Supplementary Information

Construction of pH/pectinase dual-responsive pesticide microcapsule and adhesive gel patch for sustainable plant disease management

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Supplementary experimental section

Characterization. ^{1}H NMR spectra were determined on a Bruker 400 MHz NMR spectrometer (Advance, Germany). The morphology of the samples was obtained using scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, Hitachi JEM-2100, Japan). ζ-potential and size distribution were measured by dynamic light scattering (Malvern Instruments, ZEN3700, UK). The chemical functional groups of the samples were determined by Fourier transform infrared (FT-IR) spectrometer (NEXUS, USA) in transmission mode. UV–vis spectra of the samples were measured by a UV–vis spectrophotometer in absorbance mode (Hitachi U-3900, Japan).

Preparation of PTP loaded with FITC. The hydrophobicity of PRO IL in the core of PTP was exploited to dissolve FITC to prepare PTP (FITC). Briefly, PRO IL (final concentration 5 mM), 1 mg of FITC and Tween-80 (final concentration 0.05%) were continuously added into 15 mL water, followed by vortexing for 2 min and remaining stationary for 30 min to form a stable and uniform PRO IL (FITC) emulsion dispersed in water. Copper ion (final concentration 0.11 mM) and TA (final concentration 0.07 mM) were continuously added into the above mixture, followed by vortexing for 2 min. Then the pH of the mixture was adjusted to 7.2 by MOPS buffer and then PT (FITC) was obtained by vortexing for 2 min and remaining stationary for 30 min. Finally, to obtain PTP (FITC), pectin (final concentration 0.28%) was added to the PT (FITC) suspension, followed by vortexing for 10 min. The mixture was centrifuged at 11,000 rpm for 3 min and washed three times with pure water for subsequent use.

Preparation of PTP-FITC. Different from PTP (FITC), the pectin on PTP was covalently conjugated with FITC (PTP-FITC) to characterize the connection state of pectin. The preparation of PTP-FITC was according to the reported methods with slight modification [1,2]. 20 mL of 0.5 mol/L 1,6-diaminohexane was added to 10% acetic acid, and 400 mg pectin was added and dissolved. Then 300 mg sodium cyanoborohydride ($NaBH_3CN$) dissolved in 2 mL distilled water was gradually added to the pectin solution, followed by stirring at 37 °C for 20 h. After centrifugation at 9000 rpm for 10 min, the precipitate was freeze-dried to obtain pectin-D. After that, 200 mg pectin-D was dissolved in 10 mL distilled water, and the pH of the solution was adjusted to 8.5 with 0.5 mol/L sodium bicarbonate. 20 mg FITC dissolved in 2 mL methanol was added to the pectin-D solution. The mixture was kept in the dark at 37 °C for 12 h. After alcohol precipitation, pectin-FITC was obtained. Finally, PTP-FITC can be obtained by completing the preparation process of PTP with the utilization of pectin-FITC.

Photostability investigation. The photostability of PRO EW, PRO IL and PTP under ultraviolet light irradiation was investigated using a germicidal lamp. Briefly, at the identical PRO concentration, 50 mL PRO EW, PRO IL and PTP suspension were added to a quartz glass tube under stirring, and subsequently the glass tubes were positioned 10 cm away from a 17 W germicidal lamp (wavelength 254 nm). At the regular time intervals, 0.5 mL sample was withdrawn and analyzed by HPLC.

The wettability test. The wettability test was determined based on the contact angle. All dust on the leaves was carefully removed. The leaf parts were carefully cut off and adhered to the glass slide. Regarding the preparation process of PTP, it was

categorized into two groups with the centrifugation process serving as the demarcation. One group without centrifugation retained all substances throughout the preparation process, the other group was the resuspension of the nanoparticles after centrifugation separation. 5 μL solution from the two groups was dropped onto the leaves respectively to measure the contact angle. Five measurements were performed to calculate the average value.

Spraying and leakage experiment. Leaves with basically identical size were selected and clamped at an inclination angle of 30 degrees. A glass petri dish was placed at the bottom of the leaf to collect the leaked liquid. The PRO concentration in the spraying liquid was maintained at 100 mg/L. The spraying tool and spraying angle remained unchanged (from top to bottom), and the spraying was carried out continuously for three times. In one group, a fan was used to gently blow to make the leaves tremble slightly, simulating the situation of natural wind; in the other group, a syringe was used to drip the liquid, simulating the process of natural rainfall. The process was carried out 1 h after spraying. The collected leakage liquid was used to measure the leakage rate. The experiment was repeated 3 times.

