

Supporting Information

Ultrafast Fabrication of Lignin Carbon Dots Hydrogels with Self-Mending Properties and Dehydration-Visualizable Phosphorescence for Chemical Sensing and Information Encryption

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Experimental Section

Materials

Alkali lignin was purchased from Aladdin Industrial. FeCl₃, yttrium nitrate, potassium iodide, potassium chloride, cupric chloride, zinc chloride, barium chloride, manganese chloride, potassium bromide, cobaltous nitrate, acrylamide (AM), N,N'-methylene bis(acrylamide) (MBA), ammonium persulfate (APS) were purchased from Macklin Industrial. All the chemicals were analytically pure grade and used as received without further purification.

Synthesis of lignin-based CDs (L-CDs). The synthesis of CDs-g followed the method reported elsewhere with modifications.¹ Alkali lignin (0.3 g) was dissolved in deionized water (30 ml), then 4-aminobenzenesulfonic acid (0.3 g) was mixed with vigorous stirring to form a mixed solution. After stirring for 5 min, the mixed solution was transferred to a polytetrafluoroethylene hydrothermal reactor and heated at 180 °C for 12 h. All the above reaction solutions were cooled to room temperature naturally, and filtered (using a water phase needle filter with a hole diameter of 0.22 μm), and dialyzed for 24 h (using a dialysis bag with a molecular weight of 500). Finally, freeze-dried to obtain the powder sample for further use.

Preparation of L-CDs-Fe Precursor. Briefly, L-CDs (2 ml) and a prescribed amount of FeCl₃ were added to a 30 ml beaker with ultrasonic treatment for 15 min. Finally, the precursor solution was obtained.

Preparation of L-CDs-Fe/PAM Hydrogels. L-CDs-Fe/PAM hydrogels were prepared via a one-pot process at ambient temperature without the assistance of external

stimuli. First of all, prescribed amounts of AM, MBA, APS, and deionized water were added into a 50 ml beaker to obtain a transparent precursor solution, which was followed by magnetic stirring for 60 min at room temperature until all the chemicals were completely dissolved. After that, the L-CDs-Fe precursor was added into the mixture solution and stirred for 10 s to obtain a homogeneous mixture. Finally, the mixture was poured into PTFE molds at ambient temperature to collect the L-CDs-Fe/PAM hydrogels. The detailed compositions of L-CDs-Fe/PAM hydrogels are shown in Table S1.

Characterization. High-resolution transmission electron microscopy (HRTEM) images were carried out on a JEOL-2010 electron microscope. The scanning electron microscopy (SEM) images were measured using a field-emission scanning electron microscope (FE-SEM, FEI Verios-460). UV-vis absorption spectrum was taken on a Shimadzu UV-2550 ultraviolet–visible spectrophotometer. The X-ray photoelectron spectroscopy (XPS) experiments were characterized using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatic Al Ka X-ray source. The infrared spectrum was recorded by a Nicolet Avatar 360 Fourier transform-infrared spectroscopy (FTIR). PL spectra and time-resolved decay curves were measured on a fluorescence spectrophotometer (F-7000 Hitachi) equipped with a 150 W Xenon lamp as the excitation source. Temperature dependent PL emission spectrum, afterglow emission spectrum, and afterglow decay curves were conducted by combining a heating apparatus (Oxford Instruments) with the same Hitachi F-7000 fluorescence spectrophotometer. Phosphorescence quantum yield was measured by a Hamamatsu

absolute PL quantum yield measurement system. The mechanical properties were carried out using a Shenzhen Suntest (UTM4204) mechanical tester with a 200 N load cell. The hydrogels were molded into cylindrical specimens (diameter = 20 mm and height = 8 mm) for compression tests and samples with the dimensions $35 \times 6 \times 2$ mm for tensile tests. The compression and tensile tests were carried out at a speed of 10 mm/min. The results of the compression and tensile tests were based on the average of five measurements. Cyclic Voltammetry analysis were carried out to monitor the redox reactions in the materials. The materials of L-CDs-Fe/PAM hydrogels were used as the working electrode, Ag/AgCl (KCl sat.) was the reference electrode, and Pt was the counter electrode. An aqueous solution of AM and APS was used as the electrolyte solution. The CV measurements were carried out at 5 mV s^{-1} between 0.1 and 1.1 V versus Ag/ AgCl (Figure S3).

