



Hydrogels Hot Paper

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A Urease-Containing Fluorescent Hydrogel for Transient Information Storage

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Abstract: The improper handling of decrypted information can lead to the leakage of confidential data. Thus, there is increasing interest in the development of self-erasing decrypted data. Herein, we report a urease-containing fluorescent hydrogel for multistage information security protection. Information can be input into the fluorescent hydrogel, which is based on the protonated 4-(*N,N*-dimethylaminoethylene) amino-*N*-allyl-1,8-naphthalimide (DEAN-H⁺) and doped with urease, using metal ions, such as Zn²⁺ that coordinate with DEAN. Upon exposure to urea, urease produces NH₃, which reduces the fluorescence of the hydrogel. In the presence of urea, metal-coordinated hydrogel fluorescence decreases more slowly than the fluorescence of the hydrogel alone, revealing the information. The displayed information is then automatically erased within a few minutes. This work opens up a new insights in designing and fabricating information storage materials.

Introduction

With the booming of information technology, our daily life is inundated with huge amount of data, it is easier for people to get information and to leak confidential information. In recent years, researchers have devoted great effort to exploring modern information storage strategies as well as information storage devices. From monochrome^[1] to polychromatic^[2] and panchromatic,^[3] from rigid substrate^[4] to flexible ones,^[5] from the development of printable ink^[6] to the construction of color-changing or rewritable papers,^[4,7] anti-counterfeiting materials and corresponding technologies, such as security code,^[8] fluorescent recognition,^[9] holographic anti-counterfeiting,^[10] and so on, have obtained unprecedented development.^[11] However, problems, such as secondary information leakage without proper handling, still remain. Therefore, it is urgent to design advanced information storage devices in which the information is destroyed after reading in order to enhance information security.

Smart hydrogels, exhibiting shape morphing or color switching under external stimuli, have shown significant potential applications in various fields, such as soft robotics,^[12] flexible sensors,^[13] camouflage,^[14] and information storage.^[15] Within the unique capacity of responsiveness to certain stimulus, smart hydrogels are one of the promising candidate materials for information storage, and the hidden information can be decrypted under certain circumstances.^[16] He et al.^[17] have reported a hydrogel interferometer that can change its thickness upon exposure to external stimuli, leading to instant color change. Within the capabilities of fast response, high robustness and color uniformity, this hydrogel-based platform was used for controllable information encryption. Recently, Gong and co-workers^[18] have designed an intelligent hydrogel with memorizing–forgetting behaviors, which was based on fast water uptake and slow water release upon exposure to a thermal stimulus. Through the asymmetric swelling/shrinking process as well as the dynamic and learning-strength-dependent turbidity change, this kind of hydrogel can be used as a smart display device. In our previous work, a 3D fluorescent hydrogel based on poly(vinyl alcohol) and perylene-tetracarboxylic-acid-functionalized gelatin was presented and used as anti-counterfeiting platform for multistage data security protection via the combination of Fe³⁺-induced fluorescence quenching, shape memory behavior, and self-healing properties.^[19] These elegant attempts provide new ideas for the development of hydrogel-based information storage materials. Nevertheless, if the information carrier is not destroyed immediately after displaying the information, the confidential information may still be leaked afterwards. Thus, it is highly desired but quite challenging to develop anti-counterfeiting platforms with self-erasure function.

Herein, a urease-containing fluorescent hydrogel is presented as an information storage material that self-destructs after decryption in response to an environmental stimulus (urea solution). As shown in Scheme 1, a DEAN-H⁺ fluo-