Copper ion cumulative release experiment. The prepared adhesion gel patch, containing 100 mg/L PRO, was affixed to the leaves of 5-week-old rape plants. The copper ion content within the patch was measured every two days. Specifically, the agar gel was carefully removed and placed into a 50 mL beaker. Subsequently, 40 mL pure water was added, and the mixture was heated to boiling. Finally, the pH was adjusted to 4, and magnetic stirring was conducted at room temperature for 12 h. The volume

was then made up to 50 mL, the copper ion concentration was determined by atomic absorption spectrometry, and the release rate was calculated. The instrumental parameters were set as follows: wavelength 324.7 nm, slit width 0.2 nm, acetylene flow rate 1.5 L/min, and air flow rate 5.0 L/min.

Figures

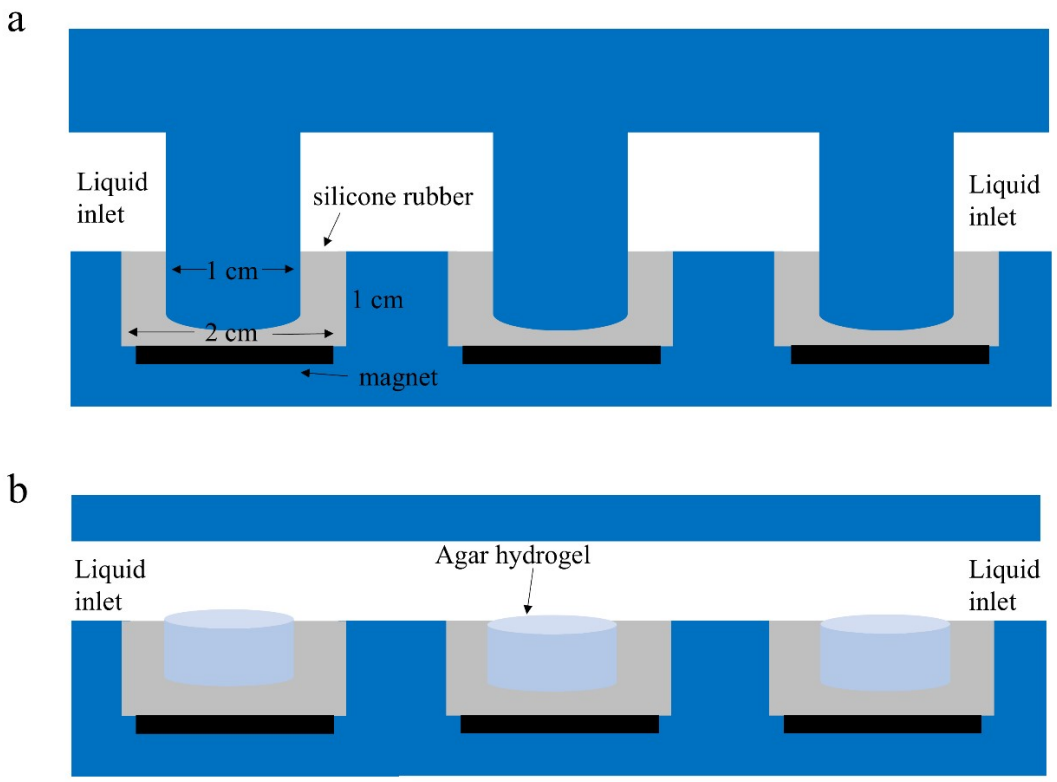

Fig. S1 (a) The design of the mold and the forming process with the addition of silicone rubber. (b) The forming procedure with the addition of agar hydrogel.

