# Supporting Information

# Gradient hydrogel actuator with fast response and self-recovery in air

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## 1. Experimental section

### 1.1 Materials

Sodium hyaluronate (HA, Mw100000-200000, BR), ethylene glycol diglycidyl ether (EGDE) were purchased from Adamas; *N*-isopropylacrylamide (NIPAM, 98.0%, RG) was provided by TCI Shanghai; *N*,*N'*-methylenebisacrylamide (BIS, AR), potassium persulfate (KPS, AR) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TEMED, AR) were purchased from Aladdin. All reagents were not further purified before use. The water used for the experiments was deionized water.

### 1.2 Synthesis of gradient HA/PNIPAM hydrogels

The gradient HA/PNIPAM hydrogels were synthesized by an asymmetric mold method consisting of glass plate and PTFE plate by free radical polymerization of NIPAM in HA solution. In detail, HA (15 mg) was first added to deionized water (4.4 mL) and dissolved under stirring, followed by the addition of monomer NIPAM (0.68 g). After mixing, the crosslinker BIS (10 mg/mL, 200 μL) was added and stirred for 5 min, followed by catalyst TEMED (10 μL) and initiator KPS (20 mg/mL, 500 μL) under stirring for 5 min. Finally, BGDE (7 μL) was added in turn and stirred for 5 min each to obtain the pre-gel solution. And then the pre-gel solution was transferred into an asymmetric mold (70×70×1 mm) consisting of PTFE plate/silicone sheet/glass plate with a syringe and reacted at 20°C for 24 h to obtain gradient hydrogel. As control, the homogeneous hydrogel was prepared in the same procedure above except a symmetric mold consisting of glass plate/silicone sheet (1 mm)/glass plate was used instead.

The hydrogels were defined as $H_xN_y$, where H and N represents HA and NIPAM respectively; x represents the mass percentage (wt%) of HA, and y represents the molar concentration (mol/L) of NIPAM in solution respectively. All mass percentages involved in the experiment are relative to the amount of water. Typically, $H_{0.3}N_{1.2}$ means the amount of HA is 0.3 wt% and the molar concentration of NIPAM is 1.2 mol/L. Unless otherwise specified, the HA/PNIPAM hydrogel is by default the concentration of $H_{0.3}N_{1.2}$ hydrogel in the text.

### 1.3 Characterizations of gradient HA/PNIPAM hydrogels

#### 1.3.1 Temperature response

The gradient hydrogels were cut into 10×1×1 mm block samples and placed in a custom-built constant temperature oven for bending performance test (the

relative humidity of 15%). And the change of bending angle(θ) with time was recorded.

The LCST of the hydrogels were measured by UV-Vis spectrophotometer (Beijing Pu-Analysis, TU-1810). The test range of temperature was 15-50℃, the heating rate was 2 ℃/min, and the transmittance of the hydrogels at 500 nm were recorded.

### 1.3.2 Water retention

The homogenous HA/PNIPAM hydrogels used for water retention test as detailed in Table S2. The water retention was tested using the weight method, and the hydrogels were cut into 20×5×1 mm samples and placed at 50°C in air. The masses were weighed at 30 s intervals and recorded, and the water retention was evaluated by the ratio ($W_t/W_0$*100) of the sample mass ($W_t$) at different time to original sample mass($W_0$).

### 1.3.3 Volume shrinkage

Two gradient hydrogel sample $H_{0.4}N_{1.1}$ and $H_{0.2}N_{1.3}$ was used to simulate the scenario of gradient hydrogel with different contents of PNIPAM and HA. The hydrogels were cut into 20×20×1 mm squares and placed in an air environment at 50°C for observation, and the degree and rate of volume change were recorded by video. The volume shrinkage (V%) was evaluated according to the equation:

$$V\% = (L_0 - L_t)/ L_0 * 100\%$$

Where $L_0$ and $L_t$ were initial diagonal length and the diagonal length at time interval t of the hydrogel.

### 1.3.4 Fourier Transform Infrared Spectrometer (FTIR)

The FITR structure analysis of NIPAM, HA and hydrogel was performed using an infrared spectrometer (Nicolet 6700, USA). Prior to the measurement, the hydrogel was fully soaked and washed with deionized water for 48 h, and then vacuum dried at low temperature and grounded into powder. The test samples were prepared by the potassium bromide pellet method. The tests were performed with pure potassium bromide as background.