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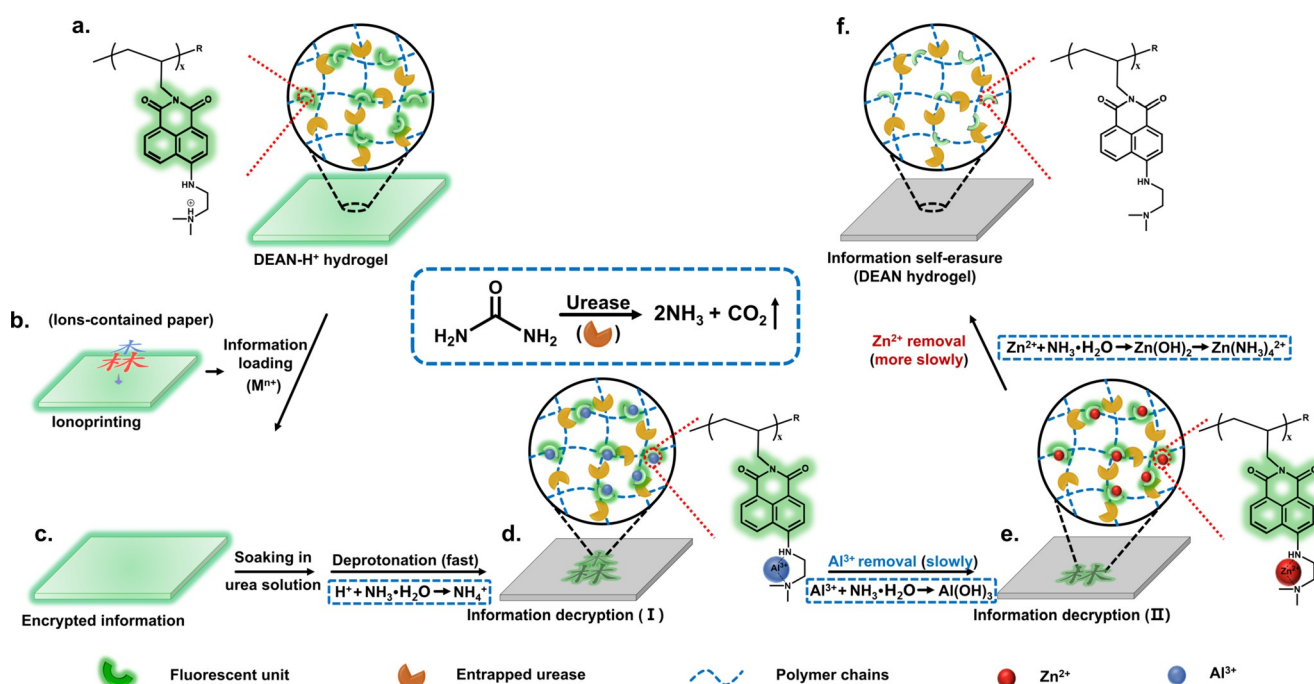
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rescent hydrogel embedded with urease is prepared (Scheme 1a and Supporting Information, Figure S2), and the DEAN-H⁺ fluorescent hydrogel can be locally transformed into DEAN-Mⁿ⁺ hydrogel after the introduction of certain ions by ionprinting, which is accompanied by a negligible change in fluorescence intensity (Scheme 1b). During the abovementioned process, Mⁿ⁺ ions (such as Zn²⁺ and Al³⁺) coordinate with the nitrogen atom of the dimethylamino group as well as the nitrogen atom of the naphthalene ring. NH₃ produced by enzyme-catalyzed reaction under the stimulus of urea solution can deprotonate the naphthalimide moieties, which leads to intensified PET (photoinduced electron transfer) effect and reduces the fluorescence intensity at a fast rate. Moreover, NH₃ can also bond with metal ions and change the DEAN-Mⁿ⁺ hydrogel into DEAN hydrogel. However, compared with the deprotonation process of naphthalimide moieties, the rate of removing Mⁿ⁺ ions is relatively slow, depending on the type of ions. Based on the difference of time dimension, the DEAN-H⁺ hydrogel ionprinted with Zn²⁺ as well as Al³⁺ can be applied as information-storing devices. Here, the Chinese character “森” (forest) is taken as an example. The character is locally printed by Zn²⁺ and Al³⁺ on DEAN-H⁺ hydrogel (blue for Al³⁺ and red for Zn²⁺), which is invisible under UV light at first (Scheme 1c). Through soaking in urea solution, the NH₃ produced by the enzyme-catalyzed reaction will first deprotonate the naphthalimide moieties and then remove the printed Zn²⁺ ions. And then Al³⁺ will be removed and the fluorescence quenching will occur sequentially. Therefore, the

encrypted information would be firstly decrypted as “森” (forest) (Scheme 1d) and then as “林” (woods) (Scheme 1e), subsequently self-erased as time goes on (Scheme 1f).

Results and Discussion

The fluorescent hydrogels are polymerized by acrylamide (AAm) and fluorescent monomer 4-(N,N-dimethylaminoethyl)amino-N-allyl-1,8 naphthalimide (DEAN) (Supporting Information, Scheme S1 and Figure S1) in the presence of urease. Since there are abundant amino groups in urease, and urease may serve as large physical crosslinkers to form non-covalent interactions, such as hydrogen bonds, with the hydrogel networks. To prove the above conjecture, the morphologies and the mechanical properties of the as-prepared fluorescent DEAN-H⁺ hydrogels were investigated. As shown in Figure S3 in the Supporting Information, the urease-containing hydrogel exhibits a more uniform structure compared with the ones without urease. Moreover, the hydrogel with urease can be stretched to more than 300% with tensile stress of 17.8 KPa, while the elongation at break of hydrogel without urease is only 150% and the corresponding tensile stress is 11.6 KPa (Supporting Information, Figure S3c). In addition, the storage modulus (G') as well as loss modulus (G'') of hydrogels with urease were much higher than those of that without urease (Supporting Information, Figure S3d). The introduction of the enzyme will not affect the optical properties, including the characteristic peaks of