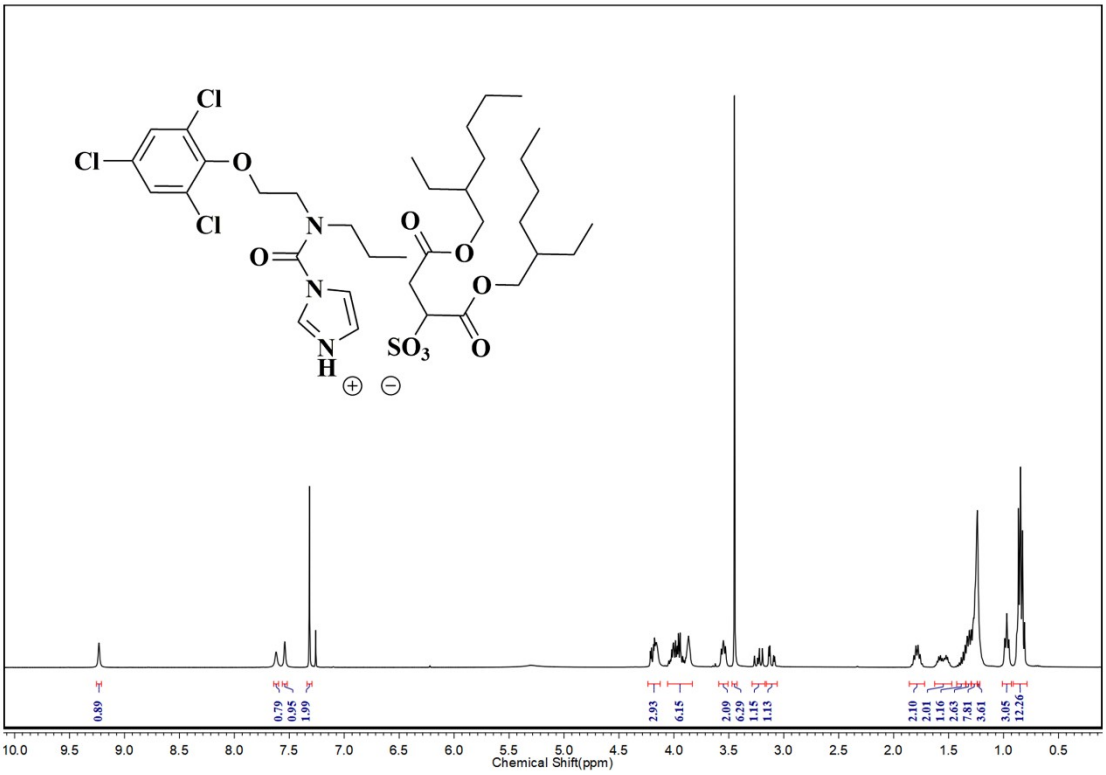

Fig. S2 ^{1}H NMR of PRO IL. ^{1}H NMR (400 MHz, Chloroform-d) δ 9.23 (s, 1H), 7.62 (s, 1H), 7.54 (s, 1H), 7.32 (s, 2H), 4.24 – 4.12 (m, 3H), 4.06 – 3.83 (m, 6H), 3.55 (t, J = 7.8 Hz, 2H), 3.45 (s, 6H), 3.23 (dd, J = 17.4, 11.3 Hz, 1H), 3.11 (dd, J = 17.4, 3.9 Hz, 1H), 1.79 (h, J = 7.4 Hz, 2H), 1.63 – 1.47 (m, 2H), 1.38 (dd, J = 14.3, 7.3 Hz, 1H), 1.34 – 1.29 (m, 3H), 1.29 – 1.24 (m, 8H), 1.24 (s, 4H), 0.97 (t, J = 7.4 Hz, 3H), 0.91 – 0.79 (m, 12H).

