

Supplementary Information

Pre-Patterning and Post-Oxidation-Crosslinking of Fe(0) Particles for a Humidity-Sensing Actuator

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Experimental Section

Materials: Sodium alginate (SA, $M_w \approx 50000$) and Fe(0) particles (FeP) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Deionized water was produced by a lab water purifier. Hydrochloric acid aqueous solution (36-38 wt%) was obtained from Jiangsu Qiangsheng Functional Chemical Co., LTD. All images and videos were recorded by a camera (JVC GC-PX100BAC).

Preparation of SA/FeP composite Film: SA aqueous solution was prepared by dissolving SA powder (1g) in deionized water (50 mL) in a 100 mL beaker under vigorous stirring by a magnetic stir bar at 80 °C. After adding FeP (250 mg), the mixture was stirred for another 2 h to ensure that the FeP dispersed homogeneously. A glass side (12 cm x 2 cm x 1 mm) was washed with ethanol and acetone and dried in a natural convection drying oven before use. The mixture of SA/FeP was cast onto the glass side and moved to magnetic field. After keeping for 30 min, the sample was dried at room temperature for 48 h to give rise to SA/FeP film with FeP patterning alignments along the magnetic direction.

Preparation of C-SA/FeP Film: Hydrochloric acid solution (10 mL) was diluted by 100 mL deionized water. The SA/FeP film was immersed in the diluted hydrochloric acid solution for 2 min. This operation turned Fe(0) into Fe²⁺ by oxidation reaction, so that the in-situ crosslinking

reaction took place between Fe^{2+} and carboxyl groups of SA, which led to different mechanical tensors of the C-SA/FeP film.

Polarized Optical Microscope (POM): SA/FeP and C-SA/FeP films were cut to rectangle strips ($35 \text{ mm} \times 25 \text{ mm} \times 40 \text{ }\mu\text{m}$) and observed by POM (Carl Zeiss, Axio Scope.A1). The observation was done under light-transmissive mode to analyze the surface and inner structures.

Scanning Electronic Microscope (SEM): SEM images were recorded on an electron microscope (Zeiss, Sigma HD) with a primary electron energy of 5 kV. The film samples were freeze-dried prior to attaching to silicon wafer with adhesive carbon tape and coated with a 5 nm thick gold layer before SEM observation.

Response to Humidity: C-SA/FeP film was cut to various rectangle strips ($25 \text{ mm} \times 5 \text{ mm} \times 40 \text{ }\mu\text{m}$) containing crosslinking patterning along different directions with respect to the long axis of the film. A mini-humidifier was utilized to change environmental relative humidity (RH) and a common camera was employed for recording the shape-changing processes of the film strips. The RH was monitored with a hygrometer (Extech, RH350). As RH was increased, the C-SA/FeP films adsorbed more humidity and showed more prominent coiling and curling motions. These kinematic processes were analyzed by measuring coiling angles and curling curvatures.

Humidity Sorption and Desorption: A mini-humidifier was used to provide humid environment. A dry C-SA/FeP film being recorded as m_0 was placed in the humid environment (RH: 99%). Its weight increased by sorption of humidity and was recorded as m at regular intervals. After the film was saturated with humidity sorption, it was transferred to a low-humidity environment (RH: 50%). The film released water molecules and decreased in its weight. The weight was recorded at regular intervals with the water release. After the film returned to the original weight, it was moved to the high-humid environment again. This operation was repeated three times. The humidity sorption and desorption were analyzed by calculating the variation of the water-sorption ratio with time according to the equation of $(m - m_0) / m_0 \times 100\%$.

Preparation of SA/FeP and C-SA/FeP Film Strips: A specialized graver from Japan was utilized to cut film to various strips. The specialized graver could make cutting edge smoother which avoided generation of shearing stress in the film strips. The shearing stress generated in the strips would have a great side effect on the shape deformations in response to external stimuli.

Contact Angle Measurement (WCA): We measured WCA with distilled water on a tester (CA100A). The top side and down side of the C-SA/FeP film were respectively tested, and their WCA were calculated based on the captured images.

Curvature calculation: The curling curvature (κ) of all film strips was monitored and calculated based on the snapshots from movies recorded during humidity-driven curling motions. The radius (r) was measured by software ImageJ v2.1.4.7. The curvature was calculated as the equation of $\kappa = 1 / r$.

