Supplementary Information

Experimental Insight into Evolutionary Mechanism of Solid-to-Hollow Hydrogel

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Experimental section

***Materials*:** Sodium alginate (SA powder, $M_w \approx 50{,}000$ g/mol), anhydrous copper(II) sulfate and dimethyl formamide (DMF), acetone, absolute ethyl alcohol , Rhodamine B, methyl green were purchased from a commercial supplier (Sinopharm Chemical Reagent Co., Ltd, China). Tris(hydroxymethyl)aminomethane (Tris) were purchased from a commercial supplier (Shanghai Titan Scientific Co., Ltd, China). Hydrochloric acid and hydrogen peroxide (30wt% in water) were purchased from a commercial supplier (Chinasun Specialty Products Co., Ltd, China). Microscopy glass slides (150 mm × 150 mm × 0.5 mm) were obtained from T&Q industry.

Tensile tests: The SA strips tubes were tested with a tensile tester (Model: HY-0580, Shanghai hengyi precise instrument limited company). A load cell of 50 N was used. The length was 4 cm for all strip samples. The strip was stretched at a speed of 5 mm/min.

ATR-FTIR analysis: Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to analyze the surface composition of the Cu^{2+}-crosslinked SA tubes. The samples were dried in a vacuum oven at 40 °C.

X-ray photoelectron Spectroscopy (XPS): The spectra were obtained using an Al K-α X-ray photoelectron spectrometer (Thermo Fischer Scientific, ESCALAB 250Xi, USA) at a work voltage of 12.5 kV, an anode current of 16 mA, and a pressure of 8×10^{-10} Pa. The pass energy was 40 eV. The measurements were carried out after one week of plasma treatment.

***Viscosity test*:** The apparent viscosity of sodium alginate/water solution was measured by Brookfield DV-2 and Pro rotary viscometer (USA). The initial concentration of sodium alginate

solution was 10 g/L at 25 °C. With H_2O_2 solution being added, the viscosity was decreased by H_2O_2-induced degradation, and was measured with time.

Supplementary Fig.s

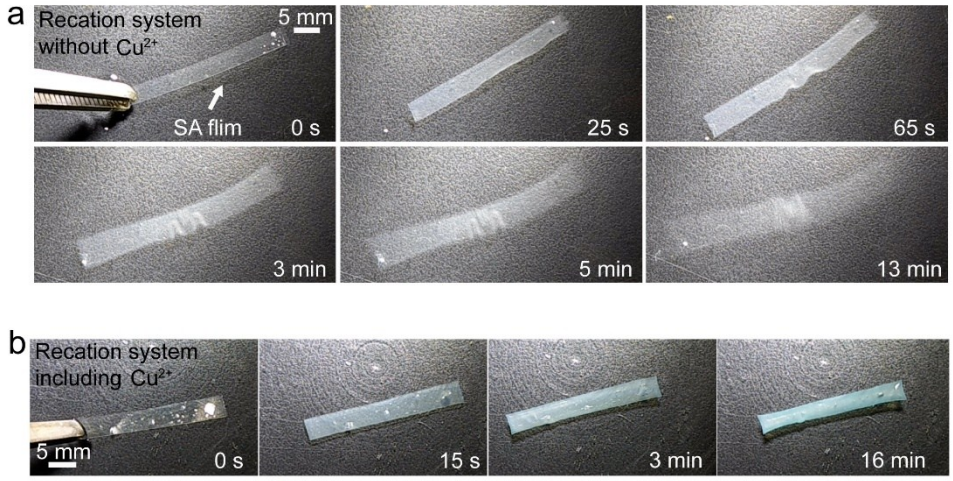

Fig. S1 Cu^{2+}-induced crosslinking. (a) An SA strip was immersed in water without Cu^{2+}, and it dissolved in 13 min. (b) As it was immersed in Cu^{2+}-containing water solution, it swelled with sorption of water, but did not dissolve owing to Cu^{2+}-induced crosslinking with carboxyl groups of SA molecules.

