Supporting Information

Visualization of Self-Healing Process by Directly Observing the Evolution of Fluorescence Intensity

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Contents

Experimental Section

Materials

Tetracyanoethylene (TCNE), 2-(N-ethylaniline)ethanol, methacryloyl chloride, triethylamine, butyl acrylate (BA, stabilized with hydroquinone monomethyl ether), and acrylamide(AM) were purchased from TCI Shanghai. Glacial acetic acid and sodium bicarbonate were purchased from Sichuan Xilong chemical Co., Ltd. 2,2-Azobis(2-Methylpropionitrile) (AIBN) was purchased from Adamas Reagent Co., Ltd. BA was filtered through a basic alumina column to remove hydroquinone monomethyl ether. All the solvents were of analytical grade.

Synthesis of TC1

The 4-tricyanovinyl-[N-(2-hydroxyethyl)-N-ethyl]aniline (TC1) was obtained by reacting 1 mol TCNE and 1 mol 2-(N-ethylaniline)ethanol in dimethylformamide at 55 ℃ for 15 min[1]. The product was precipitated from ice water and then recrystallized from glacial acetic acid.

Synthesis of TLM

The TC1-labeled methacrylate monomer (TLM) was obtained by an esterification reaction of methacryloyl chloride and TC1[1]. 0.3 mL TC1, 0.5 g methacryloyl chloride, and 0.4 mL triethylamine were dissolved in autoclaved dichloromethane, and the solution was then cooled to 0 ℃ to perform the reaction. After stirring for 2 h, the solution was washed with saturated sodium bicarbonate aqueous solution and then recrystallized from an ethanol/water solution.

Synthesis of self-healing elastomers

Copolymers of BA and AM, and copolymers BA, AM and TLM were synthesized by one-pot free-radical polymerization, and designated as p(BA-AM)-x and p(BA-AM-TLM)-x respectively, where *x* represents the molar ratio of AAm to BA. In detail, 0.0001 mol TLM and 0.4 mol BA were mixed with different molar contents of AM (10%, 15%, 20% molar ratios of AM/BA) in 15 mL ethyl acetate, which was then

injected into an argon-protected three-necked flask with a syringe. After bubbling for 30min, 2,2-Azobis(2-Methylpropionitrile) (AIBN) was added into the solution. The polymerization was conducted at 70 ℃ for 8 h under argon atmosphere. After cooling to room temperature, precipitation in n-hexane and dissolution in ethyl acetate were repeated for five times to remove the unreacted monomers.

Characterization

An Advance HD 400 MHz spectrometer (Bruker) was used to obtain the ^{1}H NMR spectra, CD3OD (δ (1H) = 3.11ppm) was used as the solvent. Methanol solution with different contents of TLM were prepared to obtain the standard curve, and the content of TLM in p(BA-AM-TLM)-10 was determined by UV-3600. The molecular weights of the copolymers were measured by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as a standard sample. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q1000 with the temperature range of -70℃-70℃, heating/cooling rate of 10 °C/min. The stress-strain curves were recorded by an Instron 5967 tensile tester with a 500 N load cell and a strain rate of 8.33 mm s^{-1} under room temperature. Rheological measurements were conducted on an MCR302 rheometer with 25 mm aluminum plates. Oscillatory frequency sweep tests were performed at a range of 0.1-100 rad/s with 1% strain measured at 25℃. The fluorescent spectra were recorded with a fluoroMax-4 spectrometer at the excitation wavelength of 488 nm under room temperature.