Tensile tests: The mechanical properties of all film strips were examined on a tensile tester (Model: HY-0580, purchased from Shanghai hengyi precise instrument limited company). A strip of the sample ($2.5\text{ cm} \times 0.5\text{ cm} \times 40\text{ }\mu\text{m}$) was gripped between two sample holders and performed at a tensile speed of $20\text{ mm}\cdot\text{min}^{-1}$.

Supplementary Figures



Fig. S1 Microscopic image of physical-patterning SA/FeP film. The image indicates that the FeP aligned orderly in SA matrix.

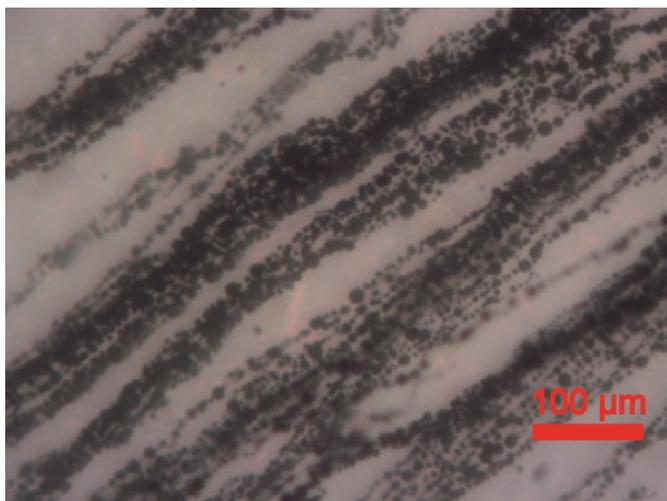


Fig. S2 Microscopic image of C-SA/FeP film. The crosslinking reaction was induced between Fe^{2+} and carboxyl groups of SA molecules, which caused chemical-crosslinking patterning inside the composite film.

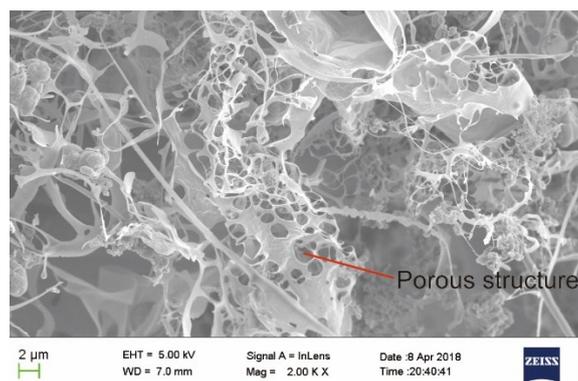


Fig. S3 SEM of Fe²⁺-crosslinked SA film. The observation was focused on the Fe²⁺-crosslinked area, where partial Fe(0) particles were dissolved and some pores left in the film.

