Supporting Information

A bioinspired layered hydrogel actuator via L-ascorbic acid-triggered interfacial self-growth from a stiff hydrogel

Rongnian Xu*, Yuxin Gao, Yingying Lai, Chengyan Zhang, Wenbo Jia, Qiangbing Wei*

Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

*** Corresponding author:** weiqiangbing@nwnu.edu.cn; xurongnian@nwnu.edu.cn

Experimental

1. Materials

Ammonium persulfate (APS, 98%) and iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99％) were purchased from Sinopharm Chemical Reagent Co. Ltd. Acrylamide (AM, 99%), Acrylic acid (AA, 99%), Sulfobetaine methacrylate (SBMA, 98%) were purchased from Shanghai Macklin Biochemical Co. Ltd. N-isopropylacrylamide (NIPAM, 99%) was purchased from J&K Chemical Ltd. L-ascorbic acid (Vc, 99.7%), N, N′-methylenebisacrylamide (MBAA, 98%), Rhodamine B (98%) were obtained from Shanghai Zhongqin Chemical Reagent Co. Ltd. All the reagents were used directly without further purification.

2. Preparation of poly (acrylamide-acrylic acid)/Fe^{3+} (PAM-PAA/Fe^{3+}) stiff hydrogel substrate

Firstly, 4.26 g AM, 1.08 g AA, 0.0534 g APS, and 0.00864 g MBAA were dissolved in 30 mL deionized water (the solution A) and degassed for 10 min to remove air bubbles in the solution. Subsequently, the solution A was transferred into a mold composed of two PET plates with a thickness of 1 mm (glass slide with the size of 1 cm × 1 cm was used as spacers in the four corners), and the chemically cross-linked

poly (acrylamide-acrylic acid) (PAM-PAA) hydrogel was obtained after polymerization for 2 h in an oven at 60 ℃. Then, the PAM-PAA hydrogel was immersed into 16.2 mg/mL $FeCl_3 \cdot 6H_2O$ solution for 24 h to obtain the PAM-PAA/Fe^{3+} hydrogel substrate. Finally, the PAM-PAA/Fe^{3+} hydrogel substrate was soaked in deionized water for 24 h to remove free monomer and Fe^{3+}.

3. Preparation of the self-growing layered hydrogel

10 mg/mL Vc solution was evenly brushed on the surface of PAM-PAA/Fe^{3+} hydrogel substrate, and the Fe^{3+} loaded on hydrogel substrate surface was reduced to Fe^{2+} by Vc. After a certain time, the hydrogel was immersed into different kinds of monomer solutions to perform surface catalytically initiated radical polymerization (SCIRP) at room temperature to grow fresh hydrogel layer and obtain layered hydrogel. The compositions of the monomer solutions are shown in Table S1-S3 in the supporting information.

4. Characterizations of morphology

The superficial and cross-sectional morphology of the samples was observed using an Ultra-Plus thermal field emission scanning electron microscope (Zeiss, Germany), and the corresponding elements were detected using energy dispersive spectrometer (EDS). Test samples were firstly frozen in the atmosphere of liquid nitrogen for 10 min and then lyophilized using a Freeze dryer (SCIENTZ-12N). The thickness of the grown hydrogel layer was monitored using a TS2 fluorescence microscope (NIKON, Japan). The layered hydrogels piece with size of 10 mm × 3 mm was placed on the slide to obtain the cross-sectional images and then the thickness of the grown hydrogel layer was measured.

5. Characterizations of surface chemical compositions

The chemical structure of the samples was assessed using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) on a PerkinElmer transform infrared spectrometer (PerkinElmer, USA). Transmittance was monitored by

UV-3600 Plus spectrophotometer (SHIMADZU, Japan). The elemental composition was characterized using X-ray photoelectron spectroscopy (XPS) using a Thermo ESCLAB 250Xi spectrometer with a monochromatic Al Kα radiation. The binding energy of C1s at 284.8 eV was as a reference. The DSA-100 optical contact angle meter (Krüss Company, Germany) was used to measure the static contact angles of sample surface at ambient temperature (25 °C) with a droplet of 5 μL deionized water in the air. Each sample was measured at least three times at different positions to get the average value.

