Supplementary Information (SI) for Journal of Materials Chemistry C.

Light-induced color changing of redox dyes assisted by photoinitiator for information encryption hydrogel paper

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Supporting Information

Figure S1 The image of the colors of DMPA/MB solution with a molar ratio of 5:1 at different exposure time.

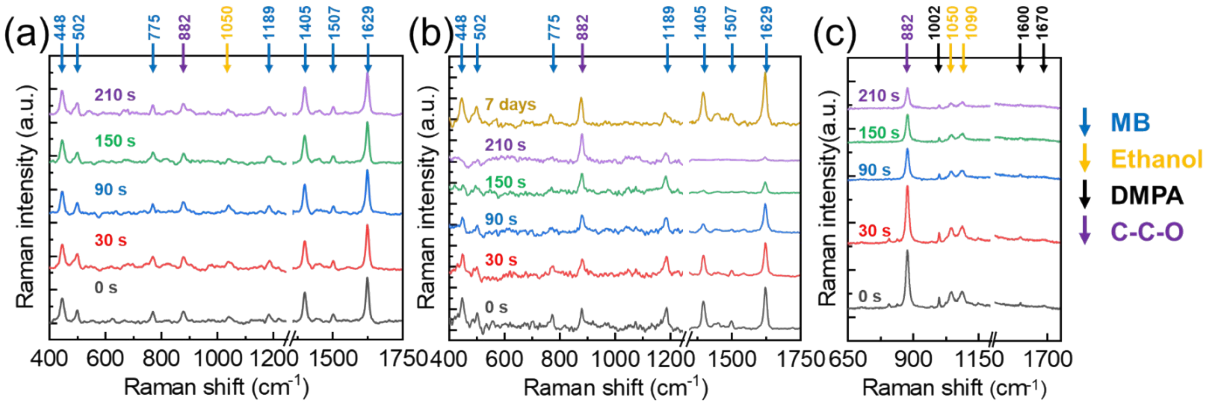

Figure S2 Raman spectra of (a) MB, (b) DMPA/MB and (c) DMPA solution before and after UV exposure.

The Raman spectra of MB and DMPA before and after UV exposure is investigated in **Figure S2**. The characteristic peaks corresponding to different materials are marked and distinguished by different colors, which are consistent with those in Figure 1 of the manuscript. It is observed that the spectra of MB solution does not show significant changes before and after UV exposure for 210 s as shown in Figure S2a. However, for the scenario of DMPA/MB solution, obvious changes in the intensity of the characteristic peaks of MB are observed as the UV exposure time increases. Notably, the peaks at 448, 502, 1405, and 1629 cm^{-1} significantly decreases, which indicates MB is substantially bleached. Additionally, in Figure S2b, the intensity reduction at 775, 1189, and 1507 cm^{-1} further supports this deduction. In Figure S2c, for DMPA solution, the peak near 1002, 1600 and 1670 cm^{-1} is typically attributed to the symmetric breathing mode of the aromatic ring (C–C vibrations), the stretching vibrations of C=C and C=O. The decreasing in the intensity of these peaks represent the cleavage of DMPA. Under UV irradiation, the decreasing in the peaks near 882, 1050, and 1090 cm^{-1} may be attributed to the consumption of ethanol during the photolytic cleavage of DMPA.