Scheme 1. Schematic illustration of DEAN-H⁺ fluorescent hydrogel for instantaneous information storage. a) As-prepared DEAN-H⁺ hydrogel with protonated naphthalimide moieties. a,b) By ionprinting to locally introduce Mⁿ⁺ ions, encrypted information can be loaded via the coordination of Zn²⁺ as well as Al³⁺ by the naphthalimide moieties. c,d) Encrypted information can be decrypted at a fast rate in urea solution due to the deprotonation of naphthalimide moieties by urease, showing the first decrypted information, the Chinese character “森” (forest). d,e) The slow removal of Al³⁺ occurs due to the NH₃ produced by urease, revealing the second decrypted information Chinese character “林” (woods). e,f) The slower removal of Zn²⁺ occurs also due to the NH₃ produced by urease to self-erase the whole information and DEAN hydrogel was obtained.

DEAN on UV/Vis absorption spectra and the transmittance of DEAN-H⁺ hydrogels (Figure 1 b), which is beneficial to the following study of fluorescent performance.

The fluorescent monomer DEAN is pH-responsive, and its fluorescence intensity decreases with the increase of pH value due to the deprotonation process (Supporting Information, Figure S4), which can be triggered by the exposure to urea solution (0.1 M) and the subsequent enzyme-catalyzed reaction (Figure 1). During the procedure of urease-urea catalytic reaction, NH₃ is produced to deprotonate naphthalimide moieties, leading to fluorescence quenching because of the PET effect. As shown in Figure 1 a, a star-shaped hydrogel can emit green–yellow fluorescence under UV illumination at 365 nm, and the fluorescence can be reduced in urea solution because of the generation of NH₃ by urease. The emission intensity of DEAN-H⁺ hydrogel weakens gradually with the elongation of immersing time in urea solution (Figure 1 c), which is accompanied by the pH value change of urea solution from 7 to 9.3 (Figure 1 d).

Besides the protonation of naphthalimide moieties, the coordination interaction between some metal ions and naphthalimide can also inhibit the PET effect, resulting in high emission intensity.^[20] The fluorescence enhancement of the DEAN hydrogel in the presence of Zn²⁺ is almost the same of that in the presence of H⁺ (Supporting Information,

Figure S5). As shown in Figure 1 a and e, Zn²⁺ could also be removed but at a slower rate through the production of NH₃ via urease-urease reaction, therefore a star-shaped DEAN-Zn²⁺ hydrogel slowly switches off its fluorescence upon soaking the hydrogel in urea solution. To understand what happened to the DEAN hydrogel after the introduction of Zn²⁺, their chemical composition and structure were characterized by attenuated total reflection Fourier transformed infrared spectrometer (ATR-FTIR). As shown in Figure 1 f (black line), the DEAN hydrogel shows characteristic peaks at 3321.9 cm⁻¹ and 3180.5 cm⁻¹, which are attributable to the stretching vibrations of -NH- groups.^[21] The peaks located at 1641.6 and 1603.3 cm⁻¹ correspond to the characteristics absorption bands of amidic groups (amide I and amide II) of the 1,8-naphthalimide.^[22] The absorption bands at 1409.9 and 1313.5 cm⁻¹ are caused by stretching vibration of C–N bond attached to naphthalene ring.^[23] A similar ATR-FTIR spectrum of DEAN-Zn²⁺ hydrogel was observed, with several differences of the peaks (Figure 1 f, red line). The passivation and fusion of peaks at 3321.9 and 3180.5 cm⁻¹, 1409.9 and 1313.5 cm⁻¹ imply the formation of coordination interaction and the emergence of peaks at 1036.6 cm⁻¹ may relate to the presence of Zn–N bonds. From these analyses, one possible conclusion is that the coordination between DEAN and Zn²⁺ has occurred.

