Electronic Supporting Information

Fabrication of Biomimetic Hydrogel Actuator with Rhythmic Deformation Driven by a pH Oscillator

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1. Materials

Acrylic acid (AA, stabilised with MEHQ) was obtained from TCL (Shanghai, China). N,N-dimethylacrylamide (DMA) and N, N′-methylenebis(acrylamide) (BIS) were purchased from Adamas Reagent Co., Ltd (Shanghai, China). Silica nanoparticle (SN) with concentrations of 50 wt% at pH 9, SiO_2/Na_2O ratios of 200-250, and radii of about 15 nm was obtained from Sigma-Aldrich (Shanghai, China). 2, 2′-Azobisisobutyronitrile (AIBN) (Sigma, 98%) was recrystallised from ethanol. Potassium persulphate (KPS) and N,N,N′,N′-tetramethylethylenediamine (TEMED) used as redox initiators were obtained from Adamas Reagent Co., Ltd (Shanghai, China). Rhodamine B and Brilliant Blue G were purchased from Huaxia Reagent Co., Ltd (Chengdu, China). hydrogen peroxide (H_2O_2) (30 wt. %) were purchased from J&K chemicals (Beijing, China). Sodium dithionite ($Na_2S_2O_4$) was purchased from TCL (Shanghai, China). The water used in this study was distilled and further purified using a filtration system. All other reagents were commercial chemicals and they were used without further purification unless otherwise noted.

2. Characterisations

Infrared spectra were recorded on a Thermo-Nicolet Avatar 370 FTIR spectrophotometer (USA) over the scanning range of 4000-400 cm^{-1} using the KBr pellet method. The cross-section morphologies of hydrogels were observed by an S-4800 field emission scanning electron microscope (SEM, Hitachi, Japan). Stress-strain measurements for the assembled gel samples were analyzed by a commercial test machine (Electronic Testing Machine, RGM-6005, China). The reactor for the pH oscillating system was fed by a Longer Dispensing Peristaltic Pump (BT100-1F, China). A PHSJ-3F pH meter (Shanghai REX, China) was used to record the pH-time curve with time intervals of 5 s using the REX DC1.0 data collection software package (Shanghai REX, China). Movies and pictures were obtained by a Canon IXUS 130 digital camera.

3. Preparation of the DA gel

The DA gel were also prepared by radical polymerisation. Predetermined amounts of DMA, AA, dyestuff (Rhodamine B) and BIS were dissolved in H_2O (25 ml). The solution was purged with

nitrogen for 15 min to remove oxygen, and then AIBN was added. The aqueous reaction mixture was injected into a mold with space of $100 \times 50 \times 1$ mm^3, which was formed by a transparent glass plate and a polytetrafluoroethylene (PTFE) spacer with thickness of 1 mm. Next, gelation was carried out in an oven at 65 °C for 10 h. The mould was then removed from the oven, and the bulk gel obtained from the mould was soaked in water for hours, then repeatedly washing with water to remove unreacted monomers and initiators. Subsequently, the gels were cut into different shapes with a knife.

Table S1 Summary of the DxAy gel composition

Sample	x	y	Molar ratio of DMA:AA
DA	0.5	0.5	1:1
DA1.5	0.4	0.6	1:1.5
DA2.3	0.3	0.7	1:2.3

The obtained hydrogels sample were denoted as DxAy, with D representing DMA, x representing the molar concentration of DMA, A representing AA, y representing the molar concentration of AA respectively.

4. Preparation of the DS gel

The DS gel was prepared by in situ free radical polymerisation of DMA using KPS and TEMED as redox initiators. The predetermined amounts of The dyestuff (Brilliant Blue G) was first dispersed in water and stirred for about 10 min, and then the SN as cross-linking agent was added into the dyestuff solution and stirred for 4 h. Subsequently, monomers DMA, initiators KPS and TEMED were added into the dyestuff and SN solution under the condition of ice-water bath with stirring. The aqueous reaction mixture was injected into a mold with space of $100 \times 50 \times 1$ mm^3, which was formed by a a transparent glass plate and a polytetrafluoroethylene (PTFE) spacer with thickness of 1 mm. Next, gelation was carried out in an oven at 30 °C for 12 h. The mould was then removed from the oven, and the bulk gel obtained from the mould was soaked in water for hours, then repeatedly washing with water to remove unreacted monomers and initiators. Subsequently, the gels were cut into different shapes with a knife.