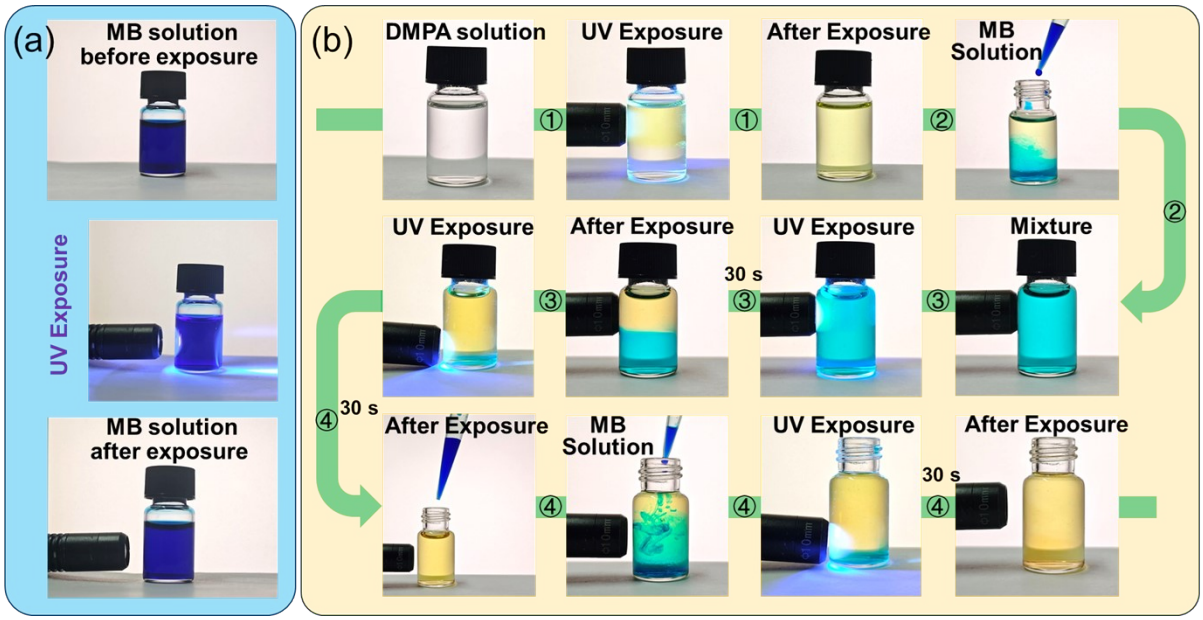

Figure S3 The color changing of (a) MB and (b) DMPA solution before and after UV exposure for 30 s.

To further explore visually the mechanism of MB bleaching, we conduct experiments on MB and DMPA solution under UV irradiation. Unless otherwise specified, the solvents are carried out as 60% ethanol and 40% deionized water (DIW) throughout this work. The results show that MB solution does not undergo color changing upon UV exposure, as shown in Figure S3a. However, for the process ① in Figure S3b, it is observed that DMPA solution turns from colorless to a faint yellow after UV exposure due to chromophores structures produced by the cleavage of DMPA. Subsequently, for the process ②, we add the MB solution into the DMPA solution under stirring to ensure thorough mixing, but observed no significant bleaching. Yet, for the process ③, upon applying UV exposure, the solution bleached completely within 30 s. These observations indicate that the bleaching of MB results from the products of DMPA during the UV exposure, such as free radicals yielding from the cleavage of DMPA, rather than from the final products of DMPA after the UV exposure. Such phenomenon is reproducible under the same conditions, and consistent results can be obtained, as shown in process ④.