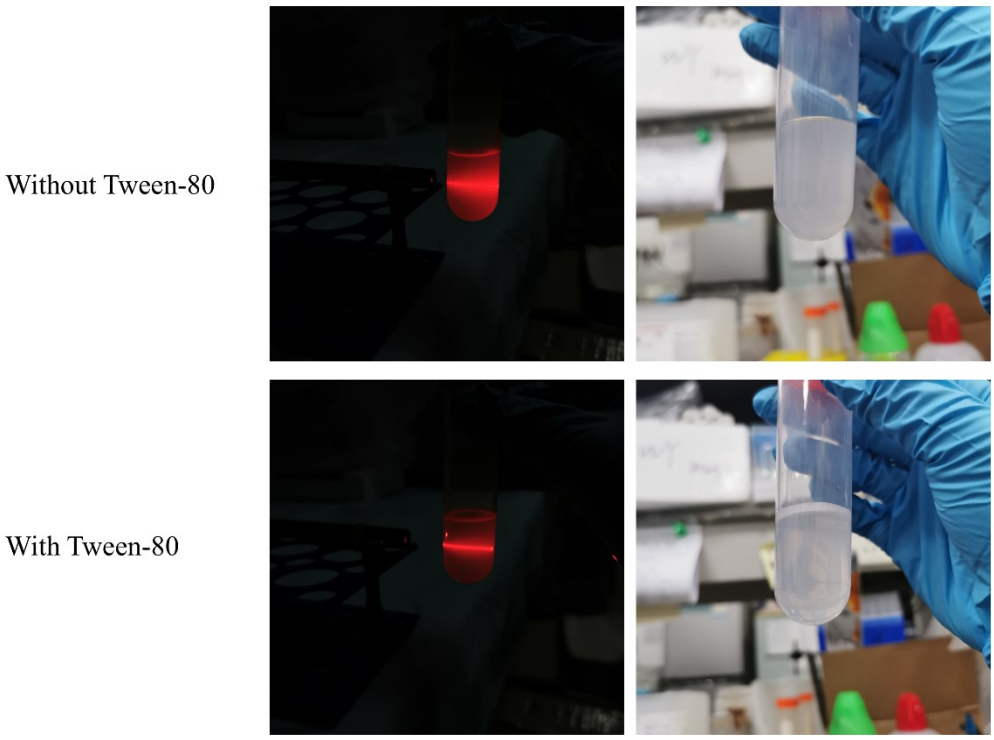

Fig. S3 The difference in preparation of PRO IL emulsion without Tween-80 and with Tween-80. After adding Tween-80, the Tyndall effect of the PRO IL emulsion is more obvious and the transparency of the liquid increases.

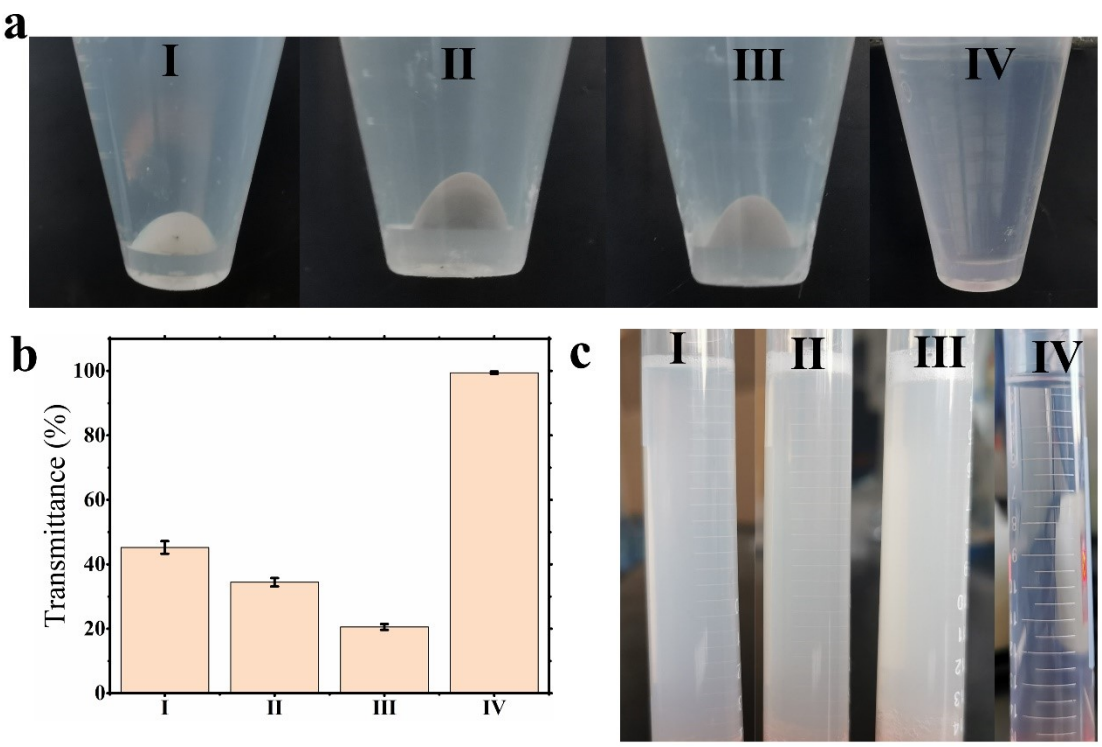

Fig. S4 (a) The bottom precipitate after centrifugation. (I: PRO IL+Tween-80+water; II: PRO IL+Tween-80+water+TA-Cu; III: PRO IL+Tween-80+water+TA-Cu+pectin; IV: Tween-80+water+TA-Cu+pectin). (b) The transmittance of samples throughout the preparation process was measured at the wavelength of 600 nm. (c) The liquid state of the samples.