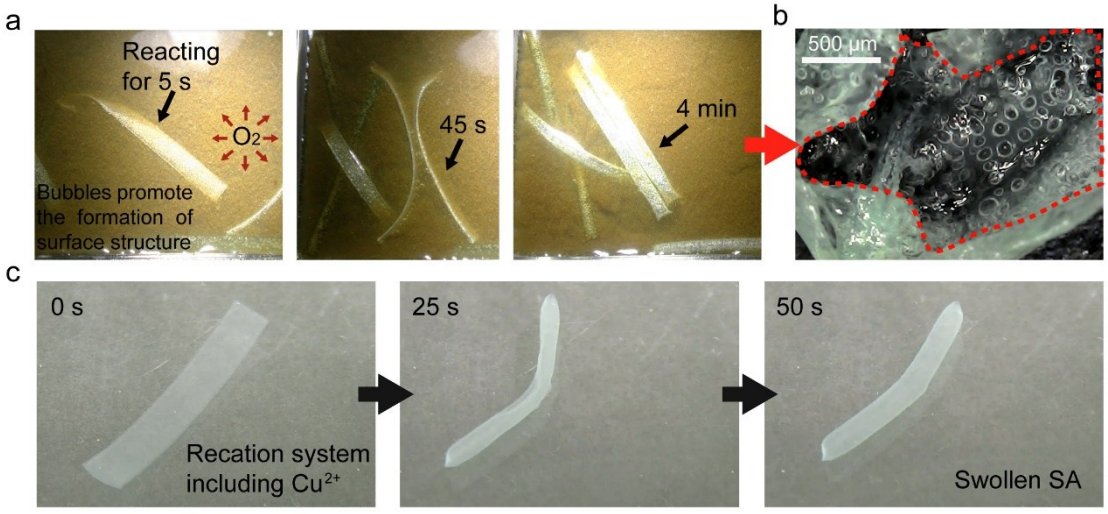

Fig. S2 Evolutionary process of a solid SA strip to a hollow hydrogel tube. (a) Snapshots showing that the SA strips were converted to hydrogel tube in 4 min. (b) A image revealing the structure of inner wall of hydrogel tube. The gas bubbles released and left many holes in the tube wall. (c) The SA strip swelled only if there was no H_2O_2 element in the reaction solution.

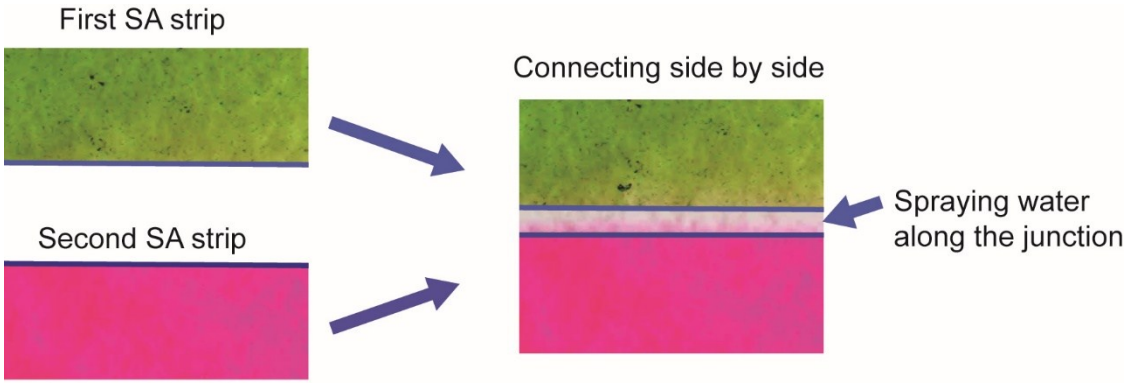

Fig. S3 Schematics showing how two SA strips were assembled together side by side. The assembled two strips self-healed into an integral piece through water-induced molecular diffusion.

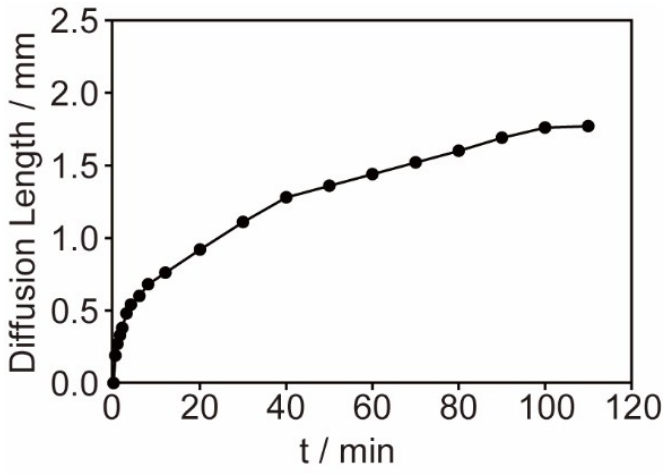

Fig. S4 Diffusion-time profile. The diffusing distance in the two phases was defined by the initial and final boundary position.

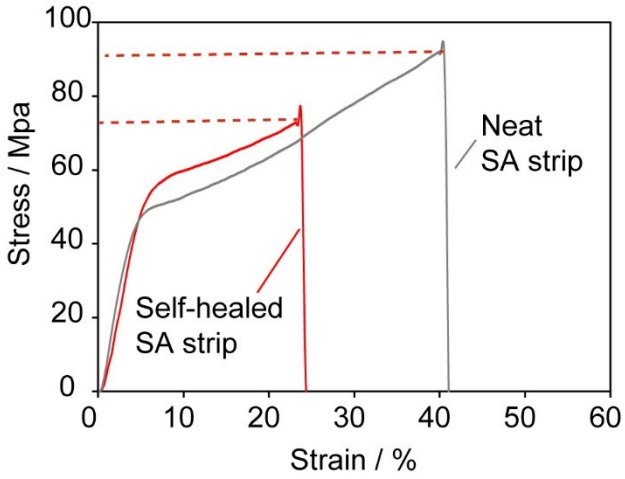

Fig. S5 Tensile curves of self-healed SA strip and the neat SA strip. The self-healing ratio was calculated based on their maximum stress values as indicated by red broken line.