### 1.3.5 Cryo-Scanning Electron Microscopy (Cryo-SEM)

Cross sections along the hydrogel thickness direction were adhered to a sample stage. The sample stage was snap frozen in liquid nitrogen slush for 30 s and then transferred to the sample preparation chamber for sublimation plating under vacuum using a Cryo-SEM (PP3000T, Quorum, UK). After sublimation at -90°C

for 10 min, the samples were sent to the sample chamber for observation in an environmental scanning electron microscope (FEI Quanta 450, FEI Inc.) with a cold stage temperature of -140 ℃ and an accelerating voltage of 10 kV.

### 1.3.6 Scanning electron microscope (SEM)

The hydrogels were cut into 3×2×1 mm strips, placed on temperature-controlled sample cups, keeping the cross-sections along the thickness direction upward, frozen at -25°C for 5 min. The morphology was observed by Scanning Electron Microscopy (Phenon ProX, Feiner, The Netherlands) with an accelerating voltage of 10 kV.

### 1.3.7 Energy Dispersive Spectrometer (EDS)

The HA/PNIPAM hydrogel samples were naturally dried at room temperature for 48 h and then transferred to a vacuum oven at 60°C for 12 h. After that, the sample sections were quenched and cooled with liquid nitrogen and analyzed by Na line scan using the elemental analysis energy spectrum EDS function of a Phenom benchtop SEM with 128 points.

### 1.3.8 Rheology

The Rheometer (TA Discovery HR-1, USA) was used to perform the angular frequency scan test on the hydrogel samples after the response at 50°C in air with the following conditions: 20 mm diameter parallel plate, strain of 1%, frequency of 1 Hz, temperature range of 25°C, and frequency scan range of 0.05-100 rad/s.

### 1.3.9 Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter (TA Q200, USA) was used to test the internal water state and water content of the hydrogels. 3 mg of hydrogel was weighed and rapidly cooled to -30℃ in a $N_2$ atmosphere of 50 mL/min. The sample was kept at a constant temperature for 3 min, and then heated to 30℃ at a heating rate of 5 ℃/min to obtain the heating curve of the hydrogels.

The melting point of water in the sample was determined by the maximum enthalpy temperature, and the water content was calculated by the following equation:

$$\text{Water Content (\%)} = Q/(\Delta H) \times 100$$

where $\Delta H$ is the enthalpy of melting of free water, which is the same as that of pure water ($\Delta H = 333.5\ J \cdot g^{-1}$), and Q is the heat absorbed by water in the sample during melting, calculated according to the enthalpy peak area of the DSC curve.

