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Actuating and memorizing bilayer hydrogels for a self-deformed shape memory function†

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A general strategy for fabricating a double layer self-deformed shape memory hydrogel which includes a thermo-responsive actuating layer and a pH-responsive memorizing layer is presented. Compared with traditional shape memory polymer systems, the temporary shape of the hydrogel could be generated by a thermo-responsive actuating layer upon the trigger of heat without the need for an external force, which could be further memorized by the pH-responsive memorizing layer.

As one of the most promising intelligent materials, shape memory polymers can stabilize their temporary shape and return to their original shape *via* external stimuli such as heat, light, pH and so on.[1–4] Therefore they have attracted increasing attention and shown promising applications in many fields, such as biomedicine, smart textiles, artificial tissue engineering and in micro-fluid controlling valves.[5–8] Traditional shape memory polymers are thermo-responsive polymers, in which the temporary shapes are fixed by vitrification/crystallization of polymer chains.[9] With the development of supramolecular chemistry,[10–12] reversible interactions have been applied as temporary crosslinks to stabilize temporary shapes, realizing shape memory behaviour at ambient temperature.[13–19] However, the temporary shapes of traditional thermo-induced shape memory polymers or innovative supramolecular shape memory hydrogels are often created as well as defined by an external force. If the temporary shape is complex or the operation environment is not suitable for direct contact, the commonly used deformation method will be limited, which would greatly restrict the potential applications of shape memory polymers. Therefore, a novel shape generating method is highly desired.

In order to realize an innovative method of shape transformation in shape memory hydrogels, another promising intelligent material, soft actuators were considered due to their ability to change their volume or shape drastically and reversibly upon the trigger of external stimuli.[20] If the soft actuators have isotropic structures, they normally undergo simple homogeneous swelling/shrinking under uniform stimuli. Alternatively, bio-inspired by the diverse anisotropic structures of living organisms in nature, many anisotropic structures have been explored to achieve various complex shape transformations. Bending and stretching behaviours have been achieved by introducing nanoparticles to fabricate gradient structures,[21,22] or accomplished by building layer-by-layer structures with interpenetrating networks. Furthermore, self-folding and buckling in 3D have also been developed using the origami technique,[23] photolithography,[24] dip-dyeing[25] and 3D printing.[26] Chu *et al.* have prepared a bilayer poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel with an asymmetrical distribution of nanoclays as a thermo-responsive manipulator.[27] Hayward *et al.* have fabricated 2D hydrogel sheets with UV-induced patterning to obtain precisely controllable 3D bucklings.[28] Lewis *et al.* have endowed the cellulose hydrogel with shape morphing capacity *via* 4D printing.[29] We have also achieved the 3D complex shape change through constructing an anisotropic hydrogel with a local second-network.[30]

Considering the variety of shape transformation behaviour of soft actuators, it can be anticipated that the introduction of an actuating system into shape memory polymers will endow them with various temporary shapes and non-contact self-deformation behaviour. Fabricating bilayer structures is an efficient way to achieve an anisotropic hydrogel and a convenient approach towards introducing the shape deformation hydrogel as one layer. Herein, we present a bilayer self-deformed shape memory hydrogel with a thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) layer as the actuating layer and a pH-responsive poly(acrylamide)-chitosan (PAAm-CS) layer as the memorizing layer (Scheme 1). When the temperature exceeds the lowest critical solution temperature (LCST), the PNIPAM layer would undergo hydrophilic–hydrophobic transition, and the shape of the bilayer

