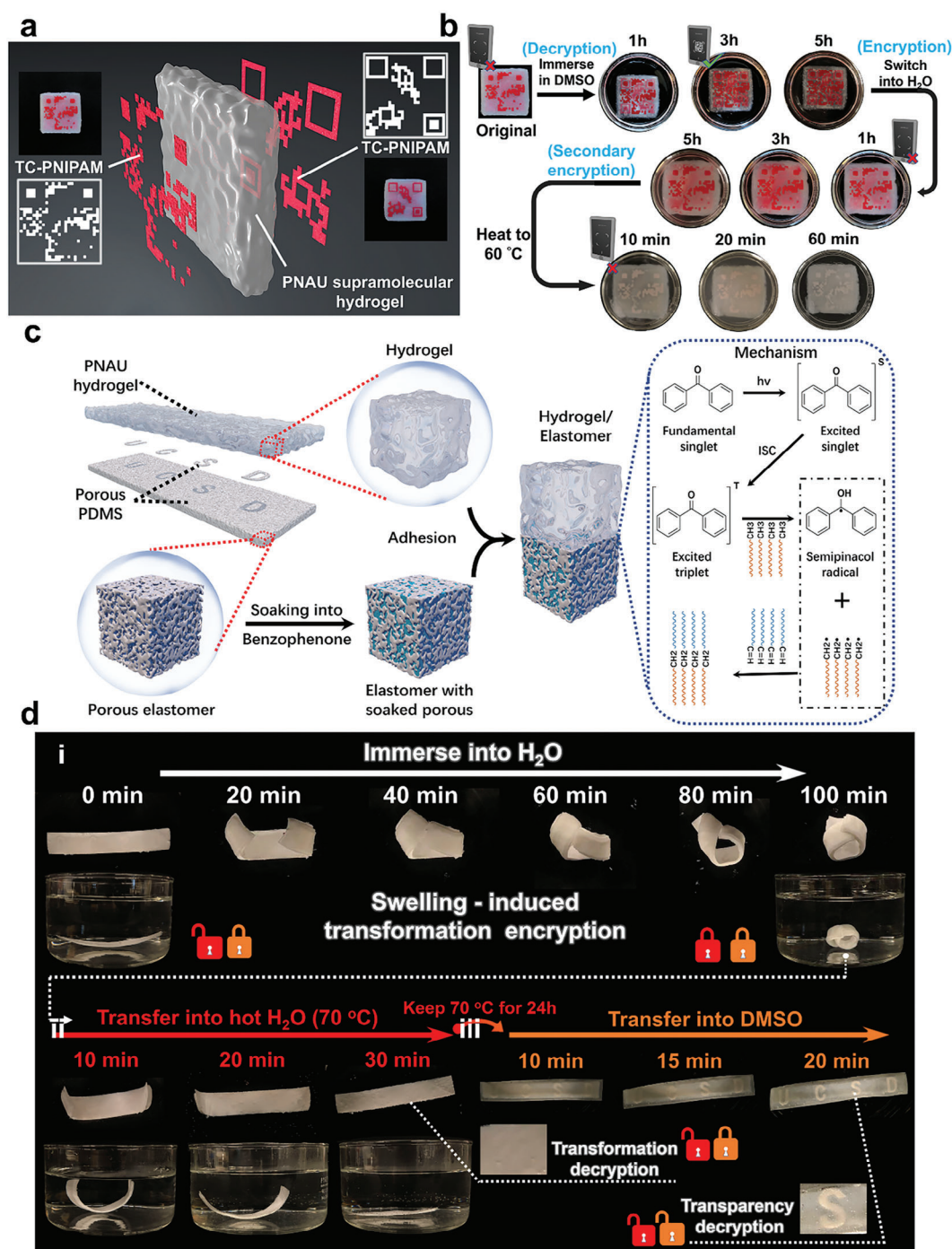


Figure 5. 3D-printed smart devices for information security and multifunctional integrated actuation. a) Schematic of the smart adaptive QR code designed for information encryption. The smart adaptive QR code was a sandwich-like structure constructed by the multi-material 3D extrusion printer. Both the left and right code pattern layers were printed with TC-PNIPAM hydrogel ink. The middle spacing layer was printed with PNAU hydrogel ink. Insert images are the top view (upper left) and bottom view (lower right) of the printed smart adaptive QR code, respectively. b) Optical photographs of the time-dependent decryption (the upper row), encryption (the middle row), and secondary decryption (the lower row) of the smart QR code. The QR code pattern obtained from the online code generator represents the official website of the University of California San Diego (UCSD). c) Schematic of the bilayer hydrogel/elastomer multi-functional actuator integrating with information protection. The bilayer structure with built-in “UCSD” letters was constructed by the multi-material 3D extrusion printer. The hydrogel layer (upper) was PNAU hydrogel, and both of “UCSD” letter (middle) and elastomer layer (lower) were porous PDMS. The adhesion mechanism is based on the formation of interfacial covalent bonds between the soaked benzophenone inside the pores of PDMS and PNAU hydrogels. d) Optical photographs of the printed bi-layer hydrogel/elastomer multi-functional actuator integrating with information protection: i) the transformation encryption induced by swelling mismatch, ii) the transformation decryption caused by deswelling of the PNAU hydrogel layer, and iii) the transparency decryption in DMSO.

the actuator are set to 50 mm in length, 10 mm in width, 1 mm in thickness of the PNAU hydrogel layer, and 0.5 mm in thickness of the porous PDMS layer. The strong adhesion between the PNAU and the porous PDMS layers was realized by the formation of covalent C—C bonds at the interface via photoinitiator benzophenone (Figure 5c). Notably, unlike the PDMS precursor doped with benzophenone in our previous work,^[68] the porous microstructure here not only whitens the appearance (Figure S16, Supporting Information) but also supplies capillary force for storing the benzophenone inside. Figure 5d illustrates the process of encrypting and decrypting information within the actuator. Optical photographs reveal that the disparity in swelling properties between the PNAU and porous PDMS layers results in the shape deformation when the actuator is submerged in H₂O. The bi-layer actuator gradually curls and eventually transforms into a ring-like structure (Figure 5d-i). The information between the PNAU and the porous PDMS layers is protected synergistically by the opaque