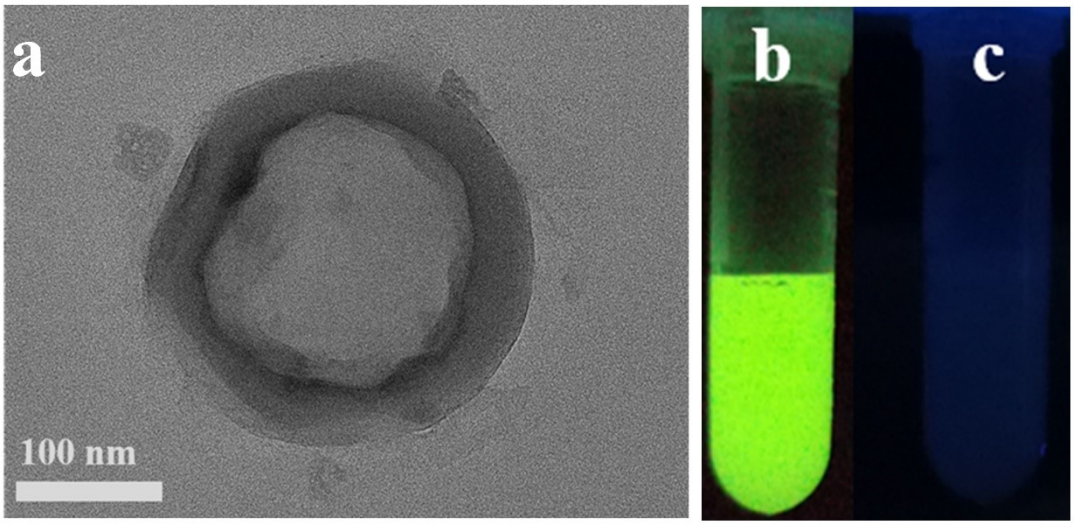

Fig. S5 (a) SEM image of TA-Cu@pectin microcapsule. (b) TA-Cu@pectin-FITC microcapsules and (c) TA-Cu@pectin microcapsules, fabricated through rinsing with ethanol.

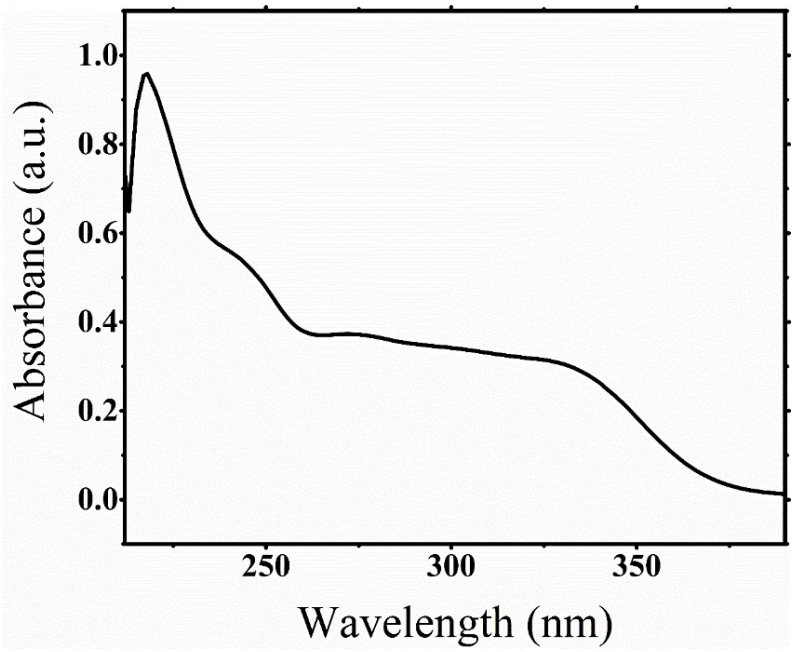

Fig. S6 The UV–vis absorption spectrum of TA-Cu at pH 7.2. A specific absorption shoulder peak at 335 nm can be observed.