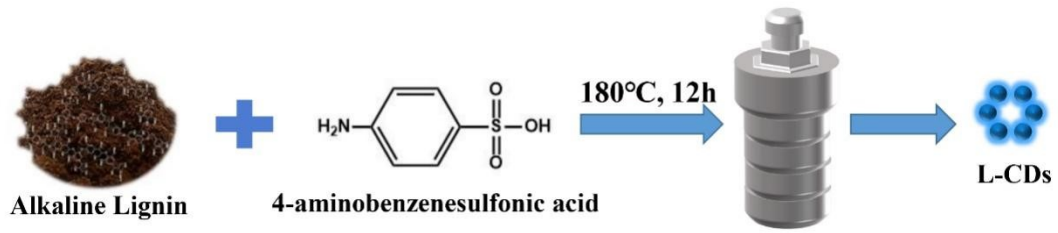


Figure S1. Schematic illustration for the formation procedure of L-CDs.

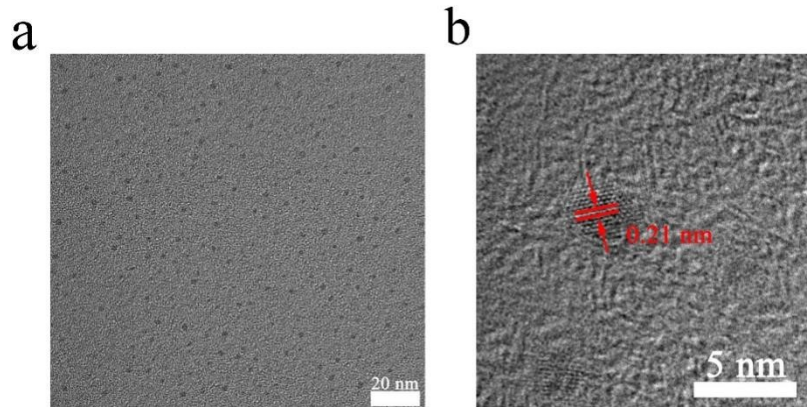


Figure S2. (a) HR-TEM images of L-CDs. (b) HR-TEM lattice fringe image of L-CDs.

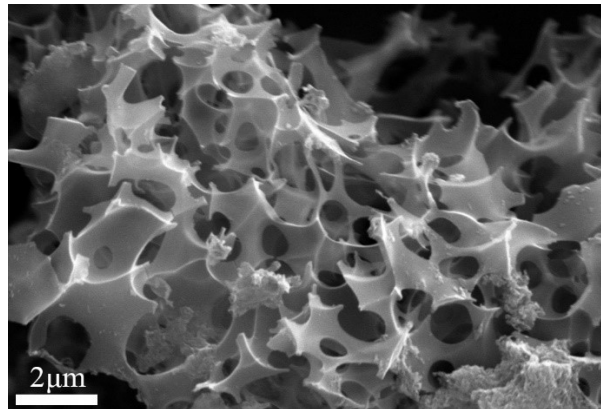


Figure S3. SEM image of the inner section of L-CDs-Fe/PAM hydrogels

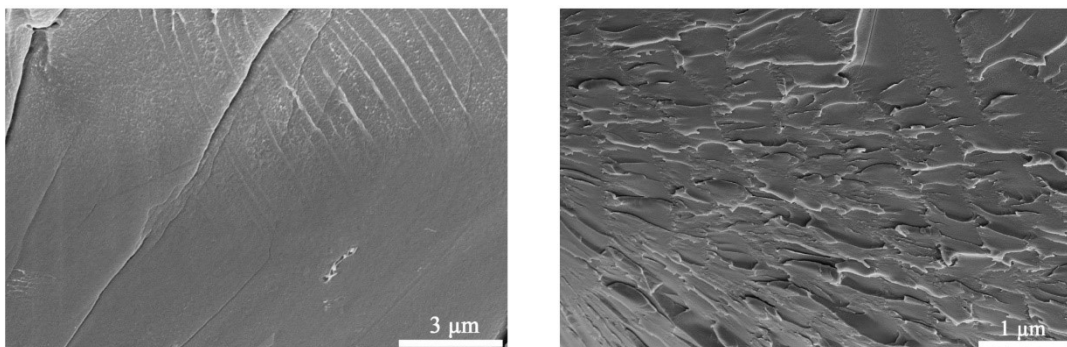


Figure S4. SEM images of the freeze-dried PAM hydrogels.

