Electronic Supplementary Material (ESI) for Soft Matter.

Bilayer Hydrogel Actuators with Tight Interface Adhesion Fully Constructed from Natural Polysaccharides

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Experimental Section

Preparation of chitosan (CS) microspheres. The CS microspheres were prepared by conventional emulsion process. To the chitosan solution in LiOH/KOH/urea/H_2O (4.5:7:8:80.5 by weight) system, 2 mL ECH was added, and stirred at -20 °C for 2 h to obtain a homogeneous CS pre-gel solution. After degassed by centrifugation at 7000 rpm for 5 min at 0 °C, the transparent CS pre-gel solution was poured into a well-mixed suspension containing 500 mL of isooctane and 5 mL Span80 in a flask. The resulting emulsion was stirred at 1300 rpm for 2h at room temperature, and the CS pre-gel micro-droplets were complete gelation. Subsequently, the emulsion was transferred into 2L ethanol/water composite solution with volume ratio (7:3). As a results, the emulsion was broken, and the CS microspheres were collected by centrifugation. Finally, the CS microspheres were successively washed with deionized water and ethanol for three times to remove the residual isooctane and Span 80. In this work, the CS microspheres was dyed by methyl orange in order to facilitate observation.

Preparation of bamboo-like hydrogels. 1-2 mL CS and C/CMC pre-gel solutions were alternately injected into a glass tube (diameter is 1 cm). After cured at room temperature for 2 hours, the hydrogels were demolded, and subsequently washed with deionized water to remove any residual. The CS sections were dyed by methyl orange.

Preparation of S-shape and wave-like bilayer hydrogels. Two or three bilayer hydrogel strips were alternately and inversely arranged along long axis on a glass plate, and a gap with width of 2 mm existed between two opposite bilayer hydrogels. Then,

the trace C/CMC pre-gel solution were dropped in and filled the gaps. After cured at room temperature for 2h, the separated bilayer hydrogel strips were jointed by the chemical bonds and strong electrostatic interaction. S-shape and wave-like bilayer hydrogels were combined from two and three as-jointed bilayer hydrogel strips, respectively.

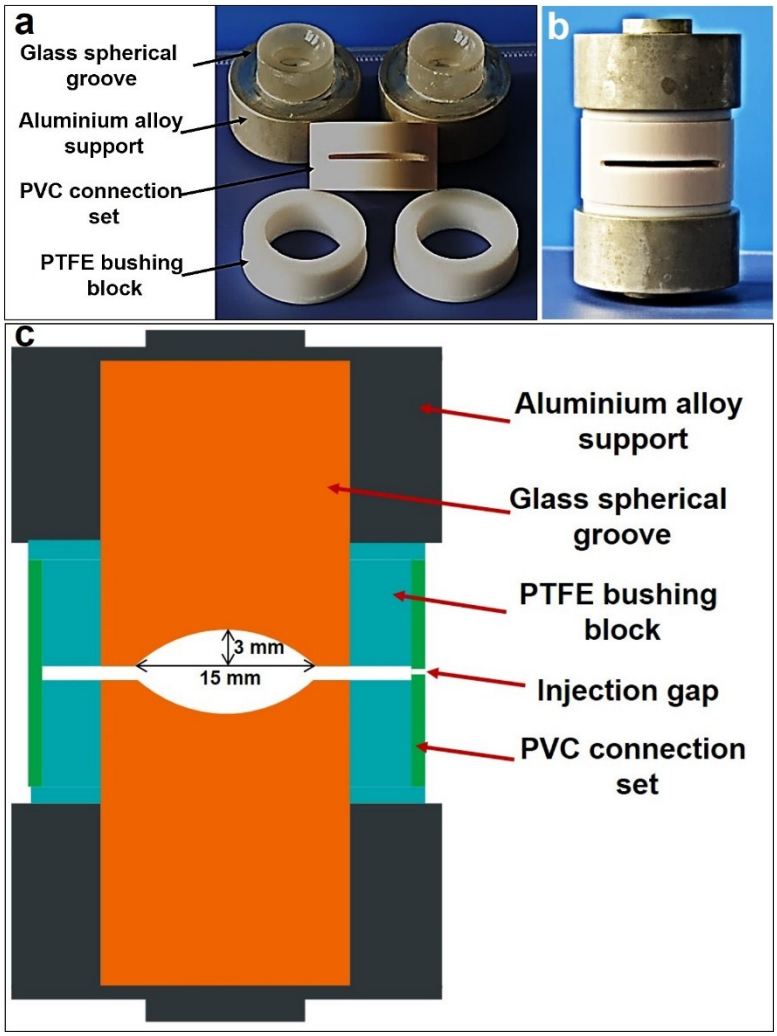

Fig. S1. Photographs of separated (a) and assembled (b) mold for bioinspired lens. The cross-section illustration of mold for bioinspired lens (c).