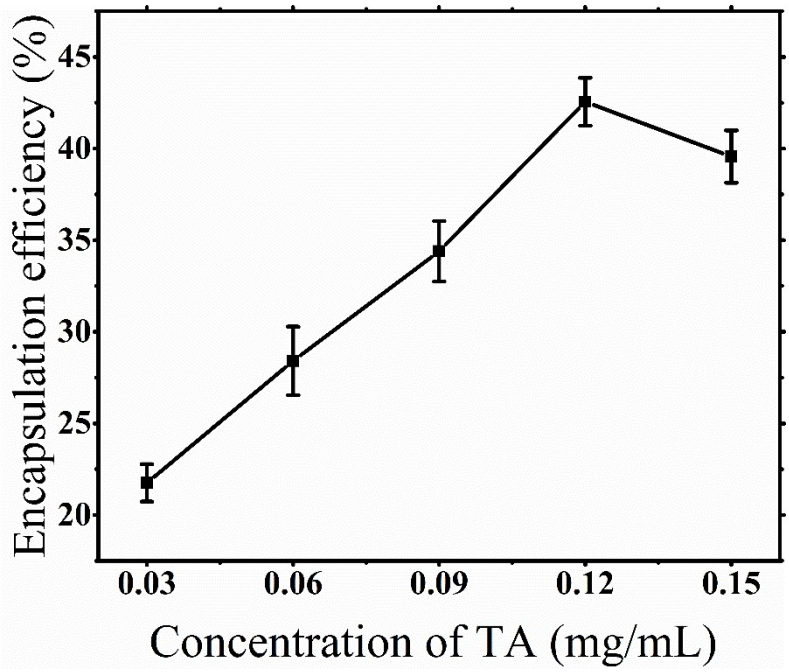

Fig. S7 The influence of TA concentration on the encapsulation efficiency of PT.

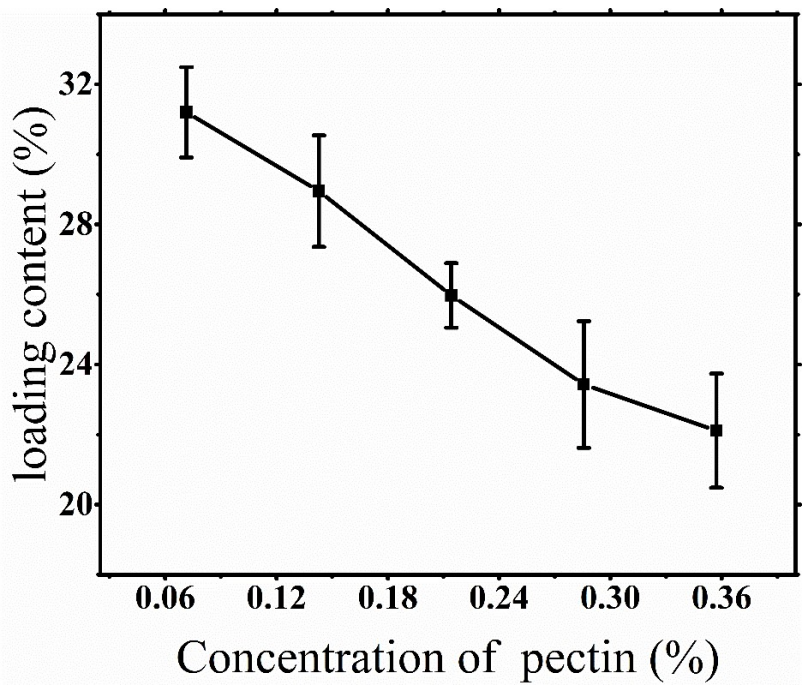

Fig. S8 The impact of pectin concentration on the loading content of PTP.