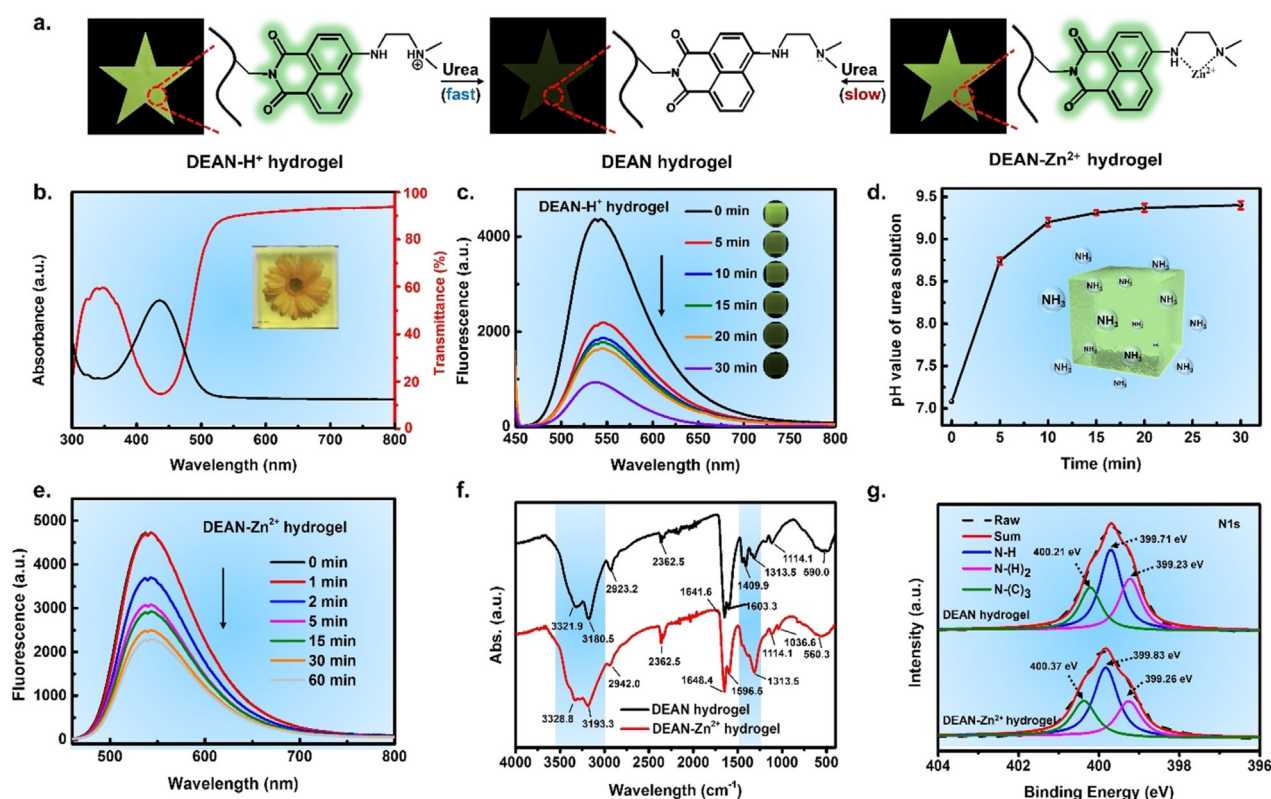


Figure 1. a) Schematic illustration and images of fluorescent switches between DEAN-H⁺ hydrogel, DEAN hydrogel, and DEAN-Zn²⁺ hydrogel. All photos were taken under a 365 nm UV lamp. b) The normalized absorption spectra and transmittance of DEAN-H⁺ hydrogel with urease. c) Fluorescence spectra ($\lambda_{\text{ex}} = 440$ nm) of urease-containing DEAN-H⁺ hydrogel treated with urea solutions as a function of time (0, 5, 10, 15, 20, 30 min). d) pH value change of urea solution during the enzyme-catalyzed reaction. e) Fluorescence spectra ($\lambda_{\text{ex}} = 440$ nm) of urease-containing DEAN-Zn²⁺ hydrogel treated with urea solutions as a function of time (0, 1, 2, 5, 15, 30, 60 min). f) FT-IR spectra of DEAN hydrogel and DEAN-Zn²⁺ hydrogel. g) High-resolution XPS fitting results for N 1s spectra of DEAN hydrogel and DEAN-Zn²⁺ hydrogel.