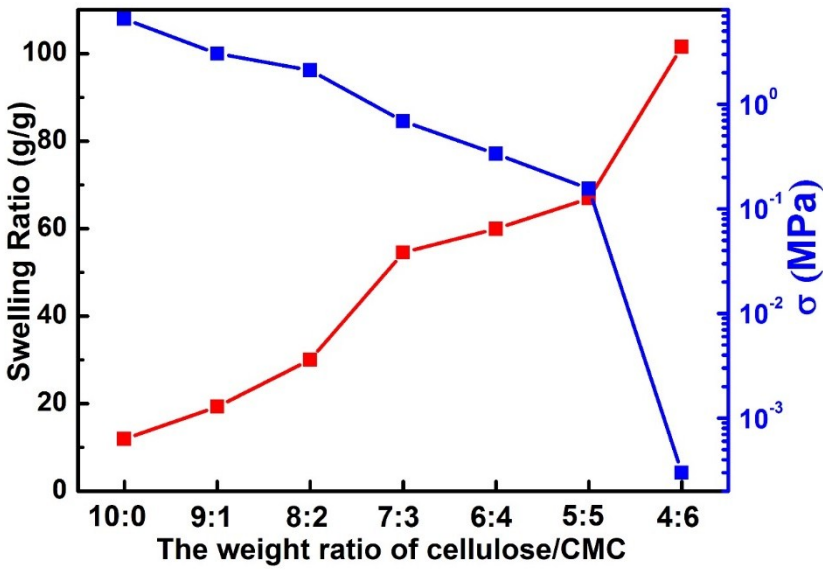

Fig. S2. The dependence of swelling ratio and compression stress of C/CMC hydrogels on their weight ratio.

As shown in Fig. S2, the compression stress of C/CMC hydrogels decreased with an increase of CMC in the composite hydrogels, whereas their swelling ratio increased with an increase of the CMC content. The results indicated that cellulose contributed to the improvement of mechanical properties of the composite hydrogels, whereas CMC enhanced their swelling behaviors. When CMC was dominated in composite hydrogels (C/CMC<4/6), the mechanical properties of composite hydrogels was very weak, and hardly tested due to their uncontrolled significantly swelling behaviors and low crosslinking density.