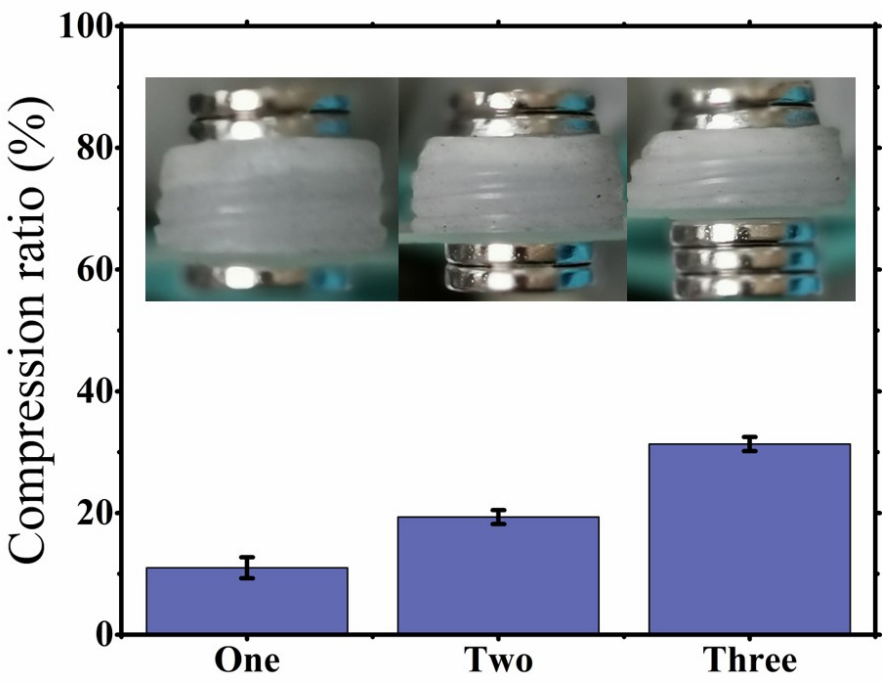

Fig. S9 The compression performance of the gel patch. Only by altering the number of magnets to compress the gel patch and comparing it with the height under natural condition can calculate the compression ratio.

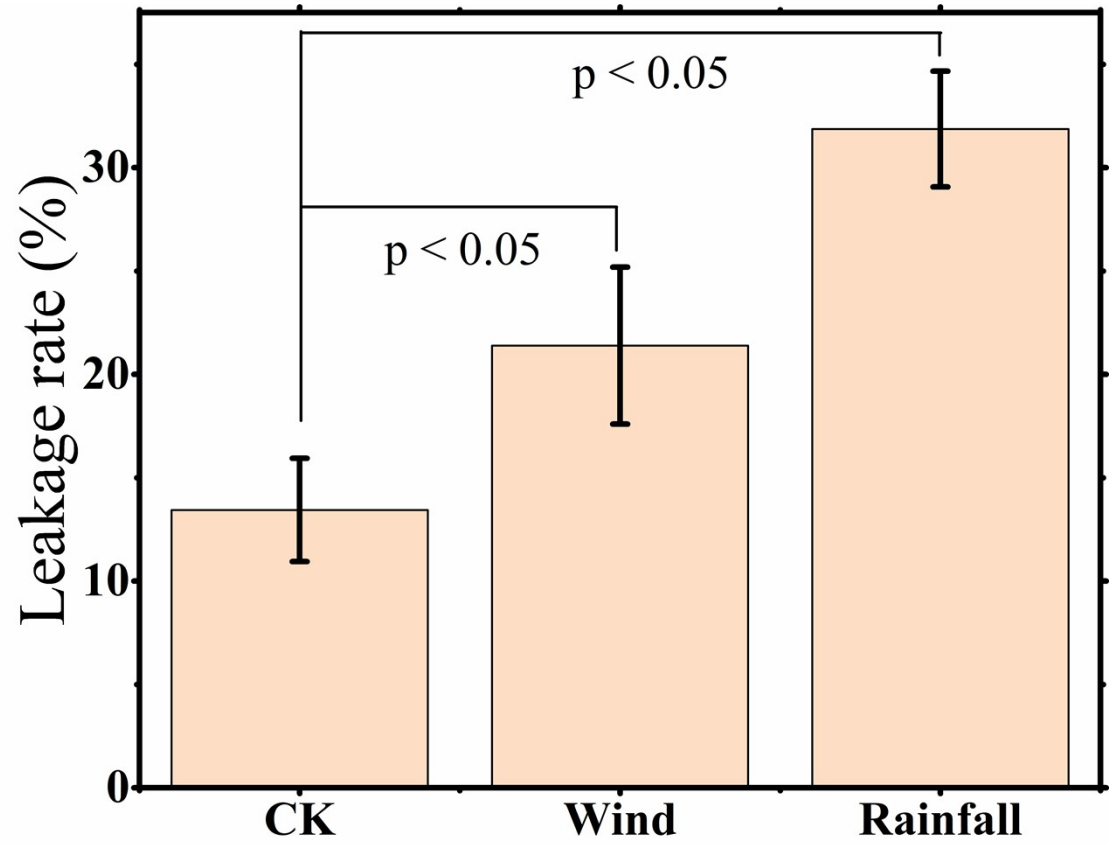

Fig. S10 The leakage rate was measured under conditions simulating natural wind and rainfall. For the control group (CK), during the spraying process, the leaves were maintained at an inclination of 30 degrees. Rainfall simulation was conducted one hour after the spraying was completed.