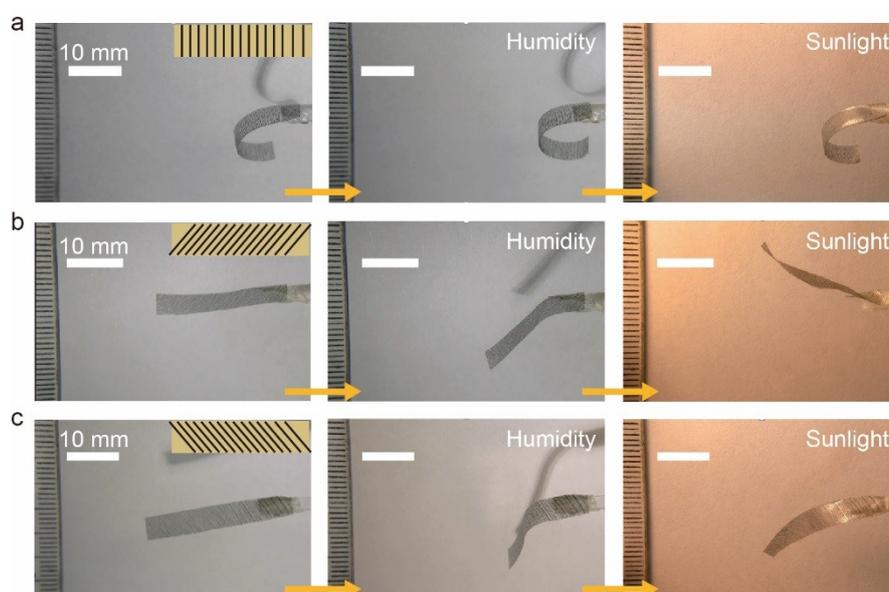


Fig. S4 Random motions of SA/FeP film. The SA/FeP film strips were cut out with FeP being aligned at (a) 90°, (b) -45° and (c) +45° with respect to the L , respectively. All film strips deformed not along the patterning direction, but in the random direction in response to humidity or sunlight.

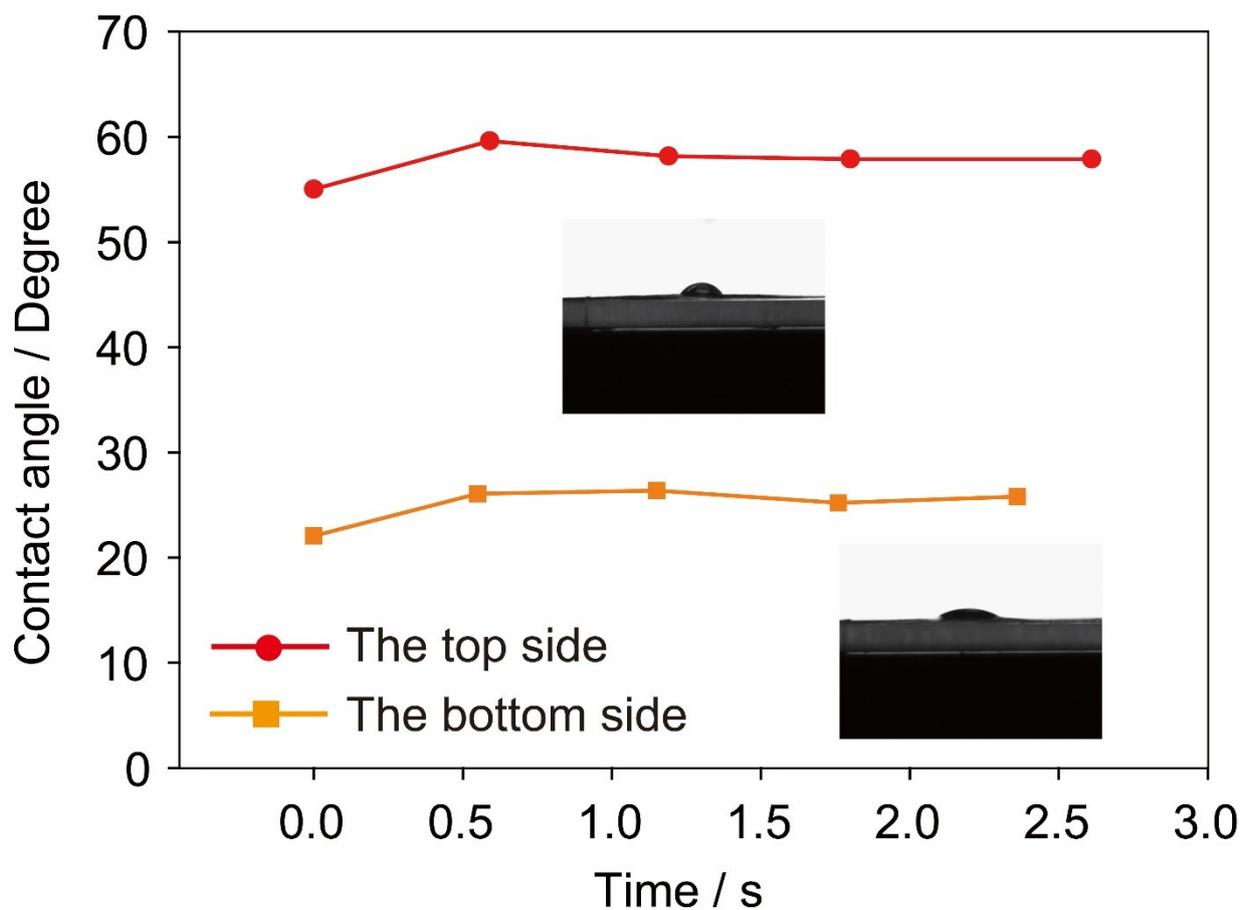


Fig. S5 Water contact angle of C-SA/FeP film. The hydrophilicity of the down side was better than the top side for the C-SA/FeP film.