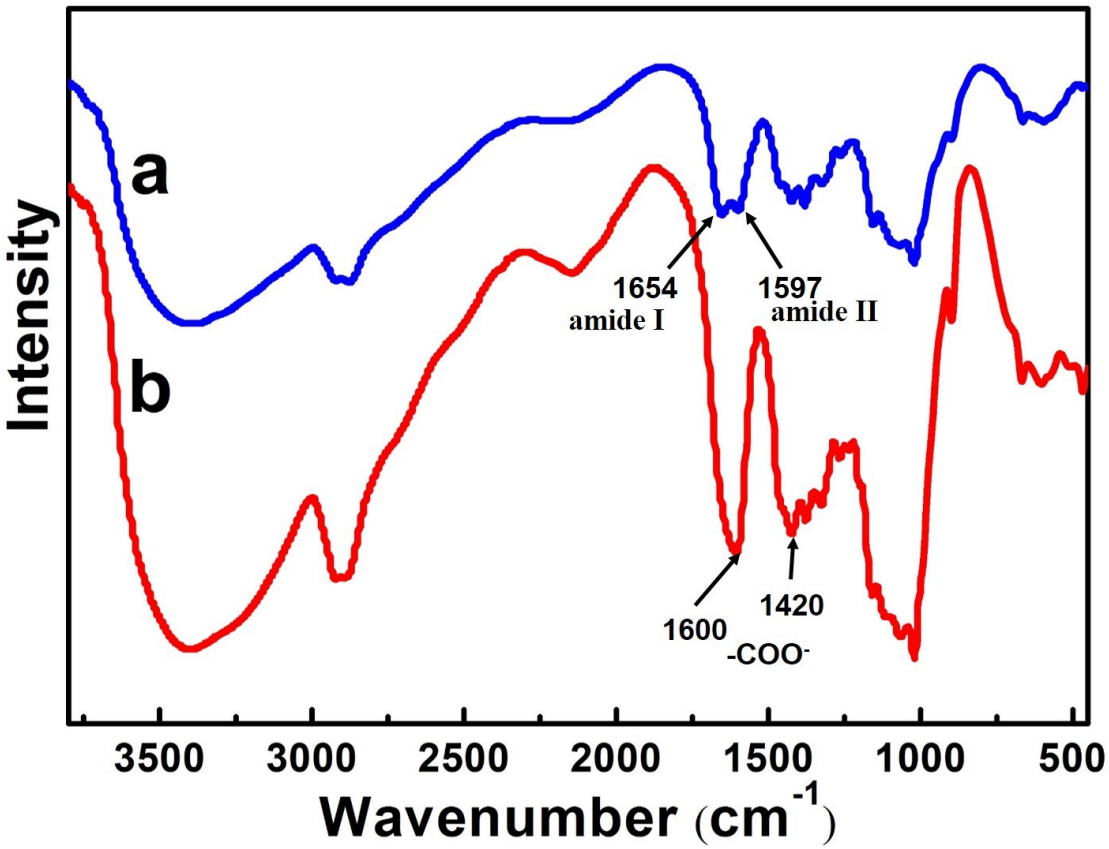

Fig. S3. Attenuated total reflection FTIR (ATR-FTIR) spectra of bilayer hydrogels, CS layer (a) and C/CMC layer (b).

As showed in Fig. S3, the bands observed at 1654 cm^{-1} and 1597 cm^{-1} in the CS layer were assigned to the amide I and N-H bending from amine and amide II, respectively.[1] The bands at 1600 cm^{-1} and 1420 cm^{-1} observed in C/CMC layer were attributed to the stretching and bending vibration of $-COO^-$, respectively.[2]

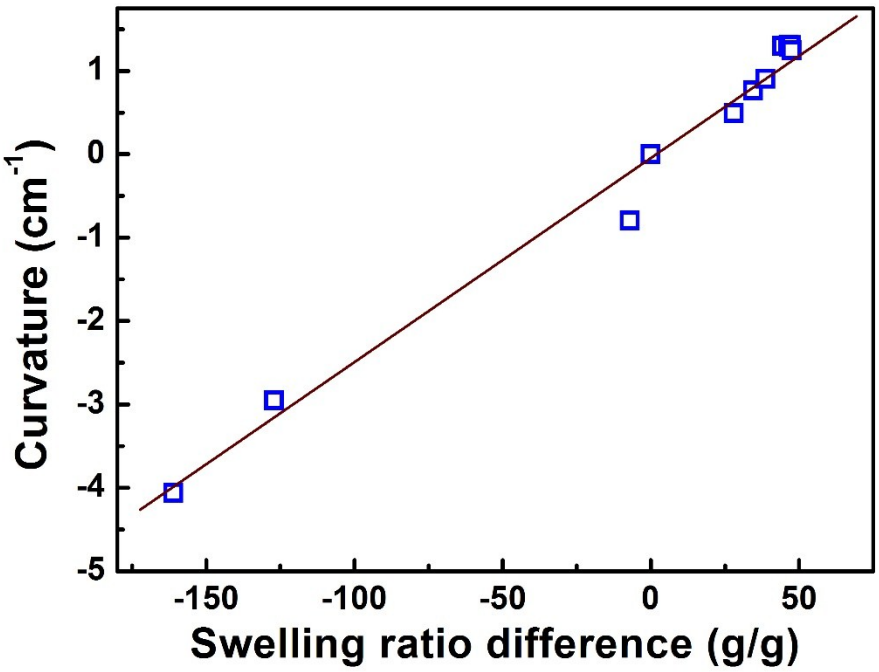

Fig. S4. The dependence of curvature of bilayer hydrogels on swelling ratio difference of CS layer and C/CMC layer.