appearance and the deformation of the actuator, by which the dual-encrypting information can be realized. That is, the correct decryption of information within the actuator necessitates the adaptive swelling property and adaptive transparency of PNAU hydrogels. The transformation decryption process should first be conducted in an H₂O bath at 70 °C, driven by the deswelling of the PNAU active layer, the deformed actuator gradually unfolds in 30 min (Figure 5d-ii). By sustaining the environmental temperature at 70 °C for 24 h, the sufficient UPy aggregation greatly enhances the crosslinking strength of the active PNAU layer. After transferring the unfolded actuator into DMSO at 23 °C, the PNAU hydrogel layer is hard to reswell, thus eliminating the swelling mismatch and allowing the actuator to maintain its flat shape in DMSO. Simultaneously, the adaptive opaque-to-transparent transition of the PNAU hydrogel layer in DMSO contributes to the transparency decryption. The “UCSD” letters can be recognized after immersing the unfolded actuator in DMSO for 20 min. Notably, the encryption and decryption of this actuator is fully reversible. When the hydrogel/elastomer actuator is immersed back into H₂O at 23 °C, its transparency and shape recover to the initial deformed state with dual encryption.

3. Conclusion

In summary, UPy supramolecular additives are incorporated into the P(NIPAM-co-AAm) hydrogel matrix to develop an environmentally adaptive PNAU hydrogel. The hydrogen bonding-induced UPy aggregation is enabled by the hydrophilic-to-hydrophobic environmental transition, thereby causing the environmental adaptiveness of microstructure, swelling behaviors, and mechanical performance of PNAU hydrogels. As the close relationship between the hydrophilic-to-hydrophobic microenvironmental transition and the deswelling of PNAU, increasing deswelling time and temperature triggers a more pronounced UPy aggregation, leading to a reduction in the reswelling ratio but enhancements in both the mechanical strength and stretchability. Especially, the tensile strength and the breaking strain of the drying-reswelling treated samples are greatly increased by 400% and 200%, respectively. Moreover, the microphase separation caused by alkanes within UPy additives endows PNAU hydrogels with environmentally adaptive transparency. The transmittance change of PNAU hydrogels closely depends on the com-

position of solvents and physical geometry. Additionally, hydrogen bonding also contributes to their applicable rheological behaviors for 3D extrusion printing, therefore versatile structures with the camouflage function can be readily and precisely constructed. Finally, the smart adaptive QR code and the multifunctional actuation are demonstrated to highlight the potential application of PNAU hydrogels.