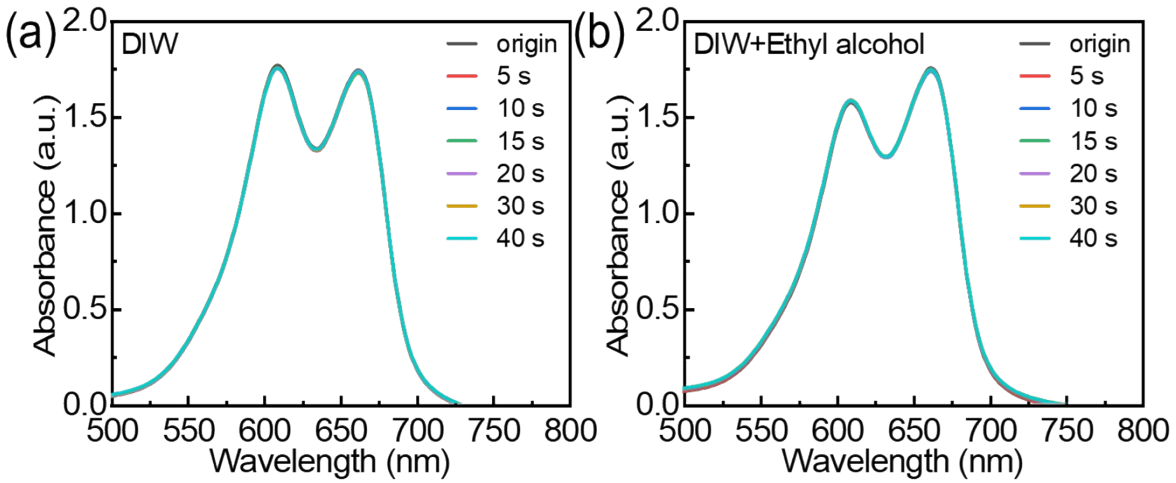

Figure S4 The relationships between the absorbance spectra and exposure time for the MB in two different solvents: (a) DIW and (b) DIW/ethanol mixture. Although ethanol has a weak reducibility, it rarely effects on the absorbance of MB through UV exposure, i.e., the ethanol is not able to accelerate the color changing of MB.

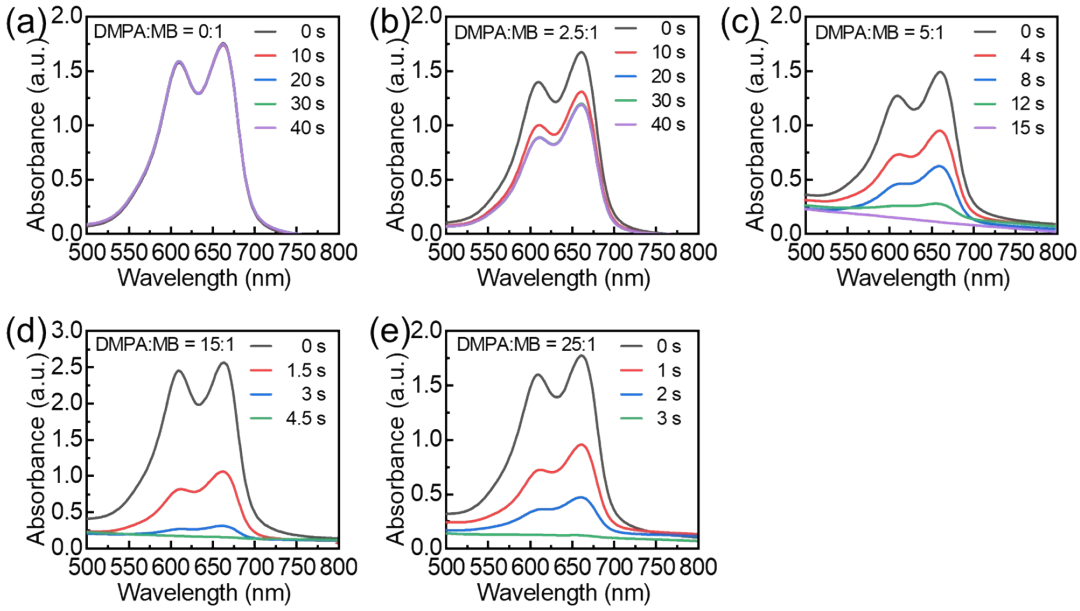

Figure S5 (a)~ (e) The effect of different exposure intensities on the decolorization rate of DMPA/MB solution with a molar ratio of 15:1. This indicates that a higher UV exposure intensity results in a faster decoloration rate of the MB.

The absorbance spectra of MB solutions show two distinct peaks at 663 and 611 nm, as shown in Figure S5a~e, corresponding to MB monomers and dimers[1]. As the UV exposure time increases, the intensity and wavelength of the absorbance spectra remain almost unchanged. However, the DMPA/MB solution with a 2.5:1 molar ratio can be significantly decolorized under UV exposure. The absorbance spectral intensity at 663 nm decreases to 77% of its original value within 30 s. In the next 10 seconds, decolorization ceases due to the depletion of DMPA (Figure S5b). The solutions with higher molar ratio of DMPA and MB are analyzed to studied the effect of DMPA content on decolorization efficiency. Figure S5c~e show the absorbance spectra of DMPA and MB solution systems with molar ratios of 5:1, 15:1, and 25:1 under the same UV exposure conditions. Higher DMPA ratios significantly accelerate the decolorization rate, so that the solution changing from blue to colorless.

