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A Novel Anisotropic Hydrogel with Integrated Self-Deformation and Controllable Shape Memory Effect

Xiao-xia Le, Yu-chong Zhang, Wei Lu, Li Wang, Jing Zheng, Israt Ali, Jia-wei Zhang, You-ju Huang, Michael J. Serpe, Xi-tao Yang, Xin-dong Fan, and Tao Chen**

Although shape memory polymers have been highlighted widely and developed rapidly, it is still a challenging task to realize complex temporary shapes automatically in practical applications. Herein, a novel shape memory hydrogel with the ability of self-deformation is presented. Through constructing an anisotropic poly(acrylic acid)–polyacrylamide (PAAc–PAAm) structure, the obtained hydrogel exhibits stable self-deformation behavior in response to pH stimulus, and the shapes that formed automatically can be fixed by the coordination between carboxylic groups and Fe^{3+}; therefore, self-deformation and shape memory behaviors are integrated in one system. Moreover, the magnitude of auto-deformation and shape memory could be adjusted with the concentration of corresponding ions, leading to programmable shape memory and shape recovery processes.

1. Introduction

Stimuli-responsive hydrogels, which are made up of water swollen 3D polymer networks, can reversibly change their shapes or dimensions upon exposure to external stimuli (temperature,[1,2] light,[3–5] chemicals,[6,7] pH,[8–12] ionic strength,[13] and so on), and realize fascinating functions such as controllable shape memory,[14–17] shape transformation,[18–21] color change,[22,23] among others.[24,25] To better mimic the performances of natural organisms and expand their applications, it is necessary to investigate the synergy of different functions of stimuli-responsive hydrogels. However, it is a great challenge to integrate multiple functions in one single system without their mutual interfering.

Among various stimuli-responsive hydrogels, shape memory hydrogels have attracted increasing research interest because of their unique ability of fixing temporary shapes and recovering to original shapes. However, their temporary shapes are often created by external forces. This method has limitation in practical applications, especially in the cases that require complex temporary shapes. Therefore, novel shape manipulating methods are highly desired. A few researchers have attempted to involve actuating behavior in shape memory polymers.[26–28] Smoukov and co-workers[26] have designed a multifunctional material consisting of interpenetrating poly(ethylene oxide) network and polycaprolactone network, which has both ionic actuation and shape memory properties. White and co-workers have introduced twisted nematic geometry into glassy liquid crystalline polymer networks to realize spontaneous deformation by heating and fix the temporary shape through rapid temperature cycling.[27] Recently, Zhuo and co-workers[28] have reported stimuli-responsive shape memory polyurethanes, which are capable of shape deformation under UV light, shape fixation in visible light as well as shape recovery by heating.

Herein, we presented a facile yet effective approach to integrate auto-deformation ability into shape memory hydrogels. As shown in **Scheme 1**, a homogeneous polyacrylamide (PAAm) hydrogel was prepared as the primary network, then a secondary inhomogeneous poly(acrylic acid) (PAAc) network was introduced via UV-initiated polymerization, leading to an anisotropic structure. The as-prepared PAAm–PAAc hydrogel could accomplish diverse complex deformations upon the pH stimulus because of the heterogeneous responsiveness of anisotropic structure. Moreover, by utilizing PAAm network to memorize the permanent shape and the complexation between PAAc network with Fe^{3+} to stabilize the temporary shape, the as-prepared hydrogel exhibits shape memory behavior.

X.-x. Le, Y.-c. Zhang, Dr. W. Lu, L. Wang, J. Zheng, I. Ali, Prof. J.-w. Zhang, Prof. Y.-j. Huang, Prof. T. Chen
Key Laboratory of Marine Materials and Related Technologies
Zhejiang Key Laboratory of Marine Materials and Protective Technologies
Ningbo Institute of Material Technology and Engineering
Chinese Academy of Sciences
Ningbo 315201, China
E-mail: zhangjiawei@nimte.ac.cn; tao.chen@nimte.ac.cn

X.-x. Le, Y.-c. Zhang, Dr. W. Lu, L. Wang, J. Zheng, I. Ali, Prof. J.-w. Zhang, Prof. Y.-j. Huang, Prof. T. Chen
University of Chinese Academy of Sciences
19 A Yuquan Road
Shijingshan District
Beijing 100049, China

Prof. M. J. Serpe
Department of Chemistry
University of Alberta
Edmonton
Alberta T6G2G2, Canada

Dr. X.-t. Yang, Prof. X.-d. Fan
Department of Interventional Radiotherapy
Shanghai Ninth People's Hospital
Shanghai Jiao Tong University School of Medicine
Shanghai 200011, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.201800019.