4. Experimental Section

Materials: 1,6-Hexyldiisocyanate (HDI, purity attain up to 99%), 2-amino-4-hydroxy-6-methylpyrimidine (MIC, purity attain up to 99%), acrylamide (AAm), thermal initiator 2,2'-azobis(2-methylpropionitrile) (AIBN), photo-initiator Iragcure 2959, crosslinker N,N'-methylenebisacrylamide (BIS), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich (St Louis, MO, USA). PDMS precursor and initiator (Sylgard 184) was purchased from Dow Corning. Thermochromic powder pigment (TC, change from red to colorless at 31 °C) was purchased from Atlanta Chemical Engineering LLC. N-isopropylacrylamide (NIPAM, stabilized with 4-methoxyphenol, $M_w = 113.16 \text{ g mol}^{-1}$) monomer was purchased from Tokyo Chemical Industry (TCI) Co., LTD. Rheology modifier nanoclay (NC) was purchased from BYK Additives & Instruments. All chemicals were used as received.

Synthesis of PNAU Environmentally Adaptive Hydrogels: Reactions were examined in typical anoxic and anhydrous reactors, where 250 mL three-neck round bottom flask, condenser tube, electric mixer, gas adaptor, and constant temperature oil bath are included. First, synthesizing UPy-NCO additives employed a public method for preparing UPy ended with active isocyanate groups, which can serve as hydrogen bond acceptors and thus provide certain interactions between additives and matrix. The reaction has already been proved that it is dependent on the nucleophilic addition of isocyanate groups and amino groups, the molar ratio of HDI to MIC was set as 1:1. Specifically, MIC (50 mmol, 6.256 g) and HDI (0.3 mol, 48 mL) were added into 250 mL three-necks round bottom flask in a nitrogen environment and kept stirring solution for 24 h at 100 °C. Then the reacted solution was slowly poured into 400 mL petroleum ether to precipitate the UPy-NCO powder. After washing with petroleum ether three times and sequentially drying in the oven at 80 °C overnight, the UPy-NCO powder could be obtained. Afterward, the poly (NIAPM-co-AAm) copolymer matrix was synthesized. 16.98 g of NIPAM monomer and 8.79 g of AAm monomer were added into a new 250 mL three-necks flask under the protection of nitrogen, then slowly injected the 90 mL DMSO solvent and kept stirring solution until NIPAM and AAm dissolved completely. Subsequently, the thermal initiator AIBN (0.156 g, 0.956 mmol) was added into the flask and heated the environmental temperature to 70 °C. After 12 h of reaction, UPy supramolecular additives were mixed to fabricate poly (NIAPM-co-AAm)-UPy (PNAU). The x value of PNAU _{x} hydrogel means the molar fraction of UPy to AAm (Table S1, Supporting Information). For PNAU_{0.5} as an example, 4.395 g of UPy-NCO was first added into the flask of the prepared poly (NIAPM-co-AAm), and the temperature was raised to reflux at 100 °C overnight to make sure UPy are fully dissolved. Next, precipitating PNAU solid was operated into the mixture of H₂O and methanol (1:3), and the product could be obtained after washing with mixture three times and drying the product in the oven at 80 °C overnight. Finally, 14 g of obtained PNAU was dispersed into 130 mL Milli-Q H₂O, and the final PNAU hydrogel ink could be received by mixing initiator Iragcure 2959 (0.2 wt%), monomer NIPAM (10 mmol, 1.13 g), and rheologic modifier NC (5 wt%) with a vortex mixer (Dlab Mx-S) at 23 °C.