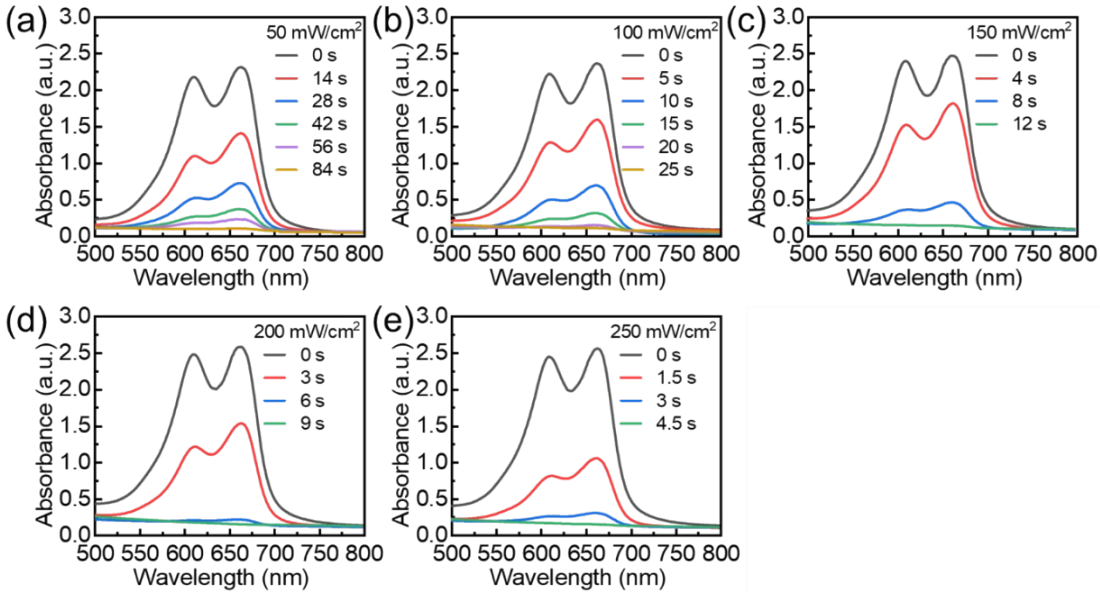

Figure S6 The absorbance spectra of DMPA/MB solution systems with different molar ratios as a function of UV exposure time are shown in (a)~(e), corresponding to molar ratios of 0:1, 2.5:1, 5:1, 15:1, and 25:1, respectively. The intensity of UV exposure is 250 mW/cm^2.

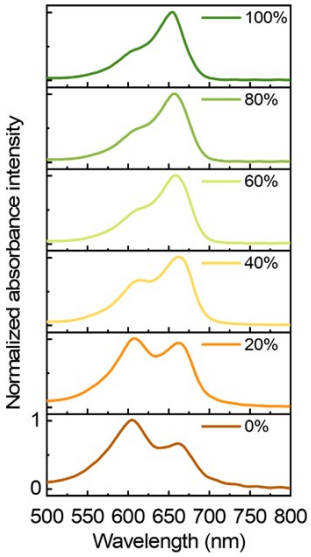

Figure S7 Normalized absorbance spectra of the MB solutions with varying ethanol contents, where the legend indicates the volume ratio of ethanol in the solutions.

The absorbance of the dimer and monomer in the MB solution is influenced by ethanol content in the solvent, which can be observed through the normalized absorbance spectra in Figure S7. A higher ethanol ratio decreases the absorbance of the dimers, which suggests that ethanol may inhibit the formation of the dimers.