Table S2 Summary of the DaSb gel composition

Sample	m(DMA)	m(SN)	Mass ratio of DMA:SN
DS0.03	0.5	0.5	1:0.03
DS0.2	0.4	0.6	1:0.2

DS0.8	0.3	0.7	1:0.8

The obtained hydrogels sample were denoted as DaSb, with D representing DMA, a representing the mass concentration of DMA, S representing silica nanoparticle, b representing the mass concentration of NS, respectively.

5. FTIR spectra of gels

As showed in Figure S1, the bands at 1610 cm^{-1} and 1631 cm^{-1} observed in DMA gel and DS gel, respectively, were attributed to the stretching vibration of -CO-. The bands at 1110 cm^{-1} and 796 cm^{-1} observed in the DS gel were assigned to the stretching and bending vibration of Si-O, respectively. The band at 3468 cm^{-1} was attributed to the stretching vibration of O-H on the SN nanoparticles surface.
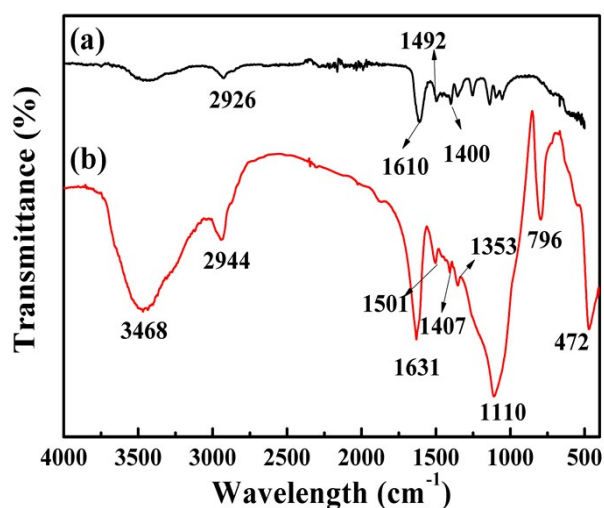

Fig. S1. FTIR spectra of hydrogels (a) DMA gel (b) DS gel
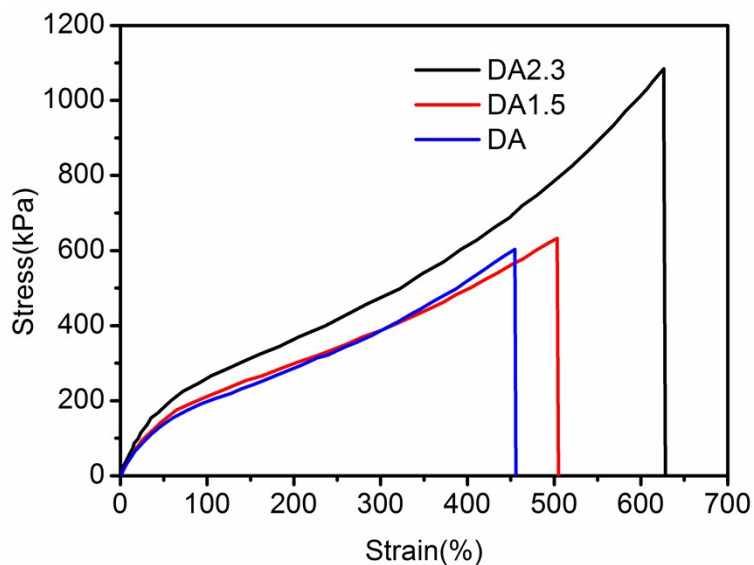
6、Mechanical tests