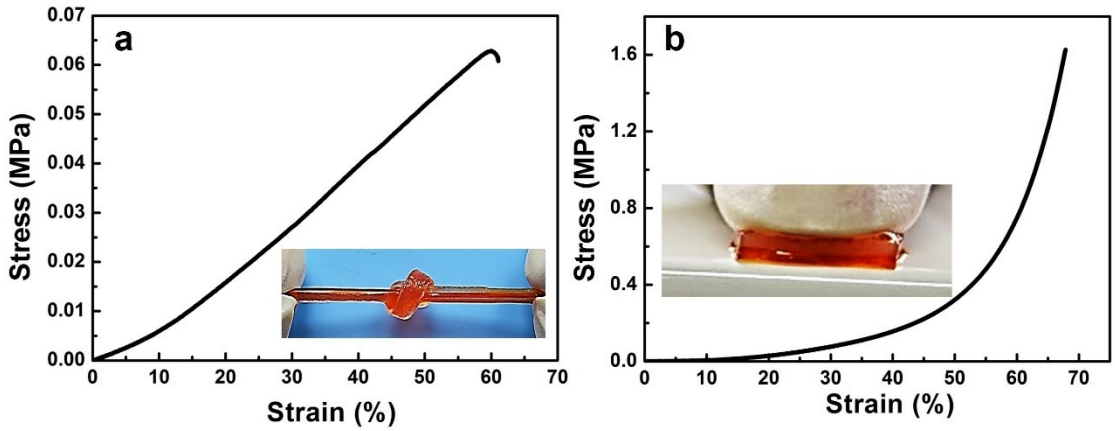

Fig. S5. Typical tensile and compressive stress-strain curves and the photographs of bilayer hydrogel: the tensile process (a) and the compressive process (b).

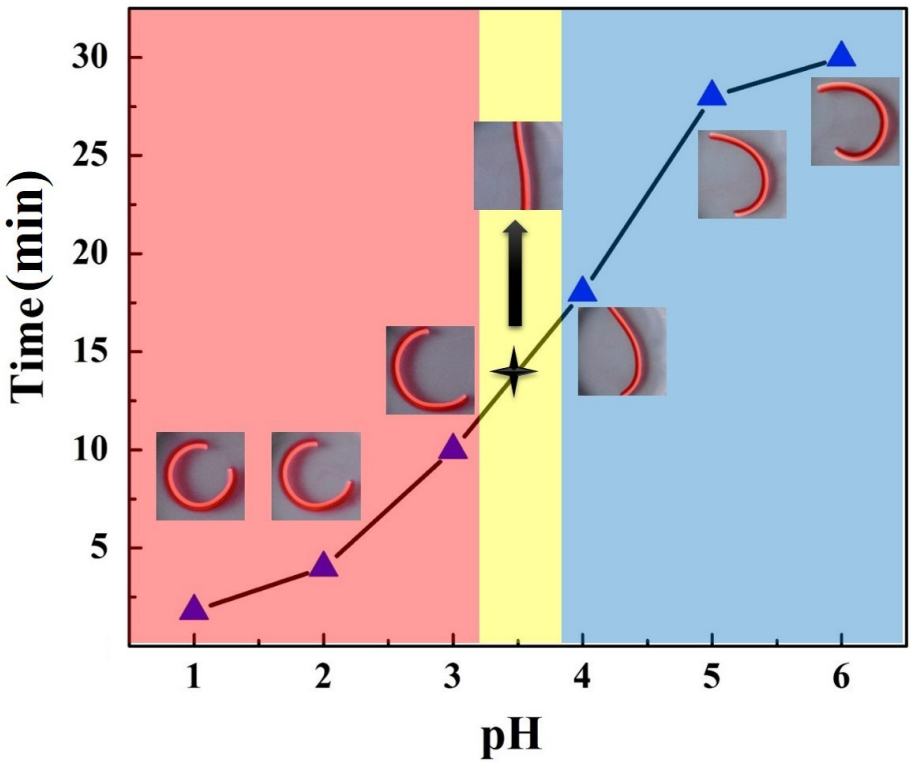

Fig. S6. The deformation equilibrium time and shapes of bilayer hydrogels in different HCl aqueous solution with different pH value.