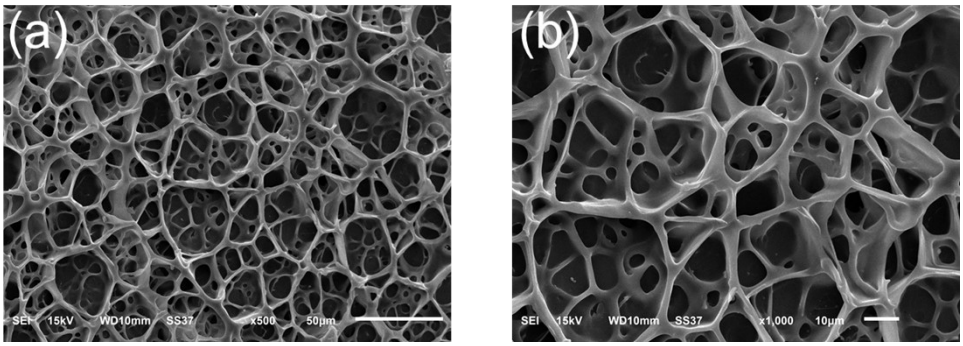

Figure S8 SEM images of macrospore network structure of the hydrogel film with different magnifications. The ability of the hydrogel to retain the DMPA/MB solution can be attributed to its intrinsic three-dimensional network structure.

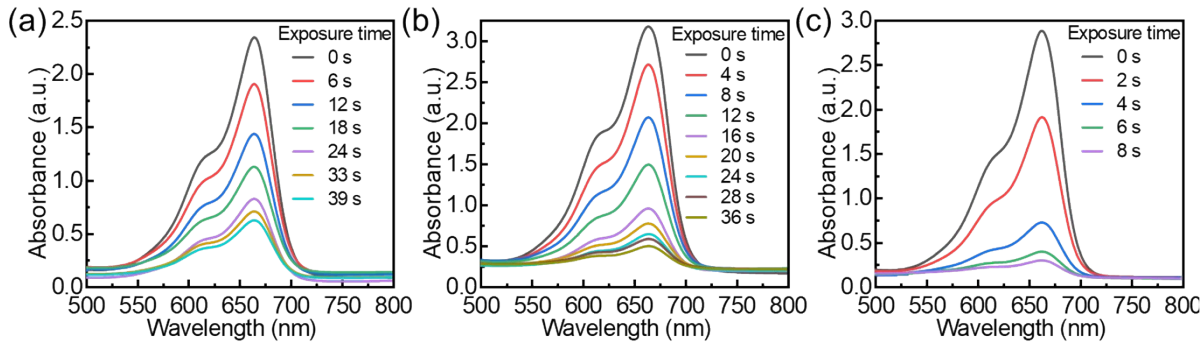

Figure S9 The absorbance spectra of hydrogels immersed in DMPA/MB solutions with different molar ratios of (a) 5:1, (b) 15:1, and (c) 25:1 with varying UV exposure time. The intensity of UV exposure is 250 mW/cm^2.

The decolorization rate of hydrogel film immersed in DMPA/MB solutions with different concentrations are investigated. At the DMPA/MB solution with molar ratio of 5:1, it takes 39 s to decolorize to only 80% of its original absorbance. The decolorization process of hydrogel film immersed in solutions with lower ratios (5:1 and 15:1), as shown in Figure S9a and b, will be early ceased or slow down due to the lack of DMPA. However, when the molar ratio is up to 25:1, as shown in Figure S9c the hydrogel film fully decolorizes in just 8 s. Meanwhile, the absorbance spectrum of the dimer in hydrogel film shows a significantly lower relative intensity corresponding to the dimer compared to the DMPA/MB solution. This may be due to the porous structure of the hydrogel, which reduces the frequency of molecular collisions, thereby affecting the formation and stability of aggregates[2].