Fig.S2 Tensile stress-strain curves of the DA gel with different AA contents
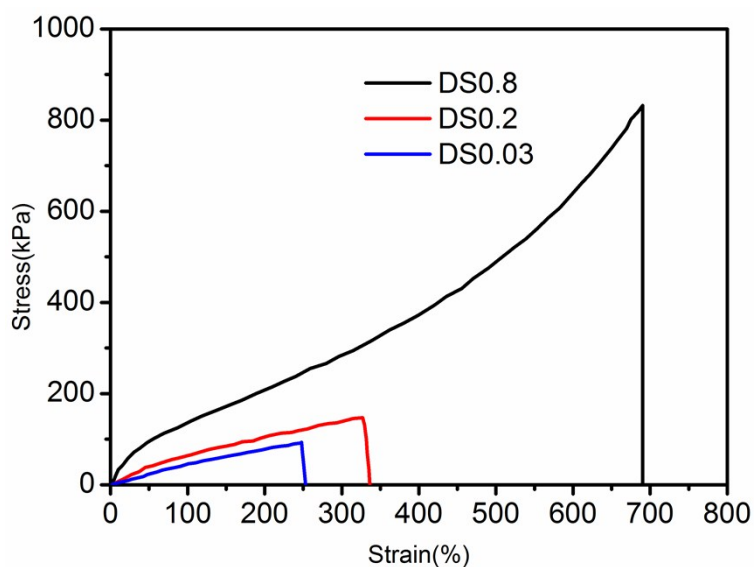

Fig.S3 Tensile stress-strain curves of the DS with different SN contents

The T-peel strength test was conducted at room temperature according to the Chinese Standard GB/T 2791-1995 with a change in the sample length to examine the adhesive strength between the DA and DS gels. A Electronic Testing Machine(RGM-6005) was used with a crosshead speed of 100 mm/min by clamping the bent and unbounded ends of the specimen. The specimen consisted of two pieces of DA gel (100 mm × 25 mm × 1 mm) adhered by one piece of DS gel (75 mm × 25 mm × 1 mm).

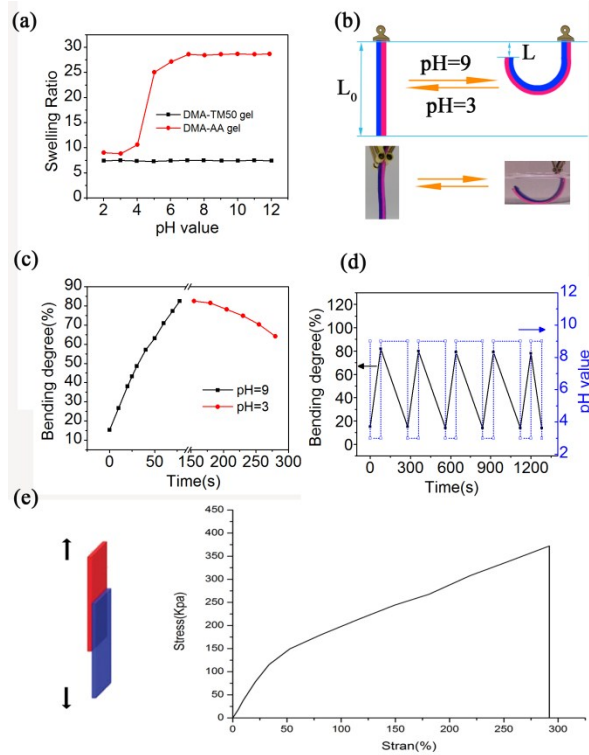## 7. Quantitative characterization of the bending behaviour of the bigel strip

Fig.S4. Quantitative characterization of the bending behaviour of the DA2.3/DS0.8 bigel strip. (a) Equilibrium swelling ratio of the DS gel and DA gel upon variation of pH value. (b) Schema and the corresponding photos for reversible bending of the DA2.3/DS0.8 bigel strip of 40 mm × 2 mm × 1 mm in different pH solutions fixed by a clip for easy observation. (c) The dependence of bending degree of the DA2.3/DS0.8 bigel strip on the soaking time in pH=3 and pH=9 buffer solution. (d) Cyclic reversible changes of bending angles in alkali solution and acid solution, alternatively.(e) The stress-strain curves of DA2.3/DS0.8 bigel overlapped at the ends with a contact area of about 6.25 cm^2 after eleven cycles of reversible bending.