6. Mechanical and friction tests

The mechanical properties of the samples were carried out on the electrical universal material testing machine (EZ-Test, SHIMADZU) with a 500 N load cell at a speed of 100 mm/min. The samples were cut into long strips for testing and were stretched completely until it broke, and the corresponding stress-strain curves were obtained. The modulus of elasticity (E) was calculated from the slope of the stress-strain curve during 5-15% strain ratio. The interface bonding force between the hydrogel substrate and grown layer was performed by180° peeling test at the speed of 20 $mm \cdot min^{-1}$ on the electrical universal material testing machine with a 100 N load cell (AGS-X, SHIMADZU). The PET was glued on the surface of sample to prevent the elongation of sample and always keep 180° peeling.

The friction test was carried out on a pin-on-desk reciprocating tribometer (CSM, Switzerland) in deionized water at 0.5 N for 300 cycles. The elastomeric poly (dimethylsiloxane) (PDMS) hemisphere with a diameter of 6 mm was used as friction pairs. The PDMS pins were prepared by pouring the mixture of PDMS and curing agent (mass ratio=10:1) into a polystyrene 96-well cell culture plate mode and then incubating in a 60 °C oven for 4 h. Measurements were taken at least three times at different locations of the sample to obtain the average value.

Table S1. The content of PAM-PAA monomer solution

Sample	AM	AA	MBAA	APS	H_2O
PAM-PAA	4.26 g	1.08 g	0.00864 g	0.0534 g	30 mL

Table S2. The content of PNIPAM-PAA monomer solution

Sample	NIPAM	AA	MBAA	APS	H_2O
PNIPAM-PAA	3.39 g	0.432 g	0.005 g	0.01 g	20 mL

Table S3. The content of PSBMA-PAA monomer solution

Sample	SBMA	AA	MBAA	APS	H_2O
PSBMA-PAA	1.50 g	4.50 g	0.02 g	0.05 g	40 mL

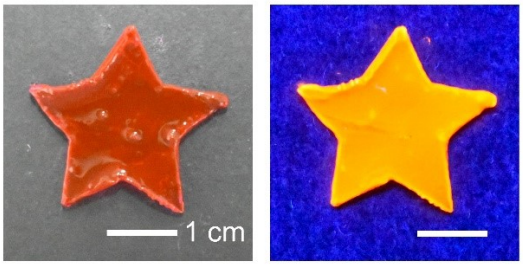

Figure S1. The photograph of the pentagon-like PAM-PAA/Fe^{3+}&PNIPAM-PAA layered hydrogel (left) and its fluorescence image dyed with 2 mg/mL rhodamine B (right).

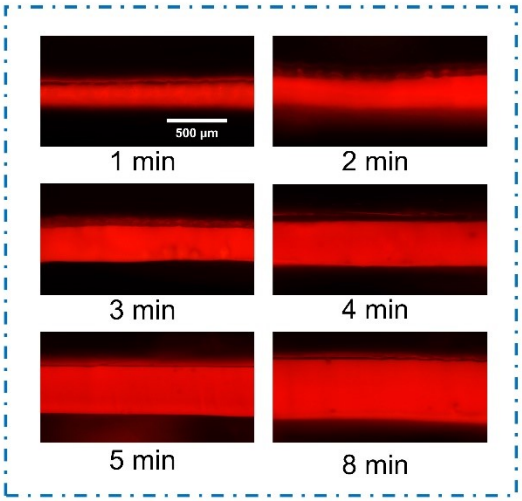

Figure S2. The fluorescence images of grown PAM-PAA hydrogel layer on the PAM-PAA/Fe^{3+} hydrogel substrate with different growth times (Vc concentration: 10 mg/mL, Vc reduction time: 2 min).