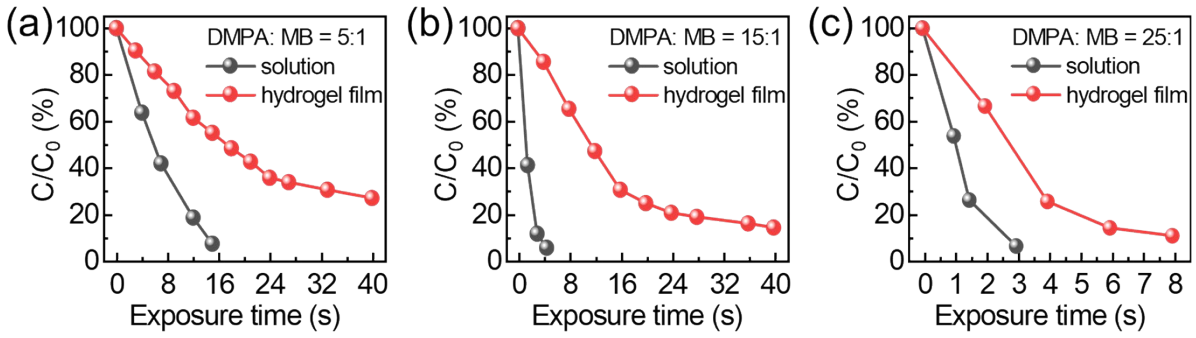

Figure S10 Comparison of the decolorization rates under the same UV exposure intensity of 250 mW/cm^2 for DMPA/MB solutions with different molar ratios and the hydrogel films immersed in these solutions.

It is noteworthy that there is a significant difference in the decolorization rate between the DMPA/MB solution and the DMPA/MB inked hydrogel films. The decolorization rate in DMPA/MB solutions are obviously faster than the one in the hydrogel films. It is due to the mobility being restricted of MB and DMPA molecules in the solid state, compared to their migration rate in solutions, that accounts for this observation [3]. However, the decolorization process still reach a time as fast as 8 s in the hydrogel film.

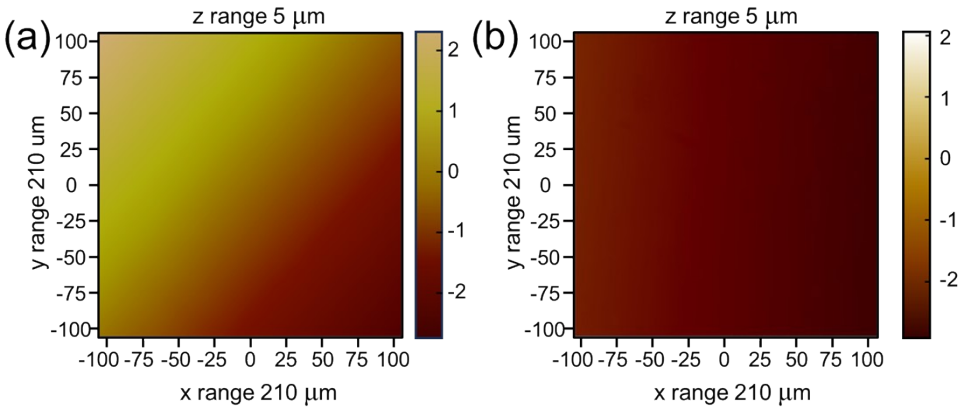

Figure S11 Characterization of the surface smoothness of the prepared hydrogel film before (a) and after (b) immersing in the DMPA/MB solution. The results illustrate an excellent flatness can be obtained before and after immersing in the DMPA/MB solution.

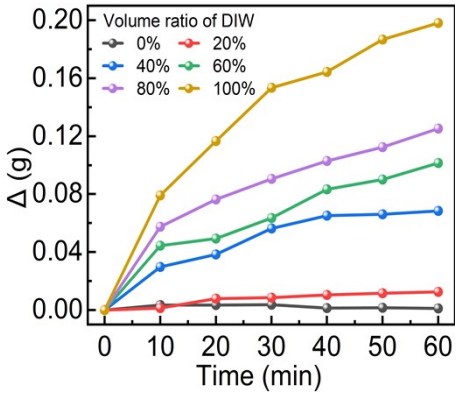

Figure S12 Weight change of the hydrogel films with the same initial mass after immersing in solutions with different volume ratios of DIW and ethanol. The hydrogel films used has dimensions of 25 mm × 25 mm × 0.4 mm.