8. The effect of the AA contents on bigel actuator response

The actuator was constituted of the DA/DS bilayer hydrogel, which was cut into a strip of 40 mm × 2 mm× 1 mm or into designed shapes. As-prepared DA (40 mm × 2 mm× 1 mm, dyed red) and DS (40 mm × 2 mm× 1 mm, dyed blue) gels were assembled into a bilayer, which was placed in a buffer solution (pH 9). The bending process was recorded and the bending angle over time was calculated according to the snapshots.
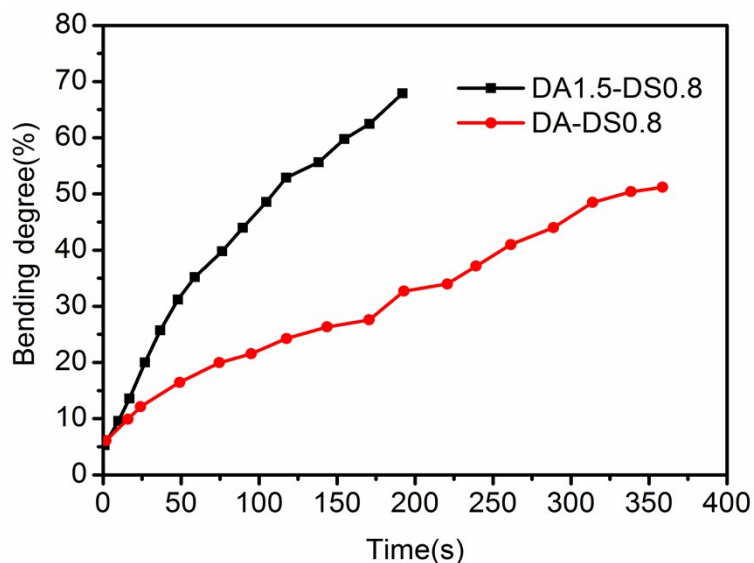
Fig.S5 the dependence of bending degree of the two bigel strip(DA1.5-DS0.8, DA-DS0.8) on the soaking time in pH=9 buffer solution

9.The construction of an oscillating system

A. Reactor

The pH oscillating system used in our studies was based on the sulfur oscillatory mechanism under a continuously stirred tank reactor (CSTR) [1]. The CSTR is a cylindrical-shaped glass reactor with a liquid volume of 24 mL with two input tubes and one output tube, as shown in Figure S5. A combination pH meter and a thermometer were connected to a computer.
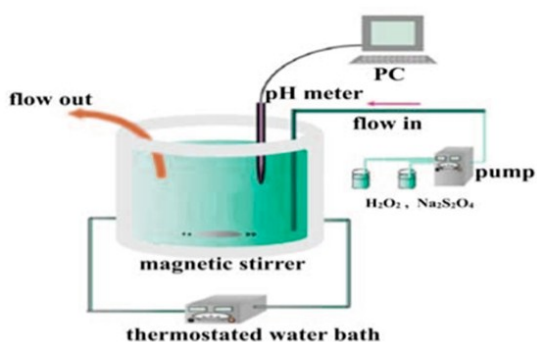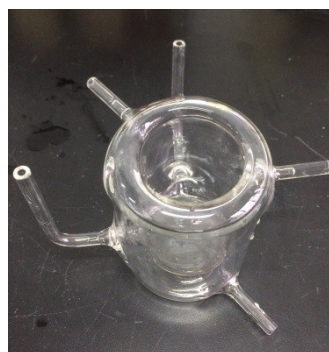
(a)   (b)

Fig.S6 (a) The illustration of the CSTR for sustainable oscillations and (b) the experimental setup.