The self-healing efficiency can be evaluated in terms of the recovered tensile strength and the original tensile strength, The healing efficiency is defined as follows:

$$Healing\ Efficiecny = \frac{\sigma_{recovered}}{\sigma_{original}}$$

Confocal laser scanning microscope (CLSM)

CLSM images were taken by Zeiss LSM 710 with a 50× objective. The excitation wavelength was 488 nm, and the emission wavelength was received at a range of 580-650 nm. A p(BA-AM-TLM)-10 film was cut into two halves using a razor blade, and

the photos focusing on the cut surfaces were taken every hour.A fresh scratch was created on the surface of p(BA-AM-TLM)-10 film, and the photos of the scratch healing process was taken every 30 minutes. All images of this experiment were captured under the same conditions in terms of objective amplification (x50), gain limit(600), and ambient temperature (25℃). Image softmare was used to obtain the fluorescence intensity evolution plot of the centre line of the CLSM photos from 0 h to 5 h. The images of three-dimensional curves were acquired through the matlab mesh function.

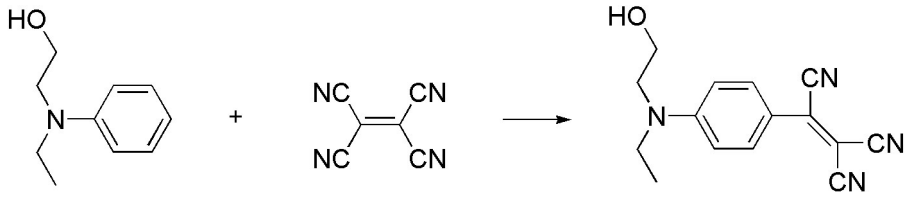


Figure S1. The synthesis of TC1

Table S1. The GPC characterization data for p(BA-AM)-x

Sample	Mn (g mol^{-1})	PDI
p(BA-AM)-10	285246	1.76
P(BA-AM)-15	314619	1.59
P(BA-AM)-20	178358	1.53

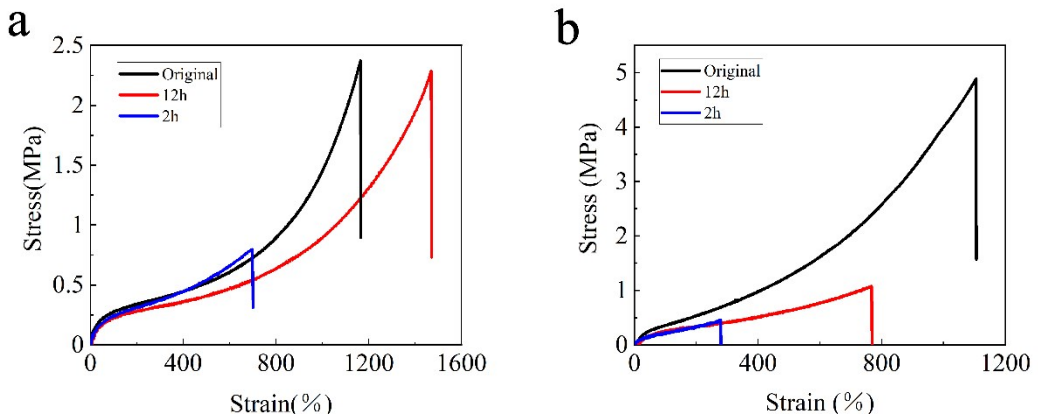


Figure S2. Stress-strain curves of the original, 2h, 12h-healed (a) p(BA-AM)-15 and (b) p(BA-AM)-20.