As the content of DIW increased, the weight change (Δ) of the hydrogel films with same shape and size due to more significant absorption of DIW. However, an excessively high proportion of DIW results in a minimal amount of DMPA being dissolved in the solvent due to DMPA is not able to be dissolve in DIW, while a higher proportion of ethanol significantly decelerates the absorption rate of the hydrogel paper. Therefore, a solvent composition of 60% ethanol and 40% DIW is selected to optimize the absorption properties.

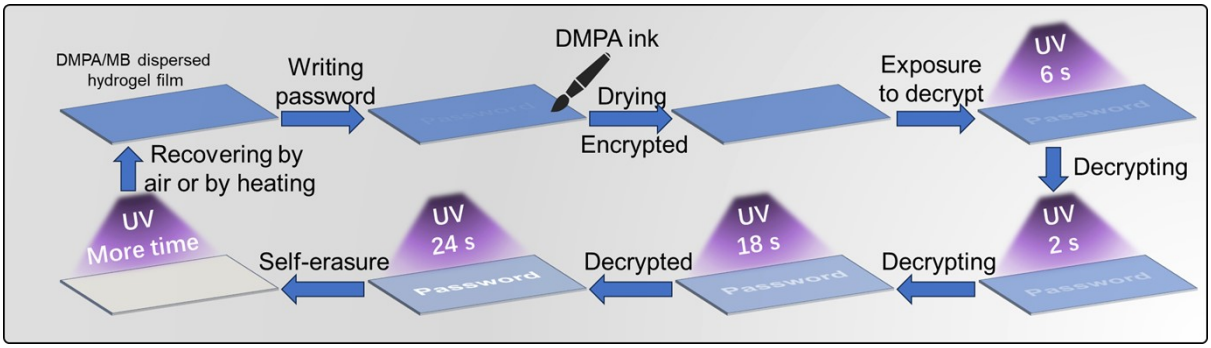

Figure S13 The schematic diagram of transient information encryption/decryption and self-erasure.

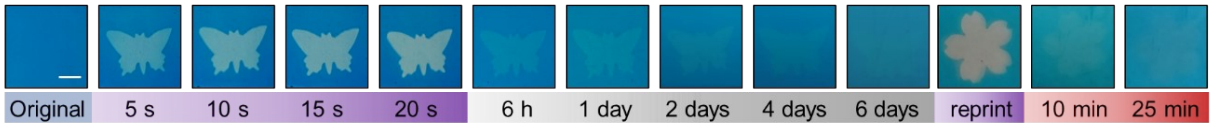

Figure S14 The patterning and rewriting processes of rewritable paper. The butterfly pattern formed by UV exposure for 20 s can be retained in air for up to 6 days. Then, the flower pattern can be rewritten on the paper and rapidly erased by heating for 25 min. The scale bar is 5 mm.

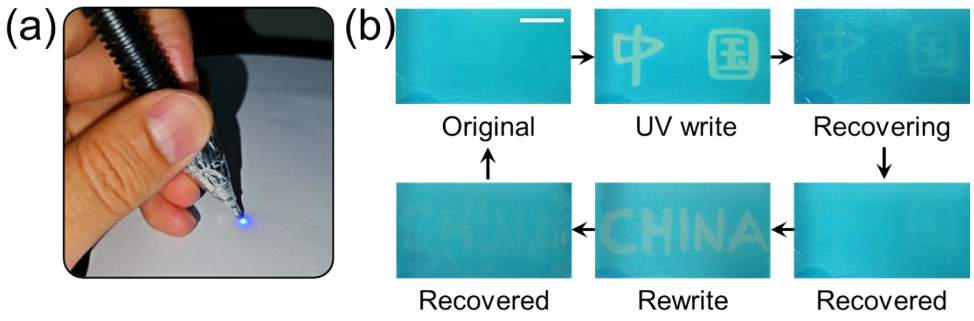

Figure S15 (a) The photograph of the homemade UV laser pen. (b) The experimental results of non-contact freely writing using the UV pen. The scale bar is 5 mm.