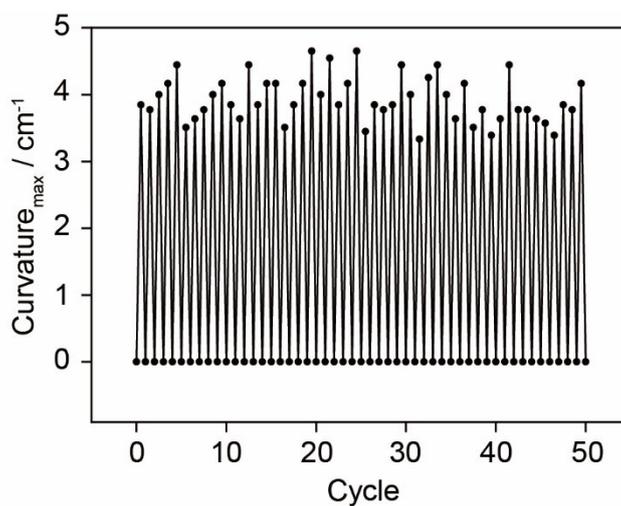


Fig. S6 Maximum curvature variation over the curling cycles in response to the same gradient of humidity.

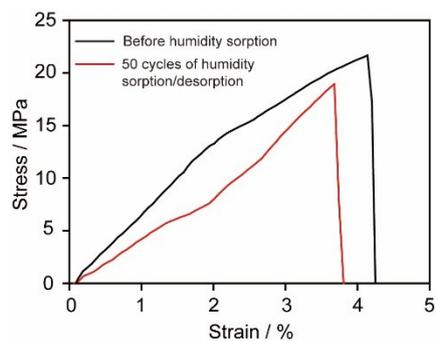


Fig. S7 Mechanical properties of C-SA/FeP film before and after humidity sorption/desorption.

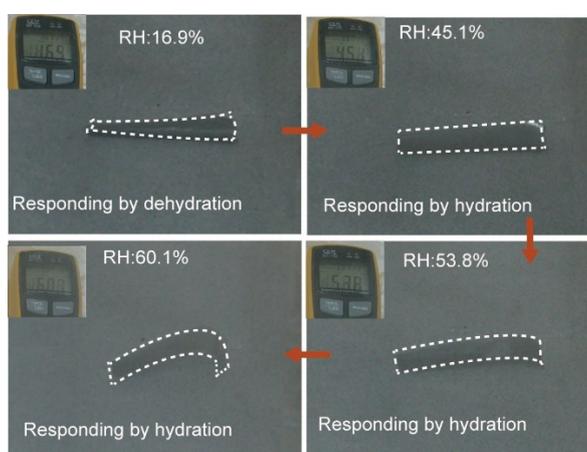


Fig. S8 Humidity-driven shape deformation of C-SA/ FeP film strip in a sealed glovebox. The lowest limit of humidity for inducing apparent shape deformation was 16.9% through the dehydration kinematics.

Supplementary Movies

Movie S1. The SA/FeP film was immersed in dilute hydrochloric acid (HCl) aqueous solution that turned partial Fe(0) particles into Fe²⁺. Lots of gas bubbles released out of the solution, which indicated the reaction between Fe(0) and HCl.

Movie S2. Humidity-driven motion of neat SA film.

Movie S3. Humidity-driven bending motion of C-SA/FeP film strip, in which the crosslinking patterns was along the direction perpendicular to the long axis L .

Movie S4. Humidity-driven right-handed coiling, in which the crosslinking patterning aligned at an angle +45° to the long axis.

Movie S5. Humidity-driven left-handed coiling, in which the crosslinking patterning aligned at an angle -45° to the long axis.

Movie S6. Humidity-/sunlight-driven uncoiling/coiling motility, in which the crosslinking patterning aligned at an angle -45° to the long axis.