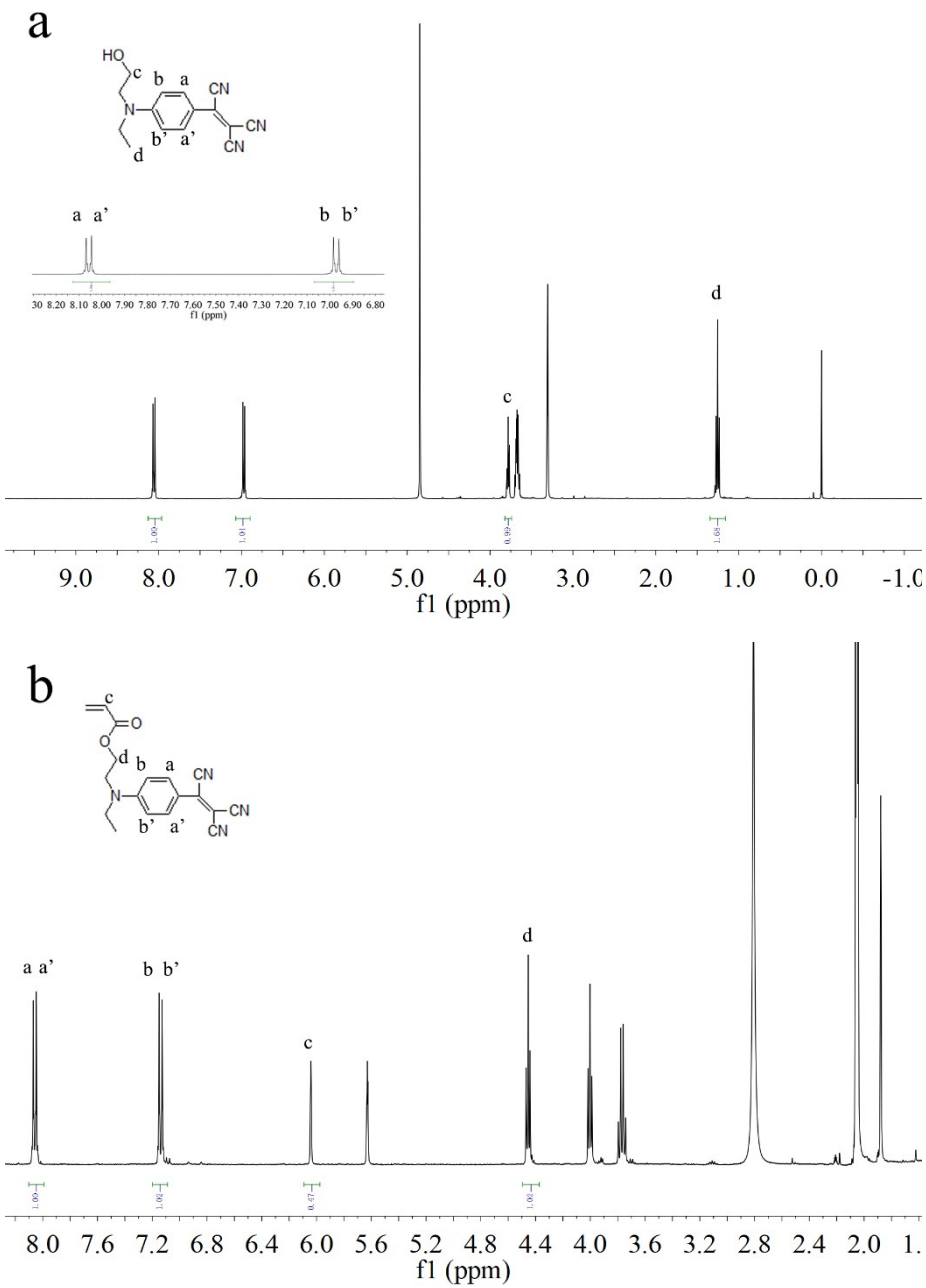


Figure S3. [1]HNMR Spectra of (a) TC1 and (b) TLM. CD3OD (δ (1H) = 3.11ppm) was used as the solvent.