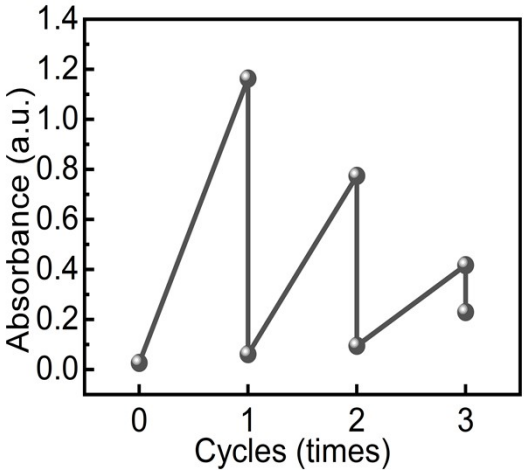

Figure S16 The relationship between the absorbance intensity at 663 nm and the number of cycles of the rewritable paper with single immersion in the DMPA/MB solution. The decreasing in rewritable ability is due to the consumption of DMPA and MB, which can be overcome by repumping the DMPA/MB ink.

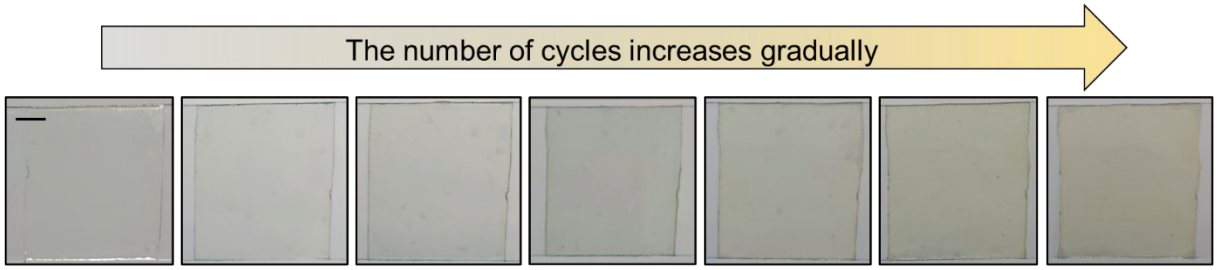

Figure S17 With the increase of the number of cycles, the rewritable paper gradually turns yellow. Scale bar is 5 mm.

With the increase in the number of cycles, the hydrogel film gradually turns yellow; however, there is no structural damage, and the printing capability remains unaffected.

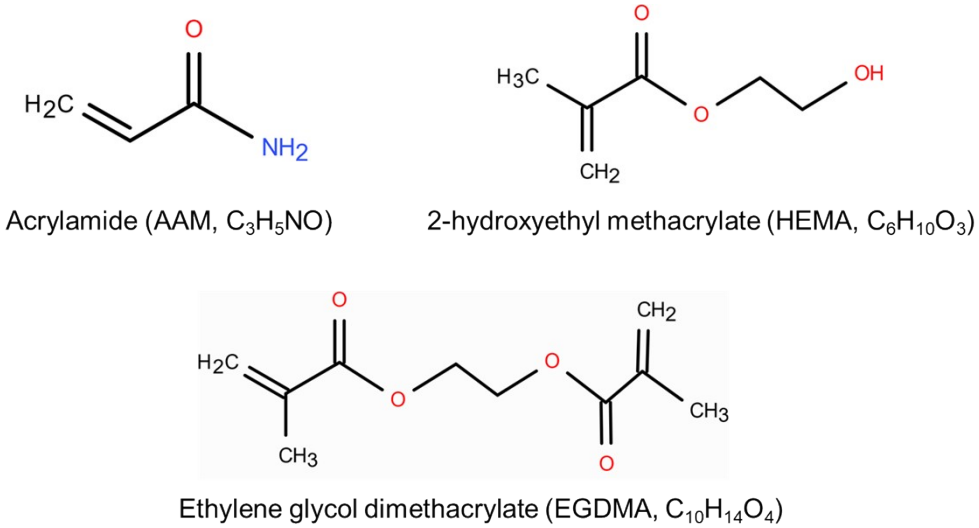

Figure S18 Molecular structures of the monomers and crosslinker used for the hydrogel synthesis.

Reference

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