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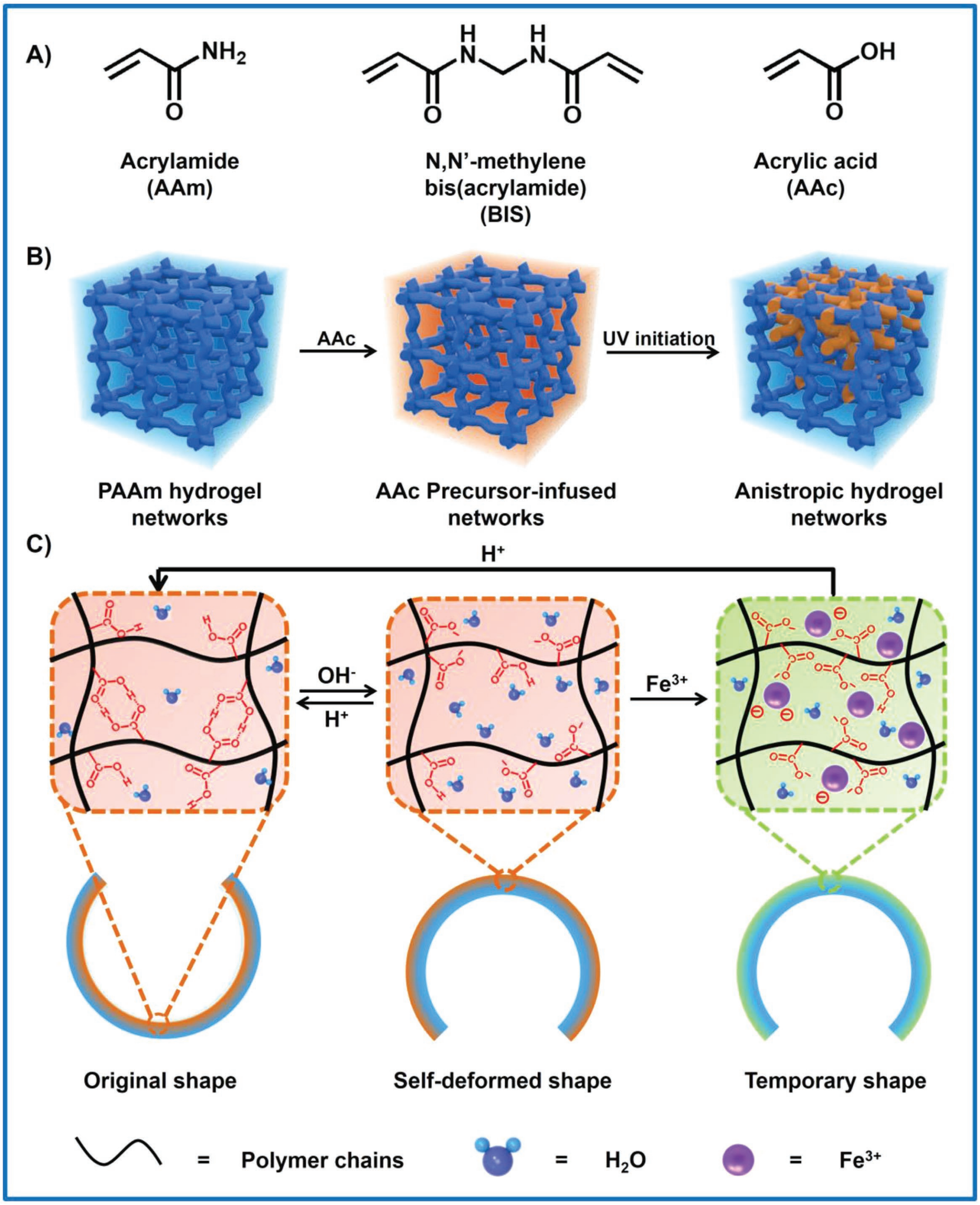

Scheme 1. Schematic illustration of controllable self-driven hydrogel with shape memory effect. A) The molecule structures of monomers and crosslinker, including AAm, AAc, and BIS. B) The preparation process of anisotropic hydrogels: PAAm homogenous hydrogel was first prepared at room temperature. After absorbing AAc precursor solution, UV polymerization was used for producing anisotropic hydrogel structure. C) The mechanism of self-driven process as well as shape memory behavior: the self-deformed shape of hydrogel was obtained by putting original hydrogel into NaOH solution to deprotonating PAAc. Then, through the interaction between carboxylic groups of PAAc and Fe^{3+}, temporary shape can be memorized, which can also be destroyed in HCl solution to recover to the original shape.