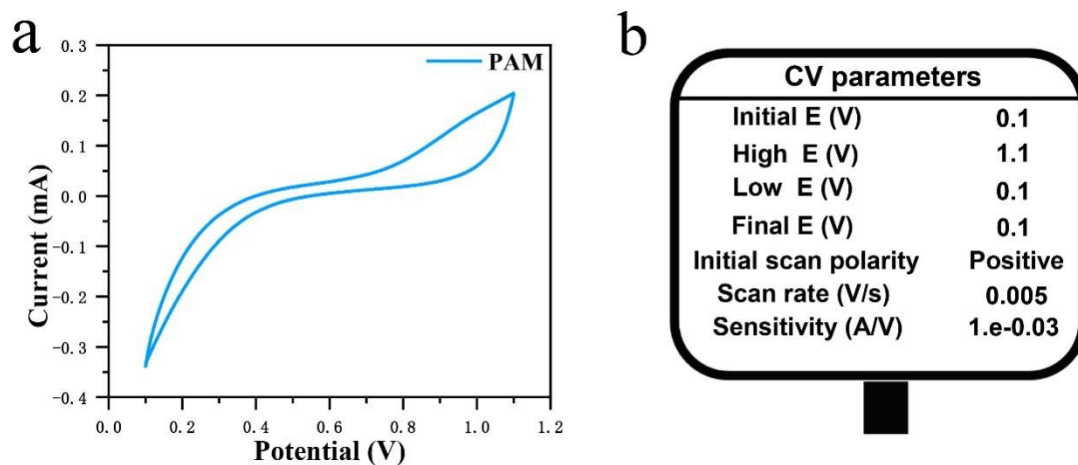


Figure S5. (a) CV investigation of the PAA with the materials as the working electrodes in a PAM/APS solution over one cycle. (b) The parameters used for the electrochemical cell in cyclic voltammetry (CV) experiments.

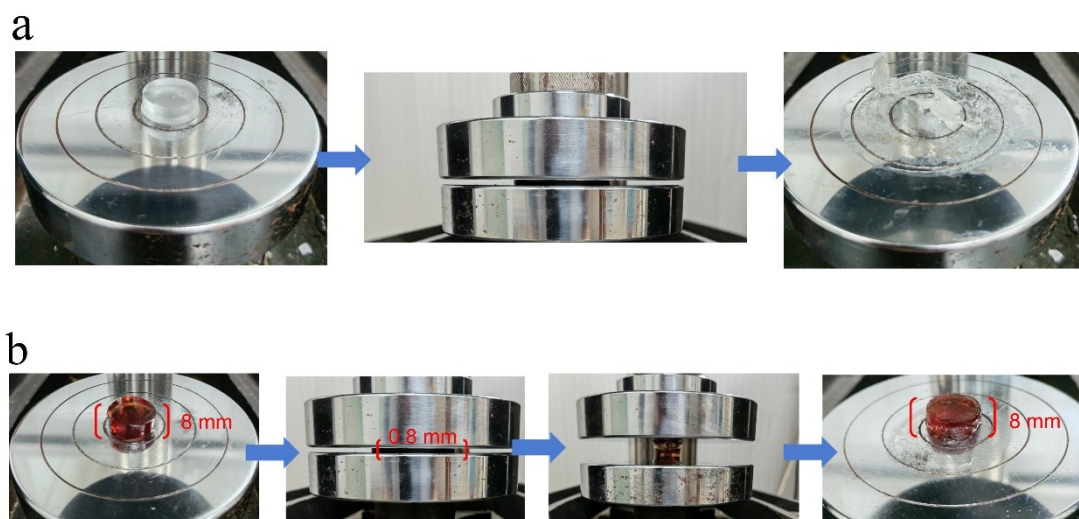


Figure S6. (a) The PAM hydrogel was destroyed by compression. (b) The lignin L-CDs-Fe-8/PAM hydrogel compressed to 90% of its height and immediately recovered.