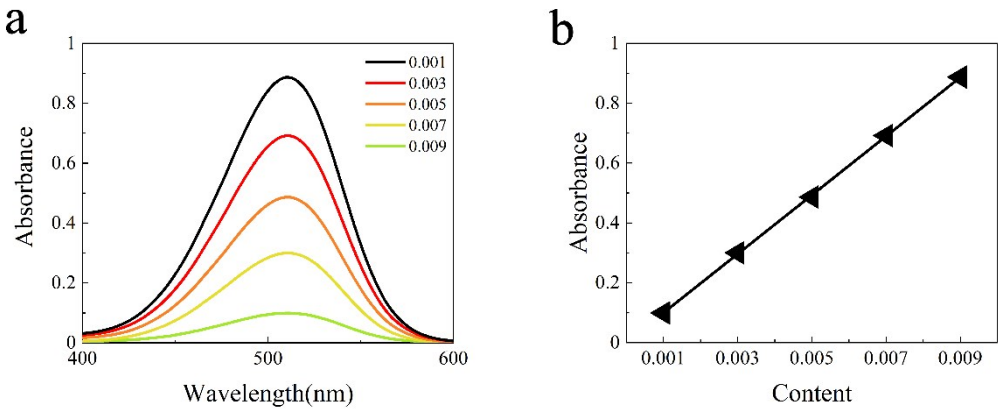


Figure S4. (a) UV-vis absorption spectrum of BA-AM-10 with gradient TLM contents (wt%); (b) TLM contents dependence of absorbance.

The stress-strain curves show that the stress-strain curves of p(BA-AM-TLM)-10 with TLM concentrations from 0.028wt% to 0.112wt % are close to each other (Figure S5a), and the small difference can be attributed to experimental error and different batches of materials. With increasing TLM content, the mechanical poperties does not show a systematic increase, indicating that the low content of TLM does not change the mechanical properties. Moreover, and DSC curves show that the mechanical and thermal properties glass transition temperatures are basically the same for p(BA-AM-TLM)-10 with different TLM concentrations (Figure S5b).

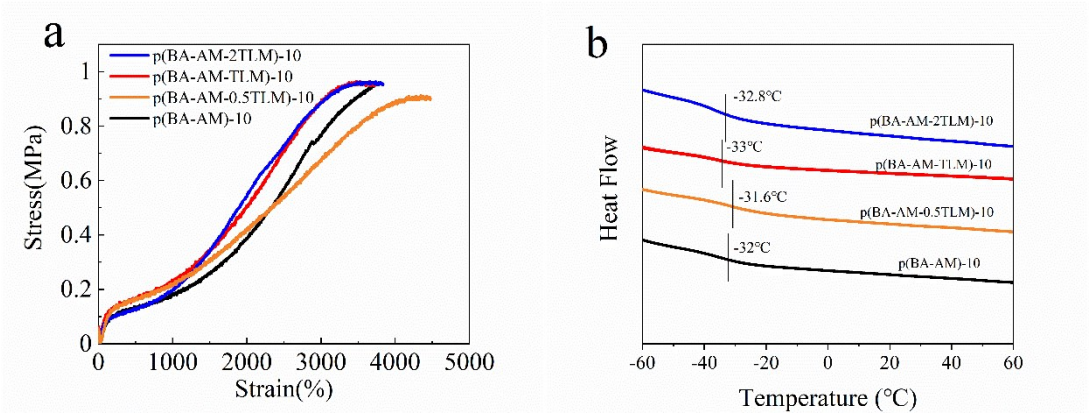
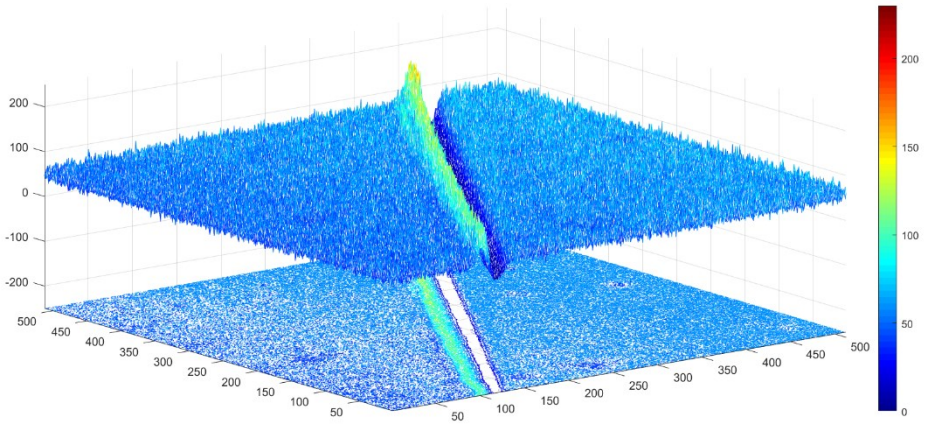