Therefore, the temporary shape of the hydrogel can be generated automatically upon pH stimulus, and then memorized by Fe^{3+}, leading to the synergy of auto-deformation and shape memory behaviors.

2. Results and Discussion

Through UV-initiated polymerization, a secondary PAAc network is introduced into the PAAm hydrogel network. Due to

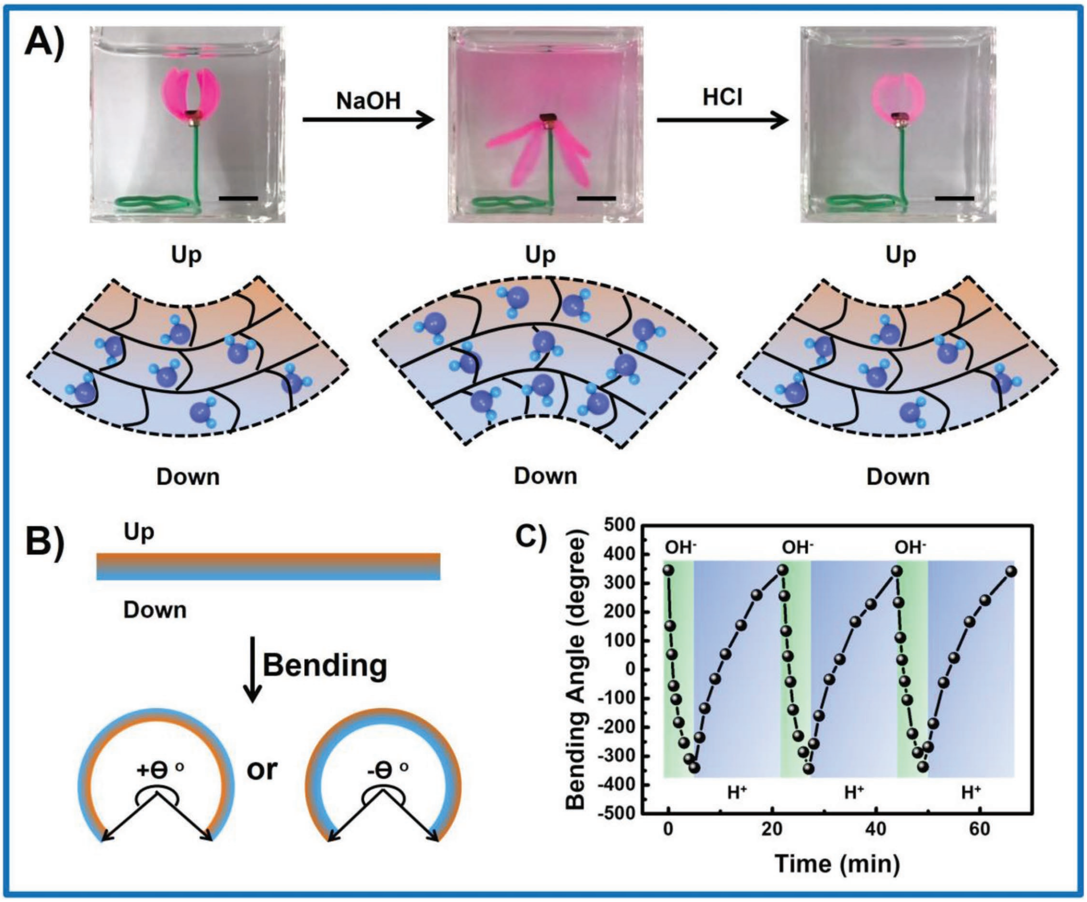

Figure 1. Self-driven process of the anisotropic hydrogel. A) The flower-shaped hydrogel opens its petals in 0.2 M NaOH solution (toward downside), and closes its petals in 0.2 M HCl solution (toward upside). B) The definition of positive/negative angles. The positive angle corresponds to the hydrogel bends to the upper side with more PAAc, and the negative angle is just the reverse. C) Cyclic reversible changes of bending angles in alkali solution and acid solution, alternatively. Scale bar: 1 cm.