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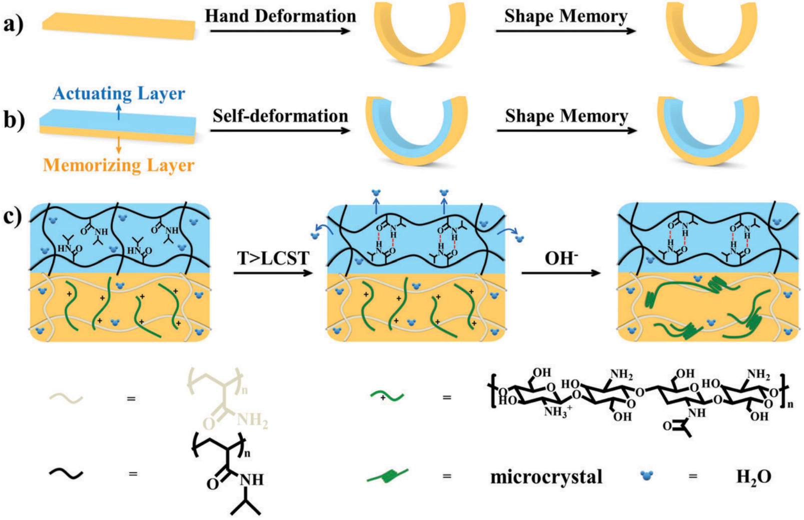

Scheme 1 (a) The traditional shape memory process of hydrogel: hand deformation is generally indispensable. (b) The novel self-deformed shape memory process: an additional actuating layer is added alternatively. The bilayer hydrogel strip automatically bends into a circle in response to heat stimulus due to the hydrophilic–hydrophobic transition of PNIPAM; and the temporary shape is memorized in alkaline condition caused by the formation of micro-crystallization of chitosan chains. (c) The mechanism of a self-deformed shape memory process.

hydrogel would deform as a result of the shrinkage of the PNIPAM layer.[31,32] Moreover, the chitosan chains would undergo micro-crystallization under alkaline conditions, which could serve as crosslink points and stabilize the deformed shape generated by the PNIPAM layer.[33,34] In addition, the bilayer hydrogel could recover to its initial shape when micro-crystallization is relieved by decreasing the pH. By integrating shape transformation and shape memory functions into a bilayer hydrogel, we demonstrate a general strategy to fabricate a shape memory hydrogel in which a temporary shape could be generated by the thermo-responsive actuating layer upon the trigger of heat without the need of an external force, which would enrich the fields of intelligent materials and promote potential applications.

The fabrication process of the bilayer hydrogel is schematically illustrated in Fig. S1 (ESI†). The PAAm-CS layer (memorizing layer) was prepared first by photo-polymerization of acrylamide (AAm) exposed to UV irradiation (365 nm) in the presence of chitosan. Then, a PNIPAM (actuating layer) layer was prepared on the top of the first layer by photo-polymerization of NIPAM in ice-water bath, resulting in a stable bilayer hydrogel. The bilayer hydrogel was detached from the mold and immersed in 0.1 M KNO_3 solution to remove any unreacted monomers. The bilayer structure of the as-prepared hydrogel was investigated by scanning electronic microscopy (SEM). As shown in Fig. 1, the PNIPAM and the PAAm-CS layer exhibit different porous microstructures. The two layers are joined together by a dense interfacial layer with a width of about 160 μm. This interfacial layer is probably an inter-penetrating-network formed during the fabrication process because the NIPAM solution permeated into the top of the PAAm-CS layer before the second photo-polymerization step. Noteworthily, the PNIPAM layer and the PAAm-CS layer are joined tightly by this junction layer and will not separate during the bending–recovering process.

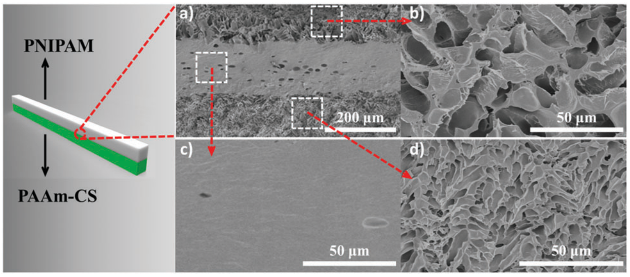

Fig. 1 (a) Cross-section SEM image of the interface of a freeze-dried bilayer hydrogel. (b) SEM image of the PNIPAM layer. (c) A dense buffer layer indicating a tight combination. (d) SEM image of the PAAm-CS layer.