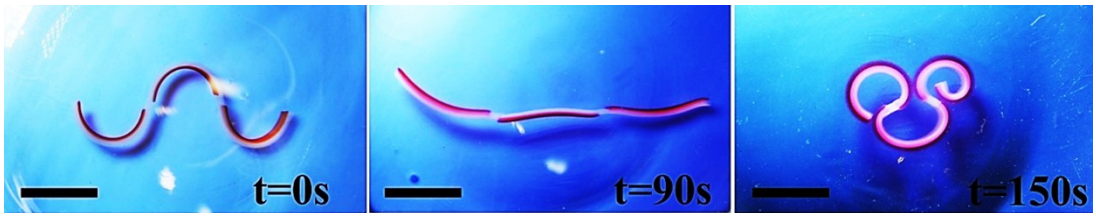

Fig. S7. The deformation process of wave-like bilayer hydrogels in 0.1M HCl aqueous solution (scale bars = 2 cm).

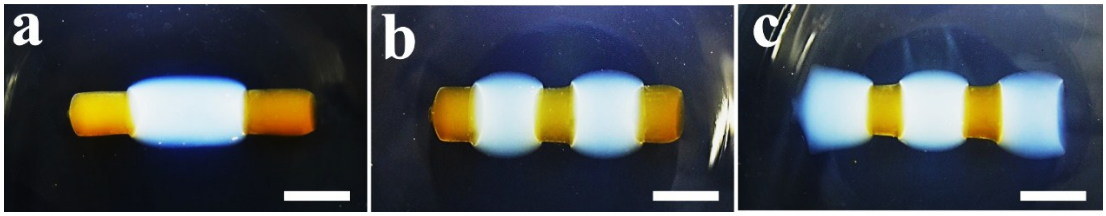

Fig. S8. Photographs of bamboo-like hydrogels at pH=7: two CS one C/CMC rods (a), three CS and two C/CMC rods (b), two CS and three C/CMC rods (c) (scale bars = 2

cm).

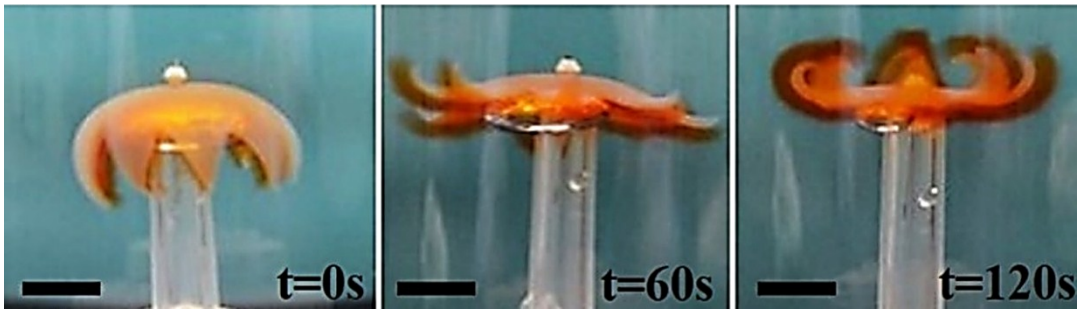

Fig. S9. The deformation process of flower-like bilayer hydrogels in 0.1M HCl aqueous solution (scale bars=3 cm).

The deformation process of flower-like bilayer hydrogels in acidic aqueous solution was displayed in Fig. S8. In brief, the as-deflexed flower-like hydrogel was fixed on the top of a plastic pillar by a pin, and then immersed into 0.1M HCl aqueous solution. Due to the combined effect of swelling/deswelling behavior of CS and C/CMC in acidic medium, the flower-like hydrogels was stretched after 60s, and finally upward bended after 120s, just like a blooming flower.

Movie S1. The adhesive force tests of two same and different free hydrogel strips.

Movie S2. The self-rolling process of a bilayer hydrogel belt in 0.1M HCl aqueous solution (four times the playback speed).

Movie S3. The slinging an object process of a soft gripper based on bilayer hydrogels in 0.1M HCl aqueous solution (two times the playback speed).

1. Lawrie, G.; Keen, I.; Drew, B.; Temple, A. C.; Rintoul, L.; Fredericks, P.; Grøndahl, L. *Biomacromolecules* **2007**, *8*, 2533-2541.

2. Chang, C.; Duan, B.; Cai, J.; Zhang, L. *Eur. Polym. J.* **2010**, *46*, 92-100.