poor penetration of UV light, the distribution of PAAc network in the hydrogel is inhomogeneous, the density of PAAc in the upper side of hydrogel is higher as compared with that of the downside (Figure S1, Supporting Information). As a result, the protonation and deprotonation of carboxyl groups is asymmetric inside the hydrogel, causing an asymmetric swelling and deswelling behavior. As shown in **Figure 1**A and Figure S2 in the Supporting Information, the petals of flower shape hydrogel bend to upside (positive angle) in water because of the inhomogeneous distribution of PAAc (closed bud) (Figure 1B). When the flower shape hydrogel is transferred into NaOH solution, the carboxyl groups will be deprotonated and the osmotic pressures between the upside and the downside will be unbalanced, leading to the blooming of the hydrogel flower (Figure S3, Supporting Information). Furthermore, the carboxylic ions will be protonated in acidic condition, and in response, the flower closes its petals and retracts to a bud again. As demonstrated with a straight hydrogel strip, the auto-deformation process is reversible for at least three cycles (Figure 1C and Figure S4, Supporting Information), indicating the stability of actuating process as well as good mechanical properties of the hydrogel.

It is well known that Fe^{3+} can chelate with AAc to form mono-, bi-, and tridentates,[29,30] and the coordination between Fe^{3+} and AAc has been introduced into shape memory hydrogels and applied as reversible crosslinks to stabilize temporary shapes.[31–35] As shown in **Figure 2**, a hydrogel bends into a circle in alkaline condition, and the circular shape could be fixed by AAc–Fe^{3+} crosslinks. When immersed in 0.02 M $FeCl_3$ solution, the shape fixity ratio can reach up to 93% (Figure 2B), which is not achieved in HCl solution with the similar pH value (Figures S5 and S6, Supporting Information). With increasing the concentration of Fe^{3+} from 0.02 to 0.5 M, the fixed angle of the hydrogel gradually converts from negative to positive (Figure S7, Supporting Information), which suggests the decreasing of the shape fixity ability. One possible reason for the lower shape fixity ratio is that mono- or bidentates of Fe^{3+} with AAc may form at higher Fe^{3+} dosage. In addition, the pH value is lowered with the addition of Fe^{3+} (Figure S5, Supporting Information), which suggests that the capacity of stabilizing deformed networks decreases. As the self-deformed shape of the hydrogel could be efficiently fixed in 0.02 M Fe^{3+} solution, it was therefore chosen for the following investigation.