In order to confirm whether the actuating layer and the memorizing layer would function as expected, a shape memory test was conducted. As illustrated in Fig. 2a, if the bilayer hydrogel is transferred to an environment with a temperature higher than the LCST of the PNIPAM network, the actuating layer will shrink. As a result, the bilayer hydrogel will bend towards the PNIPAM layer without external intervention (Fig. S2, ESI†). As shown in Fig. 2b, a straight strip of hydrogel turns into a circle and reaches equilibrium in about 8 min after the temperature increases to 45 °C. This noncontact method avoids many disadvantages of the deformation process of the traditional shape memory hydrogel, such as inaccuracy and inconvenience. Then the deformed bilayer hydrogel is immersed into alkaline solution for 20 min, the chitosan chains in the PAAm-CS network would become hydrophobic due to the de-protonation effects, and the transparent PAAm-CS layer turns opaque gradually, which is consistent with the previous report.[33,35] This colour change suggests the formation of micro-crystallization of chitosan chains, which will act as temporary crosslinking points and fix the deformed shape of the bilayer hydrogel, therefore the hydrogel with a deformed shape would not unfold

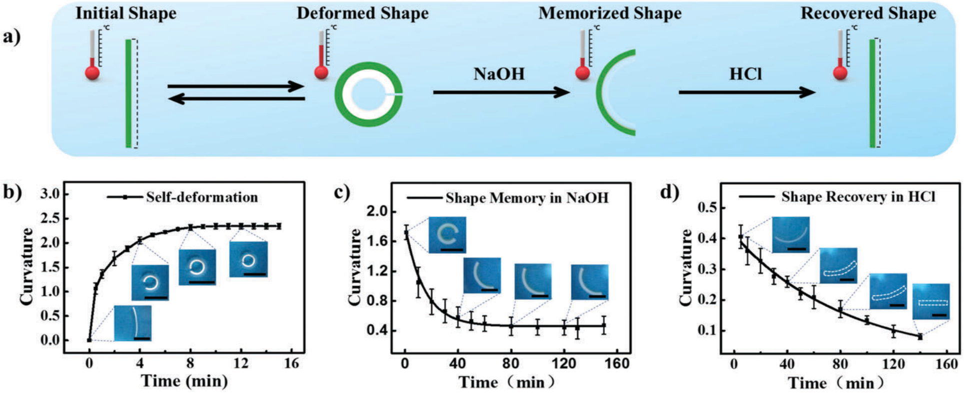

Fig. 2 (a) The hydrogel is reversibly self-deformed between 20 °C and 45 °C. The deformed shape of the hydrogel is partially maintained in NaOH solution and completely recovered in HCl solution. (b–d) The curvature of a bilayer strip against time in 45 °C KNO_3 aqueous solution, 20 °C NaOH solution and 20 °C HCl solution. The curvature is reciprocal of the radius of the corresponding circle of the deformed hydrogel (Fig. S3, ESI†) (Scale bars, 1 cm).

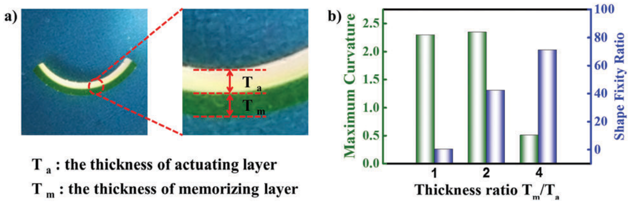

Fig. 3 (a) A picture of the bilayer hydrogel and locally enlarged vision. (b) The maximum curvature and shape fixity ratio against the thickness ratio between the memorizing layer and the actuating layer.

to a straight strip when the PNIPAM layer swells at a lower temperature (20 °C) (Fig. 2c). When the pH is decreased to 2 by replacing the alkaline solution with 0.1 M HCl, the semicircle hydrogel could become straight again due to the disentanglement of the chitosan chains. This process indicates the shape memory hydrogel with self-deform behaviour, which is significantly important to make the shape memory materials more natural, more intelligent and adaptive in response to the external environment.