## 2. Supplementary Figures

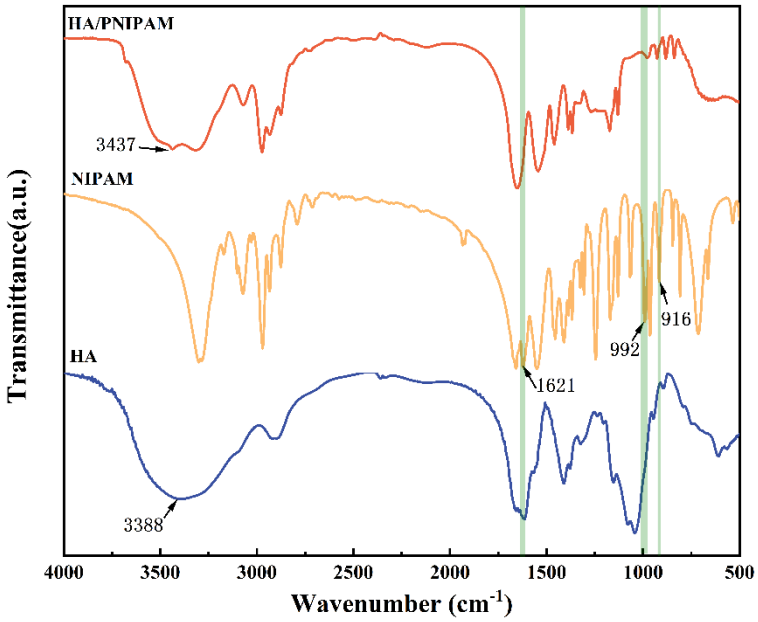


**Fig. S1.** FTIR spectra of HA, NIPAM and gradient HA/PNIPAM hydrogel.

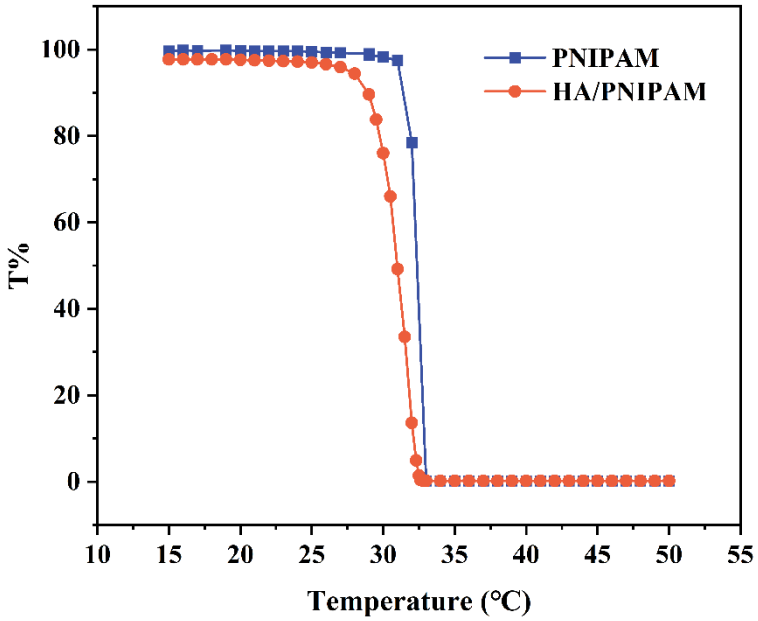


**Fig. S2.** UV-Vis curves of NIPAM hydrogels and gradient HA/PNIPAM hydrogels at different temperatures.

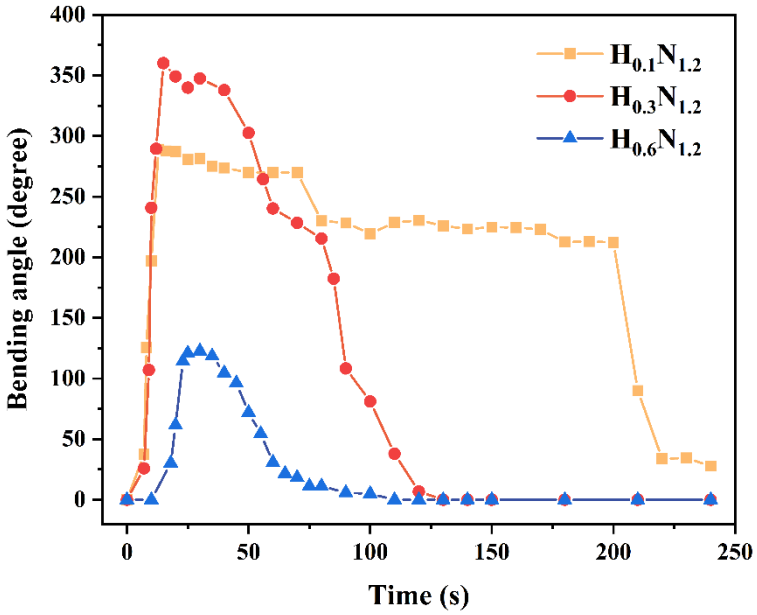


**Fig. S3.** Angular variation and self-recovery time of gradient HA/PNIPAM hydrogels with different HA mass percentages in air at 50°C.