Figure S5. (a) Sress-strain curves of p(BA-AM)-10 with different TLM contents; (b) DSC curves of p(BA-AM)-10 with different TLM contents.

1h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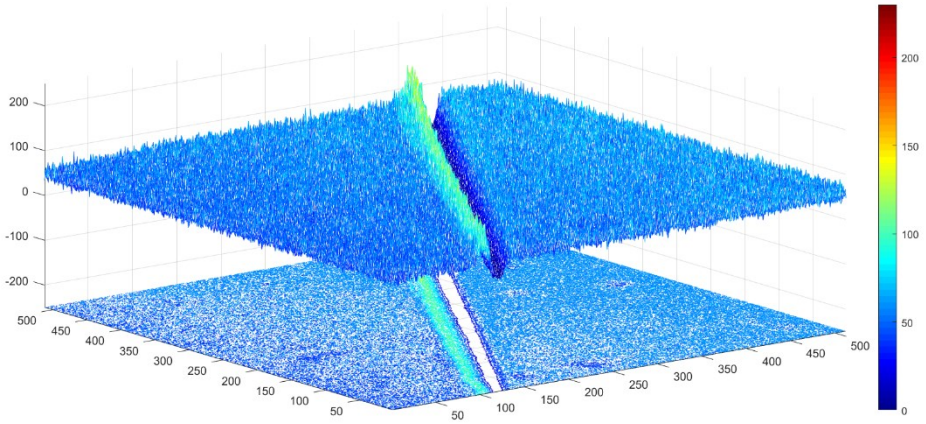