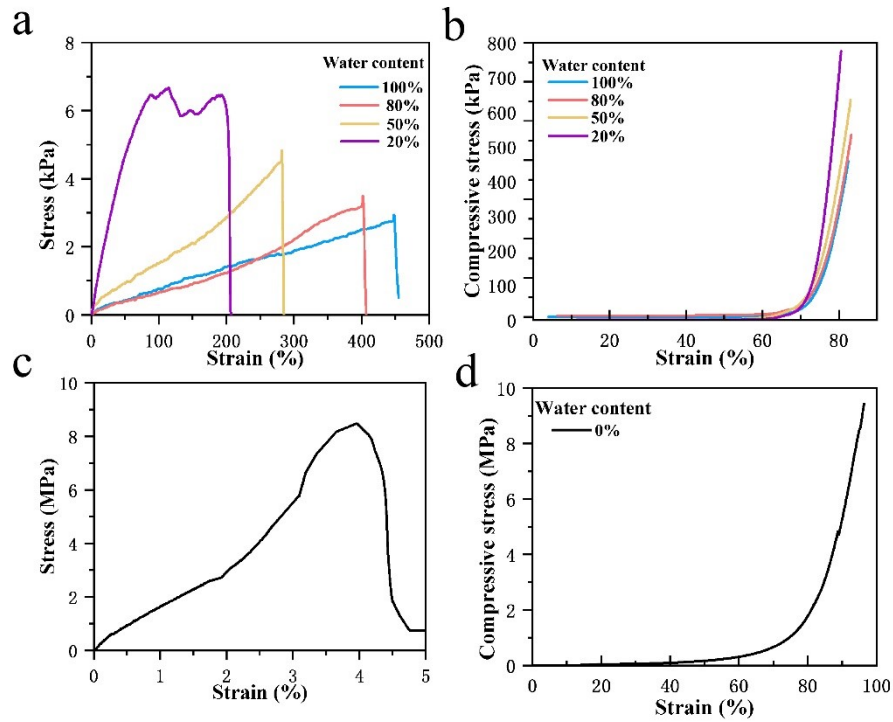


Figure. S7. (a) Tensile and (b) compressive stress-strain curves of the L-CDs-Fe-8/PAM hydrogel at different water retention rates. (c) Tensile and (d) compressive stress-strain curves of the dehydrated L-CDs-Fe-8/PAM hydrogel (water content: 0%).

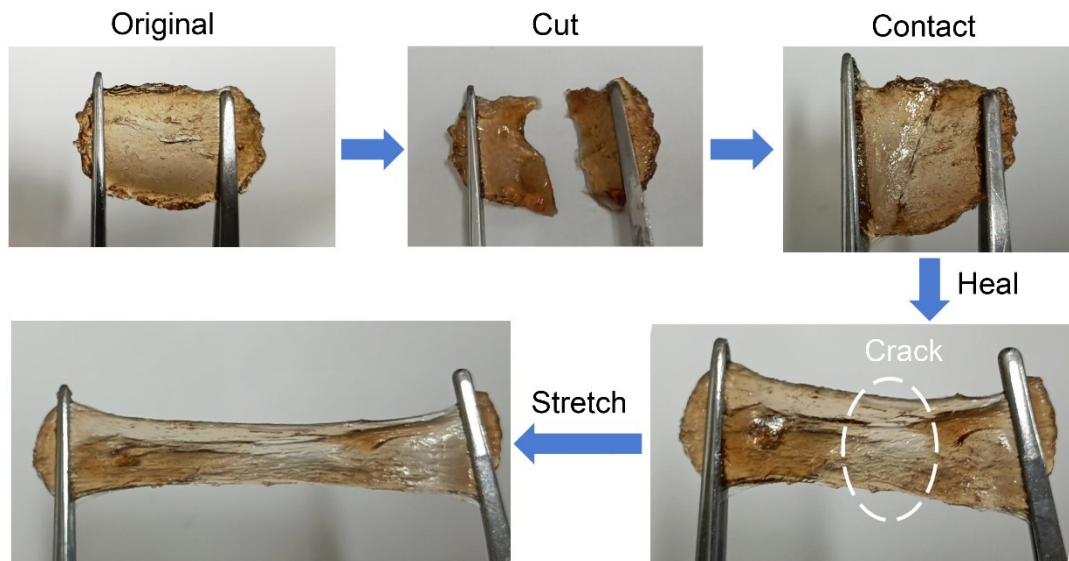


Figure. S8. Photographs of macroscopic self-healing performance of the L-CDs-Fe-10/PAM hydrogel.