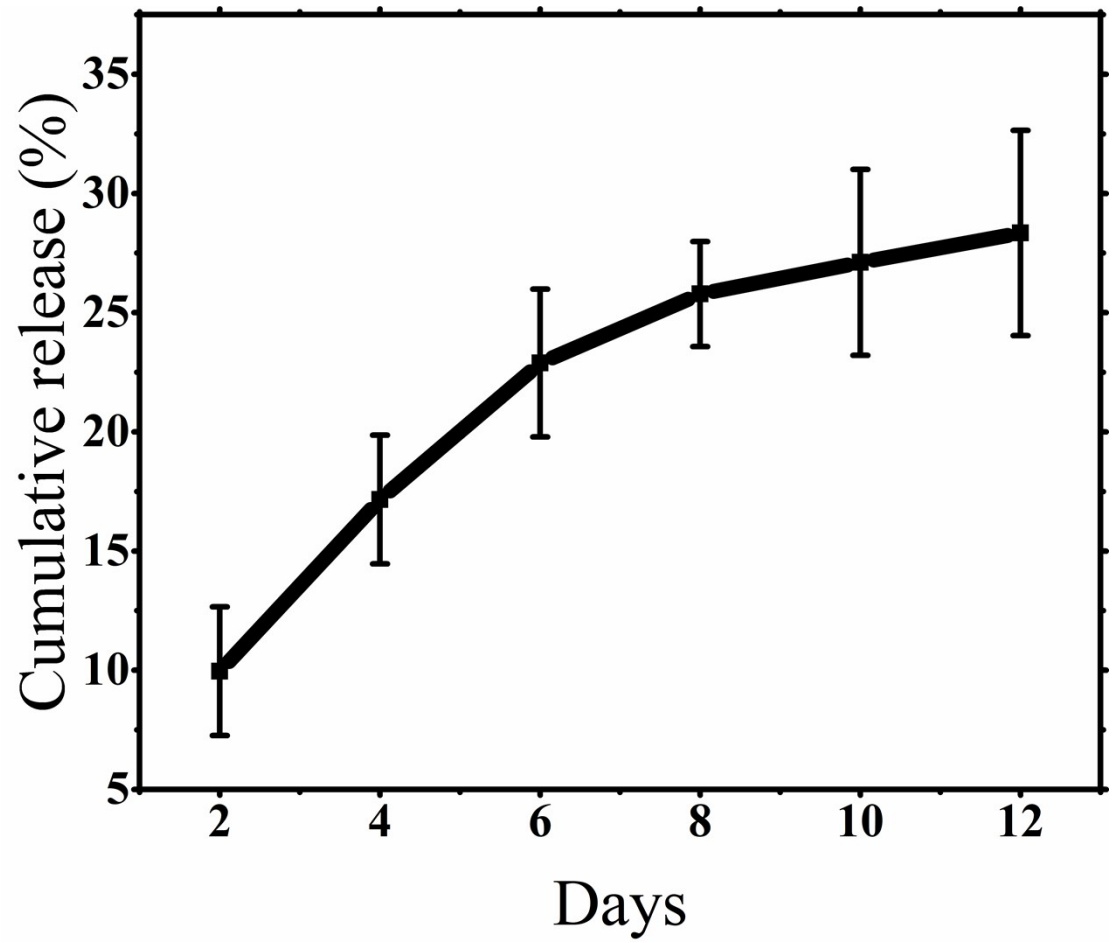

Fig. S11 Copper ion release test of the adhesive gel patch.

References

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2 P. Li, C. Li, Y. Xue, Y. Zhang, H. Liu, X. Zhao, G. Yu and H. Guan, Characterization and pharmacokinetics of fluorescence labeled propylene glycol alginate sodium sulfate, *J. Ocean Univ. China*, 2014, **13**, 683–690.