Supporting information

Actuating and Memorizing Bilayer Hydrogel for a Self-deformed Shape Memory Function

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Materials

Acrylamide (AAm), chitosan (CS), sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagent Co. Ltd. *N*-isopropylacrylamide (NIPAM), *N,N′*-methylenebis(acrylamide) (Bis), potassium nitrate (KNO_3) and lemon yellow (dye) were purchased form Aladdin Chemistry Co. Ltd. 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959) was purchased from J&K Scientific Ltd. NIPAM was used after recrystallization. Other chemicals were used without further purification.

Measurements

The microstructures of the bilayer hydrogel were analysed by field-emission scanning electron (Hitachi S-4800). The samples were frozen in liquid nitrogen for 10 min before lyophilizing with a freeze drier (FD-1C-50, Beijing BoYiKang) at −35 °C for about 48 h. The curvature of the deformed hydrogel (20 mm length, 2 mm width) was obtained from the photos taken of the hydrogel at various times.

Preparation of bilayer hydrogel

The NIPAM pregel solution was prepared by mixing NIPAM (1.00 g), Bis (5 mg), I2959 (0.01 g) with H_2O (8.64 g), and the solution was degassed by nitrogen for 10 min. The chitosan-AAm pregel solution was prepared by mixing AAm (0.45 g), CS (3 wt%, 3.00 g), Bis (10 mg/ml, 225 μL) and I2959 (4.50 mg).

NIPAM/AAm-CS bilayer hydrogel was fabricated by layer-by-layer polymerization. The PAAm-CS pregel solution was added into a glass mold that consisted of two cover glasses separated by 1 mm silicon rubber spacer, then polymerized under ultraviolet irradiation (365 nm) for 3 min. Then the covering glass slide was lifted, a second silica rubber mold was put right above the first mold, NIPAM pregel solution was injected into the mold and covered by the glass slide again. The mixture was then irradiated under UV light (365 nm) for 5 min in ice-water bath. After polymerization, the obtained bilayer hydrogel was immediately immersed in 0.1 M KNO_3 solution for 0.5 h to remove unreacted monomer and reach a swelling equilibrium, and then was cut into arbitrary dimensions.

For the patterned hydrogel, a fluorescent monomer (0.16 mg/mL) was added in the pre-gel solution, and PNIPAM hydrogel layer was locally polymerized when light through the mask.

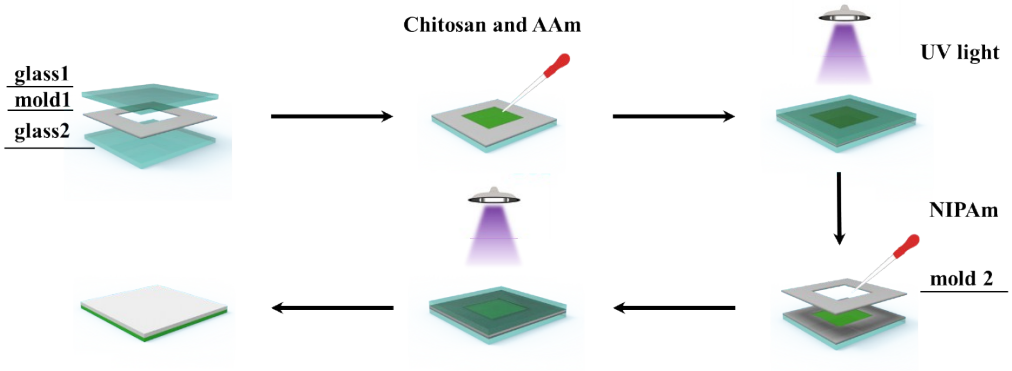

Figure S1. The preparation procedures of a self-deformed shape memory hydrogel was accomplished by a two-step photo-polymerization method. The CS-AAm pregel solution was dropwise added into a glass mold that consisted of two cover glasses separated by 1 mm silicon rubber spacer; and then polymerized under ultraviolet light (365 nm) for 3 min. After the formation of the first layer, the top glass was detached from the hydrogel sheet; and an additional silica rubber spacer was placed on the existing spacer to provide a cell for the PNIPAM layer, after 5 min polymerization, a bilayer hydrogel was obtained.

The self-deformation functionality of the bilayer hydrogel was investigated by immersing the hydrogel (20 mm length, 2 mm width, 2mm thickness) into 45 °C KNO_3 solution and then transferred to 20 °C solution, recording the deformation process by taking photos. It is noticed that the shape recovery ratio is 100 %.