Characterizations: To evaluate the synthesis of PNAU hydrogel, the Fourier transform infrared (FTIR) spectroscopy was employed to analyze the molecular structure of prepared products in each step. Specifically, the FTIR of UPy-NCO, poly (NIPAM-co-AAm), and PNAU were exactly reflected by FTIR spectrometer from Perkin Elmer Inc. in attenuated total reflectance (ATR) mode from 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹ with a total of 32 scans under 23 °C. By analyzing the appearance and dis-

appearance of peaks corresponding to functional groups in FTIR, whether functional groups that expected were acquired in the final molecular structure could be confirmed. For the swelling/deswelling/reswelling test, the precursor was cast in the mold constructed by four pieces of glass slides, followed by photocuring under UV light for 10 min, a UV system (Omnicure S2000, wavelength: 365 nm, Lumen Dynamics, ON, Canada) with a tunable output power (0–40 W) was used as curing module throughout the experiments. After demolding, the hydrogel disc with a thickness of 1 mm could be punched using a biopsy puncher with a diameter of 9.5 mm, it was then immersed into the solvent (H_2O or DMSO) at 23 °C for 24 h and the diameter change upon the swelling process was measured by the size measuring function in an optical microscope (Keyence VHX 6000). The deswelling test was examined in H_2O at 70 °C for 6, 12, 18, and 24 h (or 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C for 6 h). Reswelling test was carried out by re-immersing deswelled hydrogels into solvent (H_2O or DMSO) at 23 °C for 24 h. The linear swelling/deswelling/reswelling ratio was calculated by $\lambda = \frac{d_t}{d_0}$, where d_t is the diameter at a specific time or equilibrium diameter at certain temperature and d_0 is the as-prepared diameter. The morphology of synthetic bottlebrush supramolecular hydrogel was characterized by the scanning electron microscope (SEM, FEI Quanta FEG 250). The preparation of samples for SEM required to freeze dry in advance. The samples were first swelled in H_2O at 23 °C, then these fully swelled samples were rapidly frozen in liquid nitrogen for 10 min. Next, the frozen samples were dried by freeze dryer (Labconco FreeZone) at –50 °C for 72 h. Subsequently, the freeze-dried samples were coated with iridium for 8 s to prevent the charging of specimens during SEM imaging. For mechanical property, a punch cutter with 25 mm $\times$ 8 mm was used to cast the photocured PNAU film with 1 mm thickness. Furthermore, the casted rectangular hydrogel sample was loaded on the universal testing machine in a tensile mold (Instron, Bluehill, MA, USA), and the instrument was set as the 100 N load cell with a stretch rate of 10 mm min^{–1}. The stress–strain curve was plotted according to the displacement and applied force. Young's modulus (E) of the hydrogel at a certain tensile strain was calculated by the slope of the stress–strain curve at the breaking point. Regarding the rheological characterization, the relationship between the viscosity and shear rate was tested using TA Instruments Discovery HR-30 Hybrid Rheometer. In addition, to investigate the viscoelastic behaviors of PNAU precursor, the storage and loss modulus of samples were characterized as a function of angular frequency in the same instrument. All transmittance experiments were tested through the UV–vis–NIR spectrometer (Perkin Elmer). The wavelength was fixed at 750 nm. Coated precursor film was photocured with 1 mm thickness first, and a 35 mm $\times$ 12.5 mm cutter was then used to cast the standard sample, the resulting samples were then inserted into an instrument-specific quartz cuvette and injected solvent to the liquid level just submerged the sample. All data in swelling and mechanical tests were expressed as mean $\pm$ standard deviation (SD), where the sample number $N = 5$.

Swelling/Deswelling/Reswelling Kinetics: The swelling/deswelling/reswelling kinetics of hydrogels were examined according to previous works.^[59,60] Hydrogels with the same diameter of 4.5 mm and variable thickness (0.1, 0.5, 1, 1.5, 2 mm) were prepared in specific molds. The diameter was greater than the thickness, and their diameter change was measured by digital microscope (Keyence VHX) in all swelling/deswelling/reswelling processes. Through the $\left| \frac{R_t - R_\infty}{R_0 - R_\infty} \right| \cong A \cdot \exp\left(-\frac{t}{\tau}\right)$, where R_∞ , R_t , and R_0 is the radius of hydrogels at the equilibrium, time t , and the beginning, respectively, τ is the final relaxation time, the relaxation time of each sample from the linear fitting of data could be calculated. Afterward, using the relationship between relaxation time and equilibrium thickness, the effective diffusion coefficient (D) can be calculated by $D = \frac{h_\infty^2}{\pi^2 \tau}$, where h_∞ is the thickness of hydrogels at the equilibrium; τ is the final relaxation time; k is the exponent.