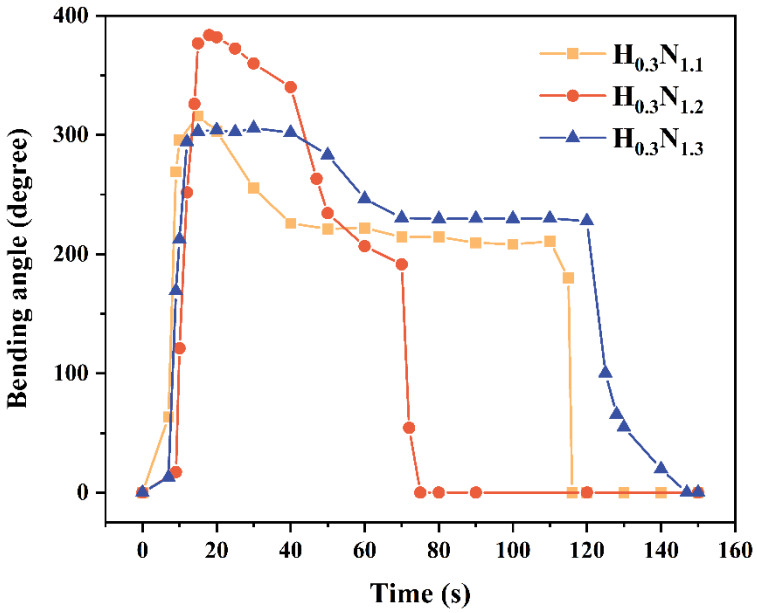


**Fig. S4.** Angular variation and self- recovery time of gradient HA/PNIPAM hydrogels with different NIPAM contents in air at 50°C.

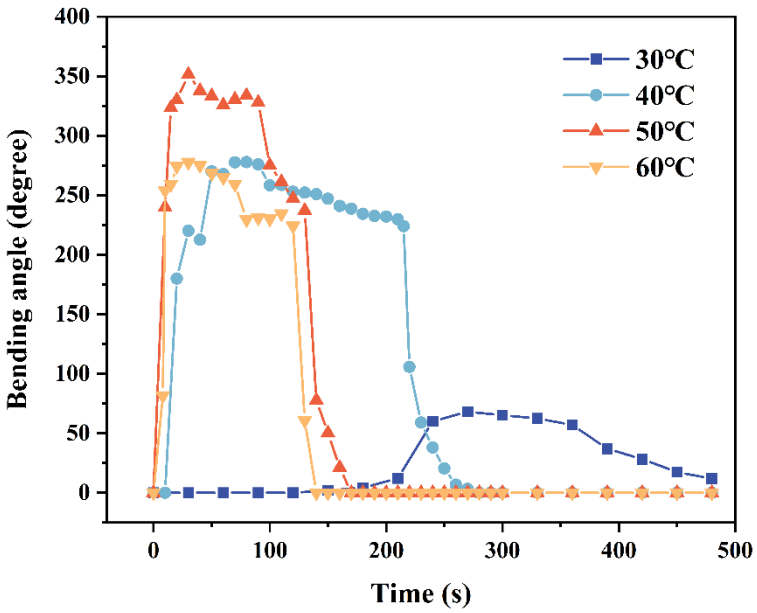


**Fig. S5.** Angular variation and self- recovery time of gradient HA/PNIPAM hydrogels ($H_{0.3}N_{1.2}$) at different temperatures in air.