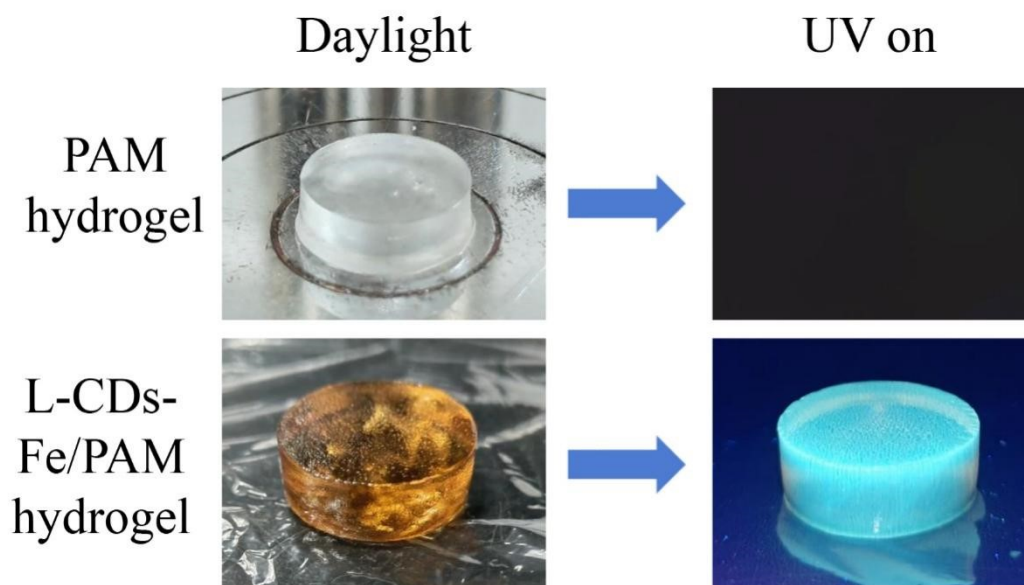


Figure S9. Photographs of the PAM and the L-CDs-Fe/PAM hydrogels under sunlight and excited with 365 nm UV lamp.

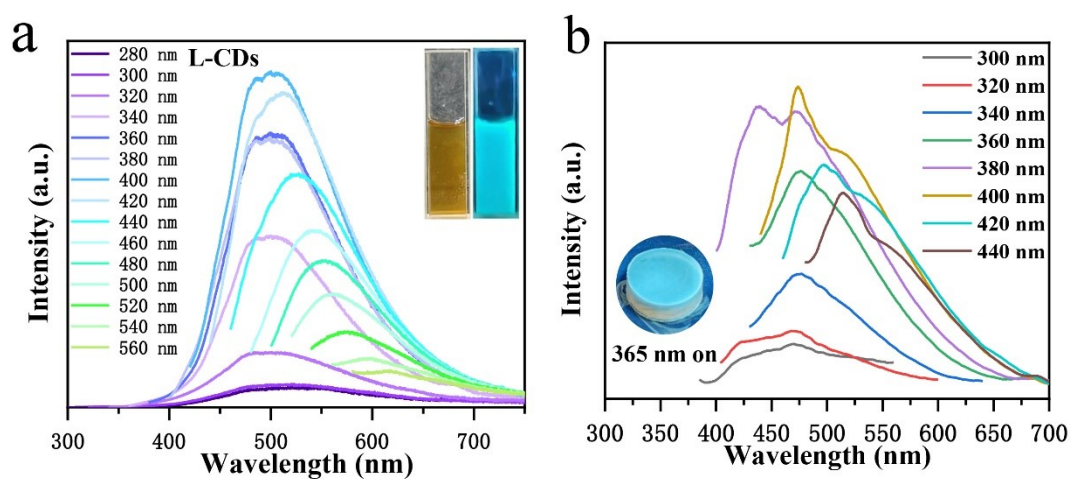


Figure S10. (a) Fluorescence emission spectra with different excitation wavelengths of aqueous L-CDs (inset: photographs were taken under daylight and UV light). (b) Fluorescence emission spectra with different excitation wavelengths of L-CDs-Fe/PAM hydrogel (inset: photographs were taken under UV light).