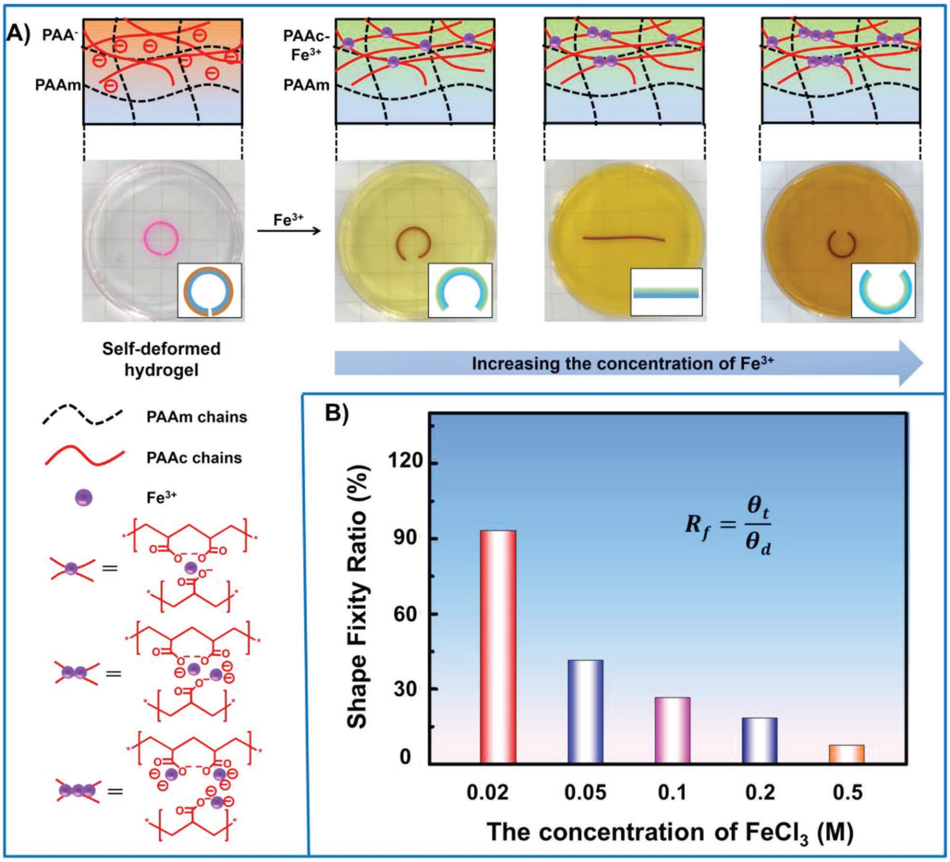

Figure 2. Controllable shape memory behavior. A) The mechanism of controllable shape memory procedure produced by changing the concentration of Fe^{3+}, in which higher concentration of Fe^{3+} corresponds to more mono- or bidentates with AAc and decreases the crosslinks. B) The shape fixity ratios triggered by Fe^{3+} with different concentrations (0.02–0.5 M), in which θ_t is the fixed angle and θ_d is the self-deformed angle.

When the hydrogel with a temporary shape is transferred into acid solution, the AAc–Fe^{3+} temporary crosslinks will be destroyed,[36,37] leading to the recovery of the original shape. As illustrated in **Figure 3**A,B and Figure S8 in the Supporting Information, by increasing the concentration of H^+ from 0.01 to 0.1 M, Fe^{3+} is gradually replaced with H^+, the ability to keep the temporary shape is deteriorated and the tendency of bending to original shape is intensified, and the hydrogel will recover to its initial shape. The shape recovery ratio can reach 93.6% when 0.1 M HCl is applied to induce the shape recovery. Moreover, the shape recovery process can be programmed by immersed into different concentrations of HCl step by step (Figure 3C).

Not limited with the simple transformation like bending from a strip to a circle, complex shape transformation and shape memory behavior are also achieved if the hydrogel is deliberately cut into a designed pattern. Inspired by the flower's blooming/falling and the butterfly's flapping wings in nature, we designed a flower shape hydrogel owning four petals and a butterfly shape hydrogel with two wings, displaying a scene of "butterfly loves flower" (**Figure 4**A). Once putting the hydrogels into 0.2 M NaOH solution, the closed flower opens the petals slowly, and the butterfly flaps its wings downward due to the repulsive interactions between deprotonated carboxyl groups. After immersing into 0.02 M $FeCl_3$ solution, the drooped flower shape and butterfly shape could be stabilized because of the formation of AAc–Fe^{3+} complexing. Moreover, the temporary shapes will recover to the permanent ones by gradually increasing the concentration of H^+. The auto-deformation behavior with predetermined temporary shapes will provide unique functionality for the shape memory hydrogels.

3. Conclusions

In conclusion, we have presented a novel strategy to incorporate self-deformation and shape memory behavior into one hydrogel system. An anisotropic hydrogel is fabricated by introducing a secondary inhomogeneous PAAc network into a PAAm hydrogel by taking the advantage of poor penetration of UV irradiation. The pH-responsiveness of carboxylic groups of PAAc is applied to induce the auto-deformation process, and the coordination between carboxylic groups and Fe^{3+} serves as reversible crosslinks to memorize the temporary shape, leading to the integration of self-deformation and shape memory behaviors. In addition, the competition of deforming force and memorizing force could be adjusted with the concentration of corresponding ions, therefore, programmable shape memory and shape recovery processes could be realized. This combination successfully endowed the hydrogel with self-transformation and shape memory properties simultaneously, and the novel