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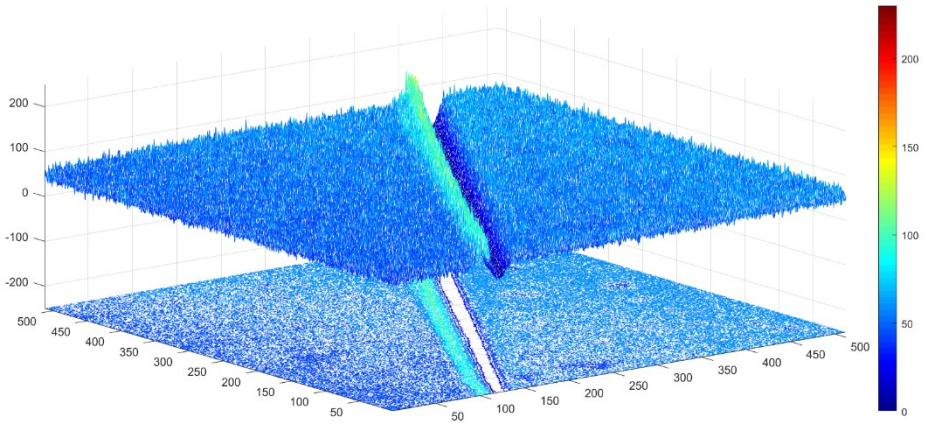
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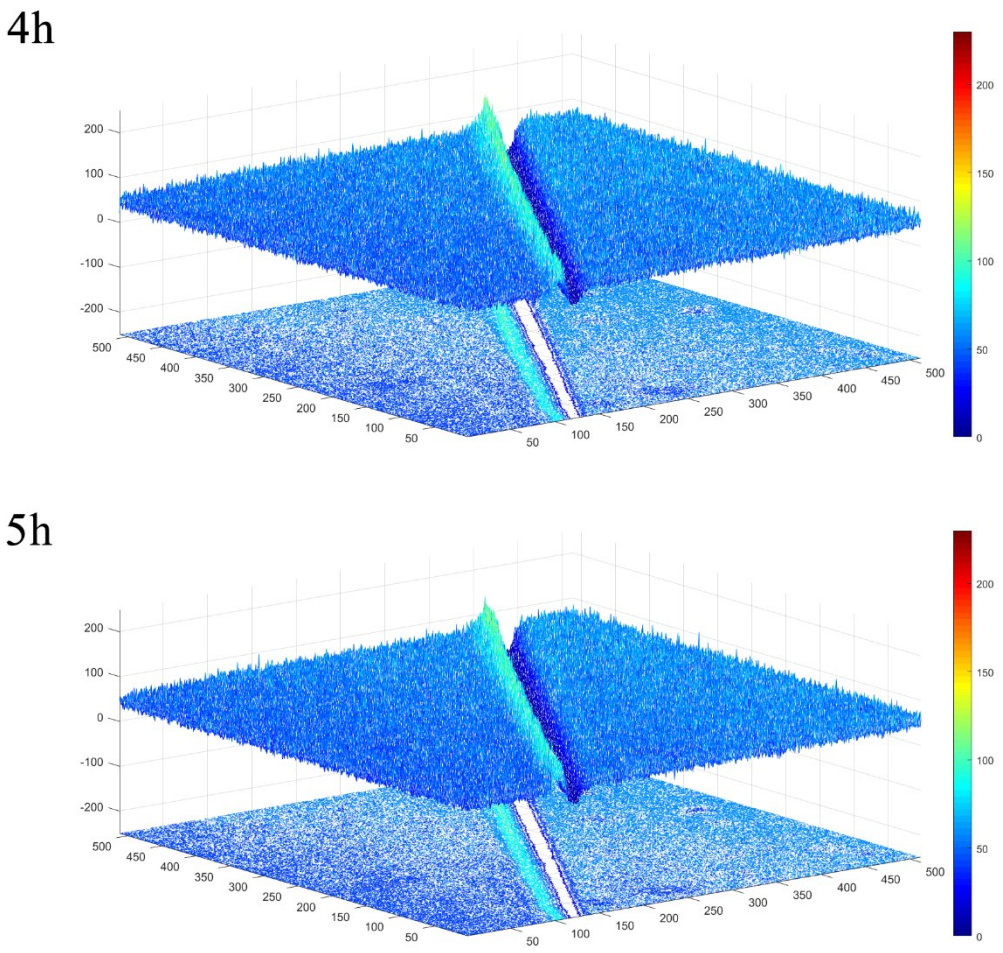