3D Printing of PNAU Hydrogels: The 3D printing of PNAU ink was achieved via a 3D extrusion printer (BioX bioprinter, produced by CELLINK) under a filament-by-filament extrusion and stack model, the synthetic ink used for printing was filled in a 5 mL syringe and squeezed out of the nozzle driven by air pressure. The nozzle size was 25 Gauge, which has

an inner diameter of 0.25 mm, the printing pressure and speed were set as 240 Kpa and 10 mm s^{–1}, respectively, and the rectangular pattern was used as the infill pattern, the infill density was set as 65%. All 3D model files were established CAD software (Solidworks, Dassault Systèmes Co., Ltd.) and could be exported as STL format, which is capable of being directly imported into BioX 3D printer. According to their shape and thickness, the imported 3D models were automatically sliced into different layers through the slicing software that comes with the printer. After printing, printed objects continued to photocure for 30 min in a UV system (Omnicure S2000, wavelength: 365 nm, Lumen Dynamics, ON, Canada) with a tunable output power (0–40 W). It is worth noting that this BioX 3D printer has three valid heads, and three heads filling in different precursor inks allow the multimaterial 3D printing of PNAU hydrogels, which facilitates the design of the application.

Fabrication of Smart QR Code: The smart QR code was manufactured by BioX multimaterial 3D printer directly. The structure was composed of three layers, the upper layer and bottom layer were split QR code patterns, and the middle layer was a spacer. The ink for the upper and bottom layer was TC-PNIPAM, which could be obtained by mixing 2 m NIPAM monomer (10 mL), 0.13 m BIS crosslinker (120 μL), NC rheological modifier (1 g), Iragcure 2959 (0.04 g), and thermochromic powder (0.75 g). The ink for the middle layer was PNAU hydrogel. First, the PNAU layer with a thickness of 3 mm and an upper QR pattern on a glass substrate was printed, then cured them together for 20 min under UV light. After curing, the bilayer structure was flipped and another bottom pattern on another side of the spacer was printed. Finally, the whole smart QR code could be acquired after UV-curing for 10 min. The printing parameter for TC-PNIPAM was shown as follows: nozzle size was chosen 25 Gauge, the printing pressure and speed were set as 75 KPa and 8 mm s^{–1}, respectively, and the rectangular pattern was used as the infill pattern, the infill density was set as 65%.

Fabrication of Multifunctional Hydrogel/Elastomer Actuator: The hydrogel/elastomer actuator also was fabricated by the BioX 3D printer directly. The actuator is a bilayer structure, the bottom layer and “UCSD” letter employed porous PDMS ink, which was prepared the same as the previous work.^[72] The top layer was PNAU hydrogel, which served as a cover and driven layer. Specifically, a porous layer with 50 $\times$ 10 $\times$ 0.5 mm was printed first, including the bottom layer and “UCSD” letters. Then, the printed PDMS structure was put into the oven at 80 °C for 2 h. After the thermal curing of PDMS, it was immersed in ethanol to generate a porous structure. Subsequently, porous PDMS was soaked into benzophenone melt for 1 h to absorb the adhesive agent through capillary effect. The adhesive mechanism is shown in Figure 5c. Next, the PNAU hydrogel layer on the top of PDMS was printed. The final structure exhibits excellent adhesion under H_2O . The printing parameter for porous PDMS was shown as follows: nozzle size is chosen 25 Gauge, the printing pressure and speed were set as 75 kPa and 8 mm s^{–1}, respectively, and the rectangular pattern was used as the infill pattern, the infill density was set as 65%.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

X.L. and J.B. designed the project. X.L. carried out most experiments, analyzed data, and prepared the manuscript draft. Z.G. characterized the rheology of hydrogels. J.Z. established the CAD blueprint of complex structures and assisted in 3D printing. J.B. contributed to the interpretation of results and supervision. All authors discussed the results and contributed to the final manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

3D printing, smart hydrogels, soft actuators, stimuli-responsive hydrogels, supramolecular interactions

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