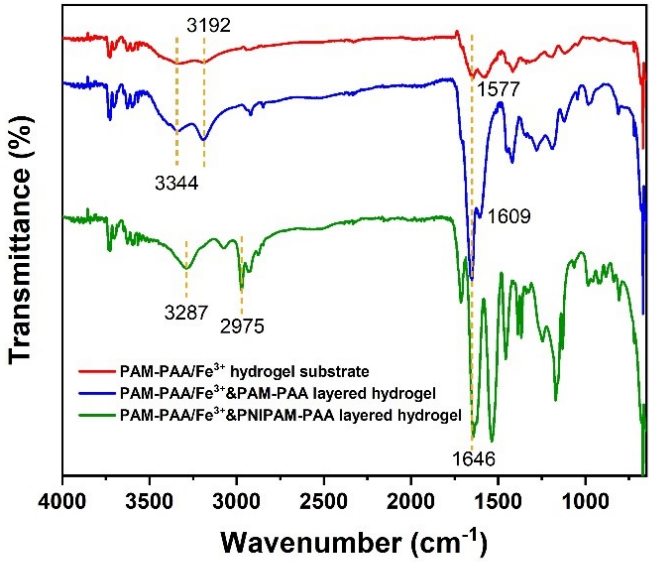

Figure S3. FT-IR spectra of the PAM-PAA/Fe^{3+} hydrogel substrate and the prepared PAM-PAA/Fe^{3+}&PAM-PAA and PAM-PAA/Fe^{3+}&PNIPAM-PAA layered hydrogel.

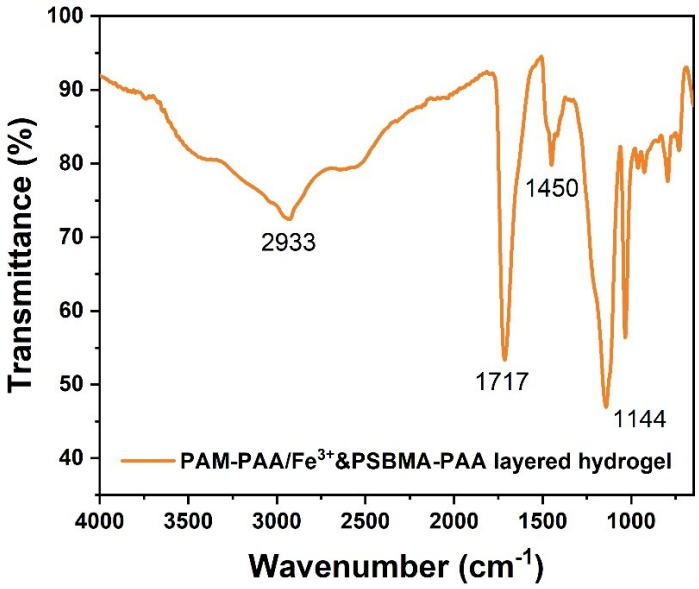

Figure S4. FT-IR spectra of the prepared PAM-PAA/Fe^{3+}&PSBMA-PAA layered hydrogel.

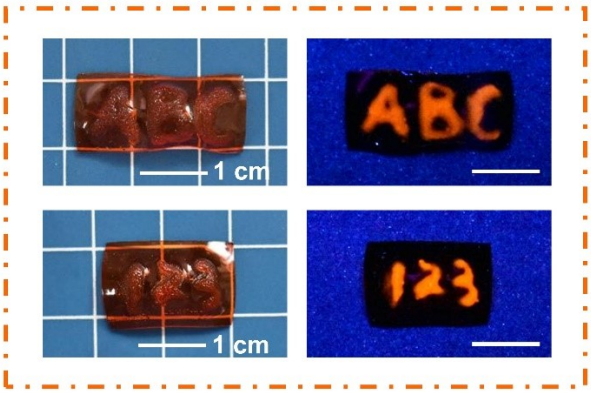

Figure S5. Optical (left) and fluorescence (right) images of patterned letters "ABC" and numbers "123" PAM-PAA hydrogel layers grown on PAM-PAA/Fe^{3+} hydrogel substrates.

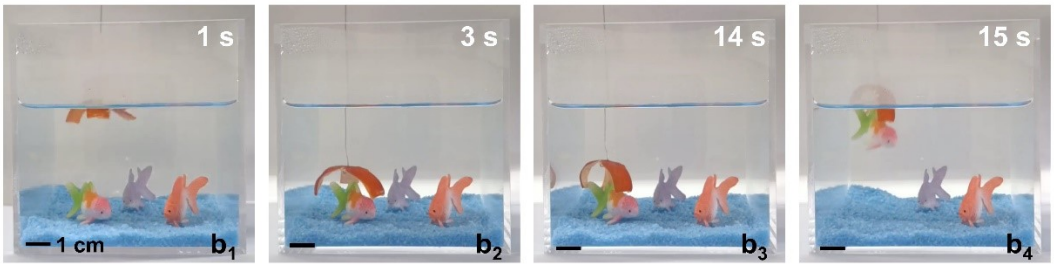

Figure S6. Photograph of a three-clawed layered hydrogel to capture a plastic fish in 60°C water bath.