Figure S6. Matlab processed images of the fracture section with different observing times.

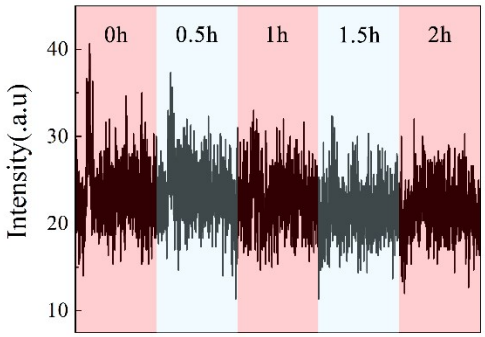

Figure S7. The plot of the fluorescent intensity of the self-healing process at the scratch.

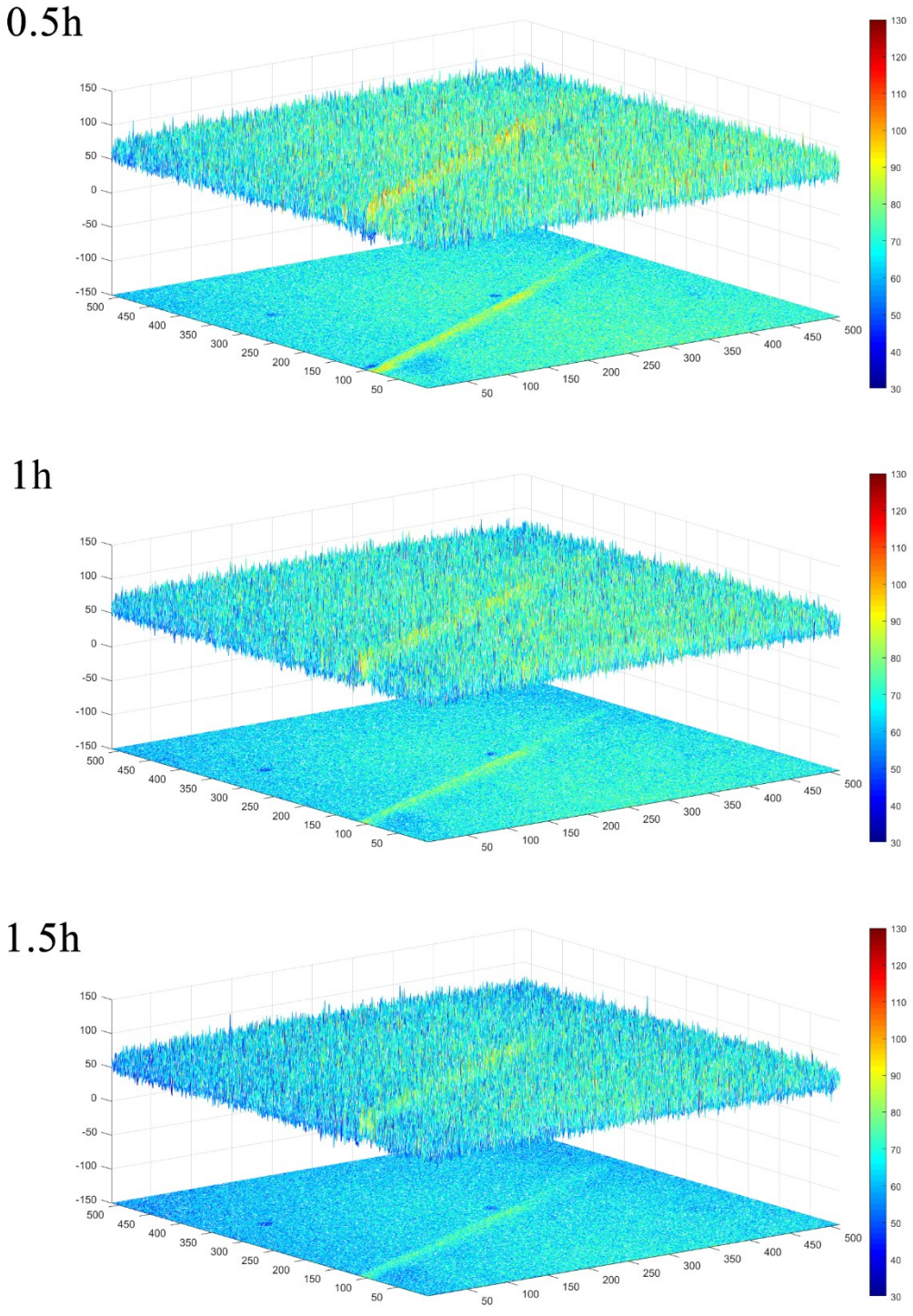

Figure S8. Matlab processed images of the self-healing process with different observing time.

REFERENCES

1 R. Priestley, C. Ellison, L. Broadbelt & J. Torkelson, *Science,* 2005, **309**, 456-459.