B. Procedures

Sodium dithionite (7.5 mmol/L) ($Na_2S_2O_4$) with pH 12 and hydrogen peroxide (23 mmol/L) (H_2O_2) solutions were prepared separately using deionized water in 250 mL volumetric flasks. Throughout the experiments, the solution of sodium dithionite in its reservoir was bubbled with nitrogen gas to prevent autoxidation. The experimental setup for the pH oscillator was shown in Figure S5. The oscillating reactions were carried out at different temperatures in the CSTR. Reactant solutions were pumped into the reactor through the inlet tubes by means of a Longer Dispensing Peristaltic Pump (BT100-1F, China). The excess reaction mixture was removed through an outlet tube. A magnetic stirrer at a constant stirring rate was used to ensure uniform mixing. The maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered to the desired value. The reactions in the batch system were initiated by the addition of the H_2O_2 solution. The pH-time data was monitored by a pH meter connected to a computer using a REXDC 1.0 data collection software package[2].
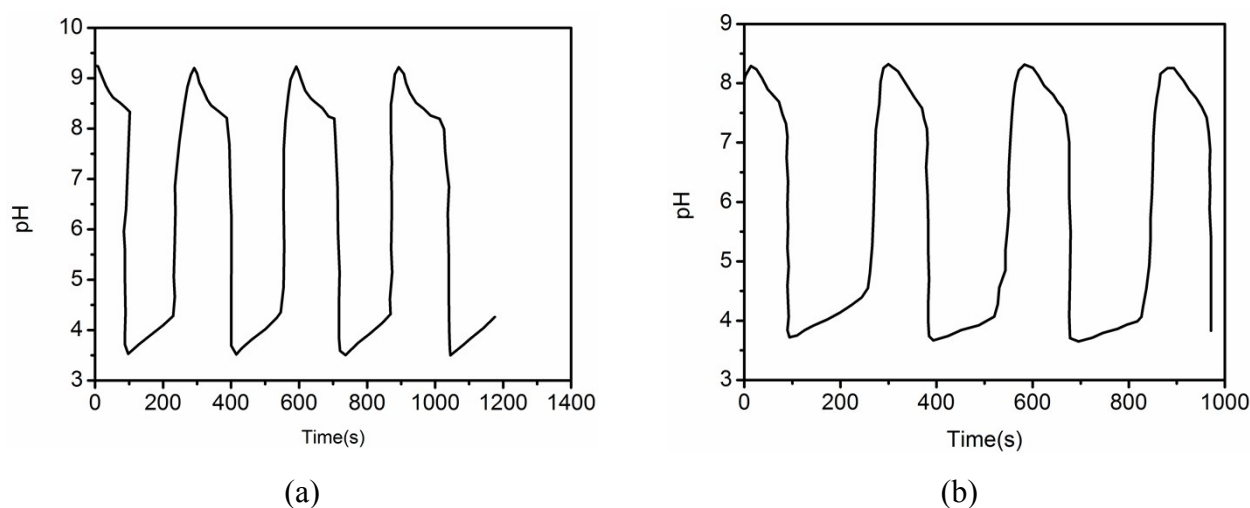

(a)   (b)

Fig.S7 pH-time series measured in a CSTR at different temperatures (a)21.5℃, (b)23℃

Table S3 The parameters of pH oscillations in a CSTR at different temperatures

T (℃)	19.7	21.5	23
pH$_{max}$	9.35	9.2	8.4
pH$_{min}$	3.46	3.5	3.6
Duration of high pH (above pKa of AA)(s)	208	175	157
Duration of low pH (below pKa of AA) (s)	120	139	144
Period (s)	305	301	285