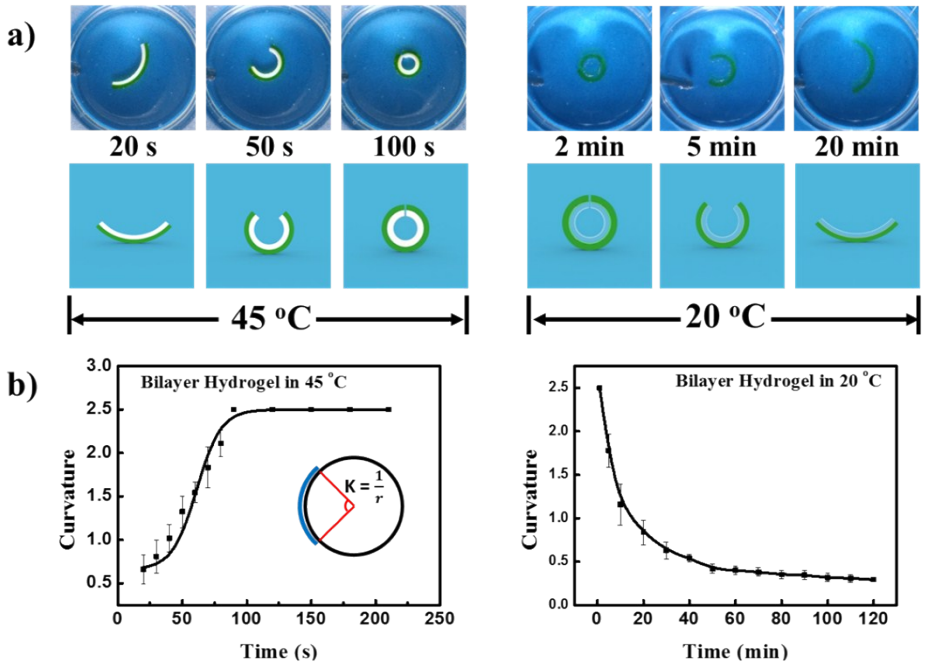

Fig S2. The reversible shape changing behavior of the bilayer hydrogel: a) The pictures of shape changing and shape recovery between straight and circle. b) The curvature of a bilayer strip against time in 45 °C and 20 °C KNO_3 aqueous solution.

The shape fixity ratio (R_f) and shape recovery ratio (R_r) were defined by the following equation:

$R_f = \theta_m / \theta_d \times 100\%$

$R_r = (\theta_d - \theta_f) / \theta_d \times 100\%$

Where θ_d, θ_m, θ_r are the central angle of the deformed shape, memorized shape and the recovered shape of hydrogel.

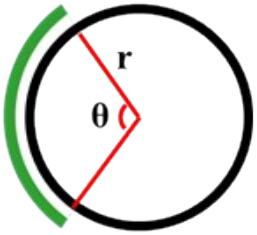

Figure S3. The curvature is the reciprocal of the radius of corresponding circle of the deformed hydrogel.

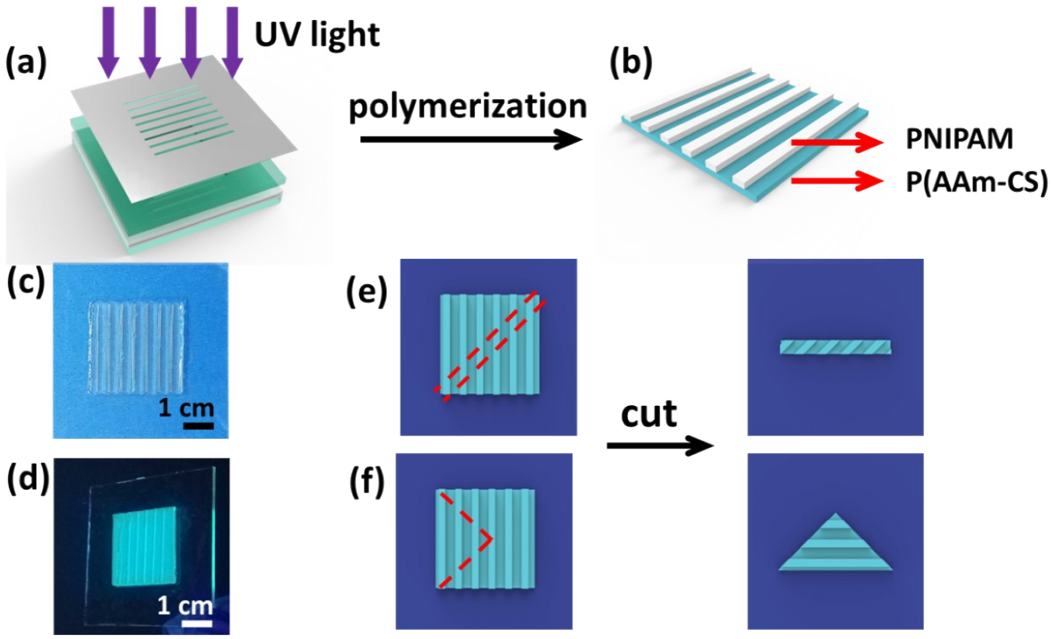

Figure S4. (a) The hydrogel was locally polymerized when light pass through the mask. (b) The PNIPAM hydrogel pattern is above the P(CS-AAm) hydrogel layer. (c) A stripe patterned hydrogel and the (d) fluorescence image. (e) A rectangle hydrogel and (f) triangle hydrogel were cut from the patterned hydrogel.

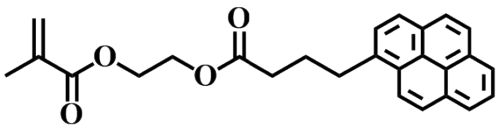

Figure S5. The fluorescent monomer that was added in the pre-gel solution.