Because the memorizing layer plays the key role in the shape memory process, the shape memory ratio can be adjusted by varying the thickness ratio between the memorizing layer and the actuating layer. As shown in Fig. 3, when the thickness ratio is 1 : 1, the bilayer hydrogel can self-deform but cannot memorize the deformed shape. That is probably because the re-swelling of PNIPAM overwhelms the stabilization effects of chitosan in the PAAm-CS layer. The maximum curvature was the same for the thickness ratio of 2 : 1 due to which the full circle was achieved. Two ends of the hydrogel touched each other and prevented further bending. With the thickness ratio increasing to 4 : 1, the shape fixity ratio concomitantly increases from 42% to 71%, however, the maximum curvature that the bilayer hydrogel could reach reduces from 2.3 to 0.5. It can be deduced that a thick memorizing layer will benefit the shape fixing process, however, if the memorizing layer is too thick, it will not be easily driven by the thin actuating layer, therefore, the thickness ratio between the two layers needs to be optimized to achieve a better performance.

Not only simple transformation from strip to circle could be realized without intervention, complex shape transformation would also occur if the cut pattern is deliberately designed. Specifically speaking, as shown in Fig. 4a, a patterned PNIPAM layer was prepared by placing a stripe grating mask above the glass cell during the second photo-polymerization step.

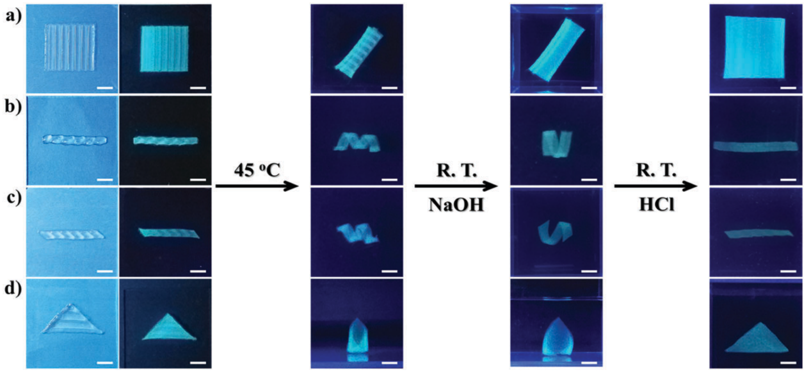

Fig. 4 Patterned hydrogels automatically transform from (a) a flat square shape into a cylindrical shape, (b) a flat shape with a 45° diagonal pattern to a right-handed helix shape, (c) a flat shape with a −45° diagonal pattern to a left-handed helix shape, (d) a flat triangle shape to a quasi-cone shape, these deformed shapes are fixed in 0.1 M NaOH solution, and could return to the original planar shapes in 0.1 M HCl. (Scale bars, 1 cm).

Noteworthily, a stripe patterned square hydrogel would automatically change into a cylindrical shape if immersed in 45 °C KNO_3 solution. After being fixed by micro-crystallization of chitosan in 0.1 M NaOH solution, the cylindrical shape could be maintained for more than 10 h at 20 °C. Finally, the temporary shape could be erased by transferring the hydrogel into 0.1 M HCl solution. Alternatively, a flat shape with a 45° diagonal pattern could transform into a right-handed helix shape, a flat shape with a $-45°$ diagonal pattern could deform to a left-handed helix shape, and a flat triangle shape could turn into a quasi-cone shape. These deformed shapes could be fixed by immersing the hydrogel in 0.1 M NaOH solution, and erased by immersing in HCl solution. In general, the shape transformation could occur from 2D to 3D, and a more complicated shape change behaviour could be expected through this approach. These automatic and predetermined shape shifting styles provide unique functionality for the shape memory hydrogels.

In conclusion, a bilayer shape memory hydrogel which can self-deform has been successfully fabricated by integrating a thermo-responsive actuating layer and a pH-responsive memorizing layer, in which a chitosan-AAm hydrogel serves as the memorizing layer and a PNIPAM hydrogel acts as the actuating layer. At a higher temperature, the as-prepared hydrogel could self-deform because of the thermo-responsiveness of PNIPAM networks, and then the deformed shape could be stabilized by the micro-crystallization of CS in the memorizing layer, leading to a self-deformed shape memory behaviour. Moreover, complex temporary shapes could also be achieved using photo-mask polymerization because of the local shrinkage. This combination successfully endowed the bilayer hydrogel with shape changing and shape memory properties simultaneously. We hope that this novel material design strategy will pave a new way for fabricating advanced shape memory materials.

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Conflicts of interest

There are no conflicts to declare.

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