C. Finite element modelling method

The results presented in Figure 4c, Figure S7 were calculated using Abaqus 6.13. Hydrogels in the simulation are set as Neo-Hookean hyperelastic materials, the shear modulus are set as 1 and the bulk modulus are set as 10-5.The slow volume change of hydrogels is formulated by a quasi-static process, and acquired in the simulation by multiplying the total volume change with the step length. 8-node biquadratic axisymmetric quadrilateral, hybrid reduced integration element (CAX8RH) is used in the simulation.
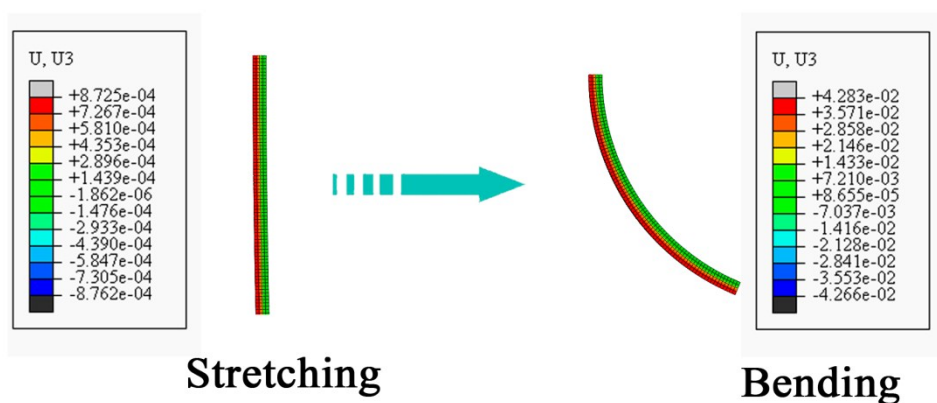

Fig. S8 Finite element modeling of the bigel strip

D. Biomimetic gel flower

The other biomimetic actuator such as gel flower could also be constructed on the basis of the same strategy. As shown in Figure S8a, the flower shaped bigel actuator, named as gel flower, was designed and prepared by the macroscopic assembly between gel building blocks tailored from the shape of the planar hydrogel sheets. Figure S8b shows the cyclic changes of the closing/blooming motion of the gel flower suspended in the aqueous solution containing the two reactants of the HPD pH oscillating reaction. The solution pH value above pKa of AA triggers the closing of the gel flower due to the obvious swelling of AA gel layer. Instead, the petals of gel flower will stretch after a change of pH from 4.25 to 3.5, and lead to the gel flower blooming. At least 10 closing-blooming cycles have been conducted without an obvious damping in responsiveness.
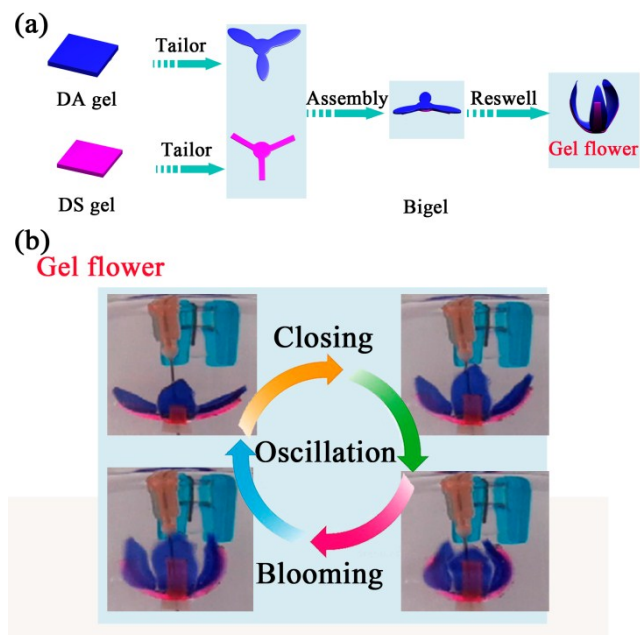
Fig. S9 Fabrication of gel flower in a pH oscillator at 23 ^{o}C(a) Schematic illustration of the process of integrating two different gel sheets into gel flower based on specific interactions between DMA chains and SN.(b) Snapshots of the gel flower closing/blooming at different times, respectively

10. References

1. K. M. Kovács and G. Rábai, J. Phys. Chem. A, 2001, 105, 9183-9187.

2. E. X. Liang, H. W. Zhou, X. B. Ding, Z. H. Zheng and Y. X. Peng, Chem. Commun., 2013, 49, 5384-5386.