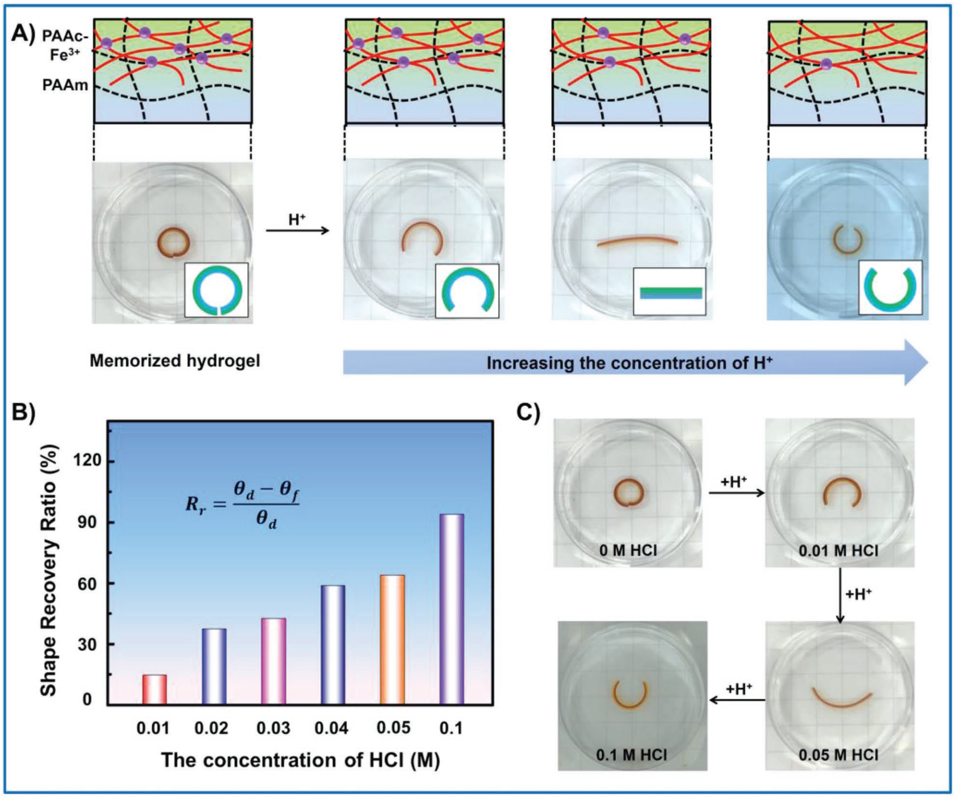

Figure 3. Controllable shape recovery process. A) The schematic diagram of mechanism for controllable shape recovery procedure produced by varying the concentration of H^+, in which higher concentration of H^+ leads to more Fe^{3+} being replaced and more crosslinks being destroyed. B) The shape recovery ratio triggered by H^+ with different concentration (0.01–0.1 M), in which θ_d is the self-deformed angle and θ_f is final recovered angle. C) The programmable shape recovery can be realized by increasing the concentration of H^+ step by step.

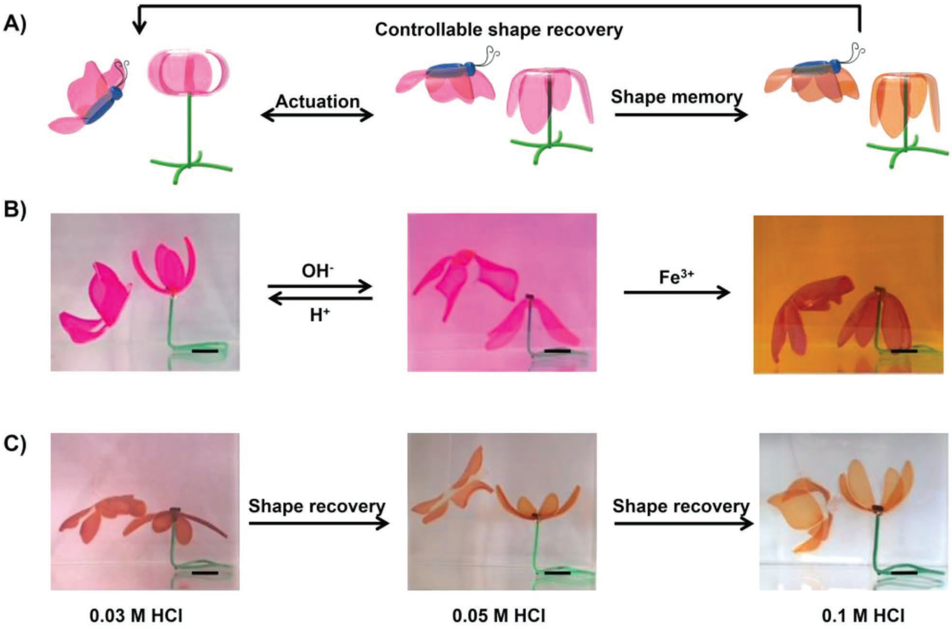

Figure 4. A) The "butterfly loves flower" cartoon picture of whole shape memory behavior, including self-driving, shape memory, and shape recovery. B) The photos of flower's blooming and butterfly's flapping wings triggered by alkaline solution, turning to bud provoked through immersing in acid solution and keeping temporary shape by adding Fe^{3+}. C) The procedure of programmable shape recovery achieved by increasing the concentration of H^+ gradually. Scale bar: 1 cm.

material design strategy will pave a new way for fabricating multifunctional intelligent materials.

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.

Keywords

complementary functionalities, self-driven, shape memory, stimuli-responsive hydrogels

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