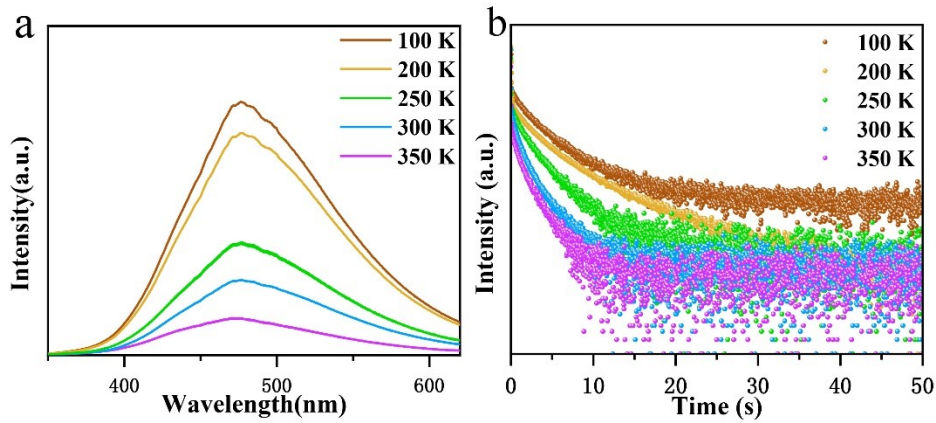


Figure S11. (a) Phosphorescence emission spectra of dehydrated hydrogel at different temperatures. (b) Phosphorescence decay curves of dehydrated hydrogel at different temperatures.

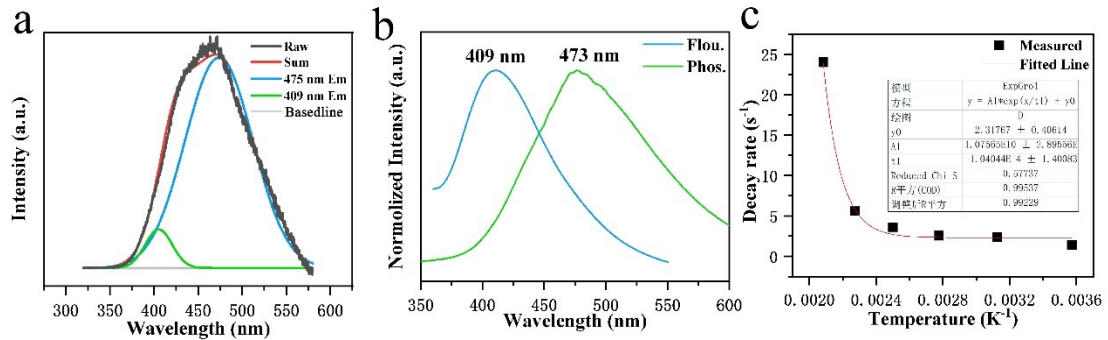


Figure S12. (a) Gaussian fittings of the phosphorescence emission spectra of dehydrated hydrogel under excitation of 337 nm. (b) The low temperature (77K) fluorescence and phosphorescence spectra of dehydrated hydrogel. (c) Afterglow decay rates of dehydrated hydrogel as a function of temperature and fitting curve.

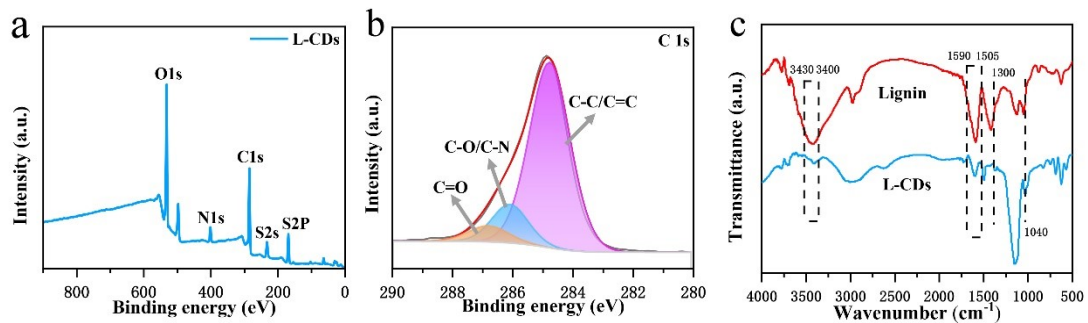


Figure S13. (a) XPS spectra of full scan of L-CDs. (b) High-resolution C 1s of L-CDs. (c) FTIR spectra of lignin and L-CDs.