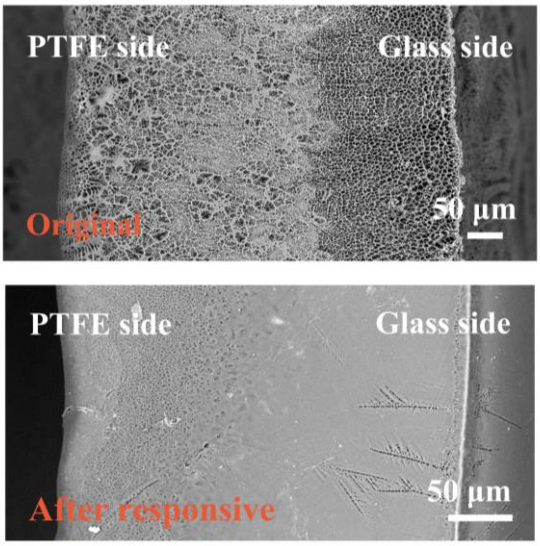


**Fig. S6.** SEM images of gradient HA/PNIPAM hydrogels before and after the response at 50℃ in air.

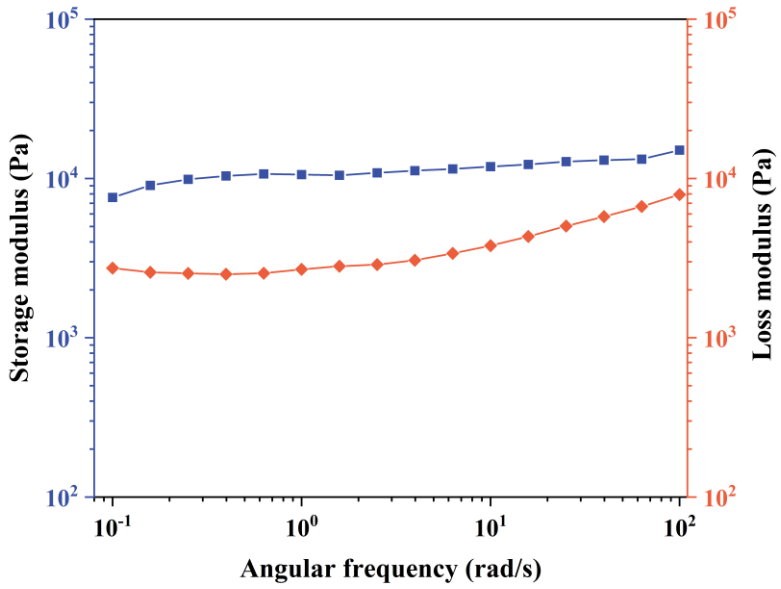


**Fig. S7.** Modulus of gradient HA/PNIPAM hydrogels after the response at 50℃ in air.

## 3. Supplementary Tables

**Tabla S1.** Formula for preparation of gradient HA/PNIPAM hydrogels.

| Symbol | HA/mg | NIPAM/g | 10 mg/mL BIS/uL | 20 mg/mL KPS/uL | TEMED/uL | BGDE/uL | $H_2O$/mL |
|---|---|---|---|---|---|---|---|
| $\mathbf{H_{0.1}N_{1.2}}$ | 5 | 0.68 | 200 | 400 | 10 | 5 | 4.4 |
| $\mathbf{H_{0.3}N_{1.2}}$ | 15 | 0.68 | 200 | 400 | 10 | 7 | 4.4 |
| $\mathbf{H_{0.6}N_{1.2}}$ | 30 | 0.68 | 200 | 400 | 10 | 10 | 4.4 |
| $\mathbf{H_{0.3}N_{1.1}}$ | 15 | 0.62 | 185 | 365 | 9 | 7 | 4.5 |
| $\mathbf{H_{0.3}N_{1.2}}$ | 15 | 0.68 | 200 | 400 | 10 | 7 | 4.4 |
| $\mathbf{H_{0.3}N_{1.3}}$ | 15 | 0.74 | 220 | 430 | 11 | 7 | 4.4 |

**Tabla S2.** Formula for preparation of HA/PNIPAM hydrogels with different HA mass contents on water retention properties.

| Symbol | HA/mg | NIPAM/g | 10 mg/mL BIS/uL | 20 mg/mL KPS/uL | TEMED/uL | BGDE/uL | $H_2O$/mL |
|---|---|---|---|---|---|---|---|
| $\mathbf{H_{1.0}N_{1.2}}$ | 50 | 0.68 | 200 | 400 | 10 | 12 | 4.4 |
| $\mathbf{H_{0.6}N_{1.2}}$ | 30 | 0.68 | 200 | 400 | 10 | 10 | 4.4 |
| $\mathbf{H_{0.2}N_{1.2}}$ | 10 | 0.68 | 200 | 400 | 10 | 6 | 4.4 |
| $\mathbf{H_{0}N_{1.2}}$ | 0 | 0.68 | 200 | 400 | 10 | 0 | 4.4 |

**Tabla S3.** Formula for preparation of gradient HA/PNIPAM hydrogel used to simulate the different response behaviors.

| Symbol | HA/mg | NIPAM/g | 10 mg/mL BIS/uL | 20 mg/mL KPS/uL | TEMED/uL | BGDE/uL | $H_2O$/mL |
|---|---|---|---|---|---|---|---|
| $\mathbf{H_{0.4}N_{1.1}}$ | 20 | 0.62 | 160 | 400 | 10 | 7 | 4.5 |
| $\mathbf{H_{0.2}N_{1.3}}$ | 10 | 0.74 | 250 | 400 | 10 | 7 | 4.4 |