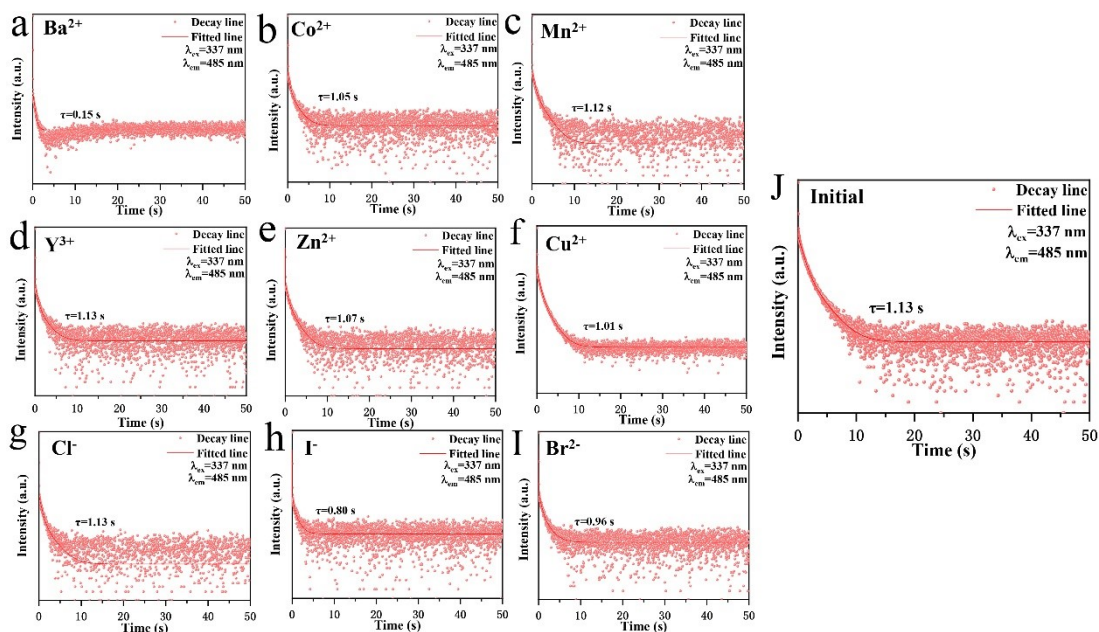


Figure S14. The phosphorescence decay curves of dehydrated hydrogel treated by (a) Ba^{2+} , (b) Co^{2+} , (c) Mn^{2+} , (d) Y^{3+} , (e) Zn^{2+} , (f) Cu^{2+} , (g) Cl^- , (h) I^- , and (i) Br^{2-} . (j) The phosphorescence decay curves of untreated dehydrated hydrogel.

Table S1

Sample	AM (g)	APS (mg)	MBA (mg)	L-CDs (ml)	FeCl_3 (mg)	H_2O (ml)
PAM	3	30	6	0	0	8
L-CDs-Fe-4/PAM	3	30	6	2	4	6
L-CDs-Fe-8/PAM	3	30	6	2	8	6
L-CDs-Fe-10/PAM	3	30	6	2	10	6

Table S2 Dehydrated hydrogel treated by different ions and the corresponding

phosphorescence lifetimes ($\lambda_{\text{ex}} = 337 \text{ nm}$, $\lambda_{\text{em}} = 485 \text{ nm}$).

Sample	τ_{avg} (s)
L-CDs-Fe-4/PAM + Ba ²⁺	0.15
L-CDs-Fe-4/PAM + Co ²⁺	1.05
L-CDs-Fe-4/PAM + Mn ²⁺	1.12
L-CDs-Fe-4/PAM + Y ³⁺	1.13
L-CDs-Fe-4/PAM + Zn ²⁺	1.07
L-CDs-Fe-4/PAM + Cu ²⁺	1.01
L-CDs-Fe-4/PAM + Cl ⁻	1.13
L-CDs-Fe-4/PAM + I ⁻	0.80
L-CDs-Fe-4/PAM + Br ⁻	0.96
L-CDs-Fe-4/PAM	1.13

Reference

- 1 L. Zhu, D. Shen, Q. Wang and K. H. Luo, *ACS Appl Mater Interfaces*, 2021, **13**, 56465-56475.