To further confirm the ATR-FTIR analyses, X-ray photoelectron spectroscopy (XPS) was applied to investigate the DEAN hydrogel as well as DEAN-Zn²⁺ hydrogel. The XPS N1s spectra of DEAN hydrogel is fitted with three components that can be assigned to N-(H)₂ (399.23 eV), N-H (399.71 eV), and N-(C)₃ (400.21 eV), while those peaks of DEAN-Zn²⁺ hydrogel are at 399.26 eV, 399.83 eV, and 400.37 eV, respectively. According to the N 1s fitting result, obvious increases of the peaks related to N-(C)₃ and N-H indicate that Zn²⁺ coordinate with DEAN through sharing the electron pair of nitrogen atoms, which attribute to Zn-N binding (Figure 1 g).^[24] These results are in good agreement with the ATR-FTIR analysis, implying the coordination interaction between DEAN and Zn²⁺. In addition, when keeping the concentration of fluorescent monomer DEAN fixed, and varying the molar ratio of Zn²⁺ to DEAN from 0:10 to 9:1, the fluorescence peak gradually shifts toward blue with an increase in the concentration of Zn²⁺ (Supporting Information, Figure S6), which confirms the metal-ligand coordination.

By treating the DEAN-H⁺ hydrogel with Zn²⁺ ions, the coordination between Zn²⁺ and naphthalimide can be directly formed, obtaining the DEAN-Zn²⁺ hydrogel. As shown in Figure 2 a, through information loading process, DEAN-H⁺ hydrogel was locally ionoprinted by Zn²⁺, which can gradually transform into DEAN hydrogel and go through information decryption and self-erasure procedures due to the enzyme-catalyzed reaction process. Different from the deprotonation process of naphthalimide moieties, the destruction of the coordination between Zn²⁺ and naphthalimide by NH₃ is much slower. Hence, a secret pattern, such as a star, could be locally printed on the surface of the DEAN-H⁺ hydrogel by Zn²⁺, while the pattern is invisible because of the equivalent fluorescence intensity before and after treating with Zn²⁺. Taking advantage of the difference in time dimension of fluorescence off triggered by NH₃, hidden pattern such as a star printed by Zn²⁺ can firstly emerge and then gradually fade with the help of the catalytic reaction between urea and the embedded urease (Supporting Information, Figure S7). The transient appearance of information can effectively prevent information leakage. Notably, due to highly reversible fluorescent on-off performances through cyclically treated by urea solution and citric acid solution (pH 6) as well as the reusability of enzyme, secret patterns can be sequentially loaded. For example, the printed pattern A (the rose) has experienced appearing and disappearing process in urea solution (0.1 M), after which citric acid buffer solution was used for the regeneration of DEAN-H⁺ hydrogel (Supporting Information, Movie S1). As seen in Figure 2 c, the “encryption–decryption–self erasure” cycle can be manipulated again by reprinting pattern B (the sun) (Supporting Information, Movie S2) and pattern C (Chinese character “龍”, which means “dragon” in English) (Supporting Information, Movie S3). It is worth pointing out that with the same concentration, compared with NH₃·H₂O and NaOH solution, urea solution exhibits superior controllability in the time dimension due to relatively slow enzyme-catalyzed reaction process, the decrypted information will disappear quickly in the presence of NH₃·H₂O and NaOH because of the rapid

deprotonation process, making it difficult to obtain the secret information (Supporting Information, Figure S8 and Movie S4).

As DEAN moieties can coordinate with many other metal ions (Supporting Information, Figure S9), such as Al³⁺ (Supporting Information, Figures S10 and S11), and display different fluorescence properties in urea solution (Supporting Information, Figure S12), through the introduction of both Al³⁺ and Zn²⁺, the fluorescence intensity of hydrogels would undergo hierarchical changes, by which programmable information decryption can be realized (Supporting Information, Figure S13). The unique phenomenon can be explained according to the Precipitation–Dissolution Equilibrium.^[25] The pH at which metal ions begin to precipitate can be calculated according to the following equation:

$$\text{pH} = 14 + \frac{1}{n} \lg \left(\frac{K_{sp}}{[M^{n+}]} \right) \quad (1)$$

The pH at which Al³⁺ ions begin to precipitate into Al(OH)₃ is 3 ([Al³⁺] = 0.1 M), while as for Zn²⁺, it starts to turn into Zn(OH)₂ at 5.93 ([Zn²⁺] = 0.1 M) first and further transforms into a complex compound Zn(NH₃)₄²⁺, indicating that the former compound is much easier to be removed than the later. To further illustrate the stability of coordinated configuration, the optimized geometries of DEAN, protonated DEAN and DEAN coordinated with Al³⁺, Zn²⁺ are shown in Figure 3 a and Figure S14 in the Supporting Information. Within the higher total energy of 9.08 × 10⁴ kcal mol⁻¹, the molecular DEAN coordinated with Al³⁺ is less stable compared with DEAN-Zn²⁺ (9.07 × 10⁴ kcal mol⁻¹), indicating Al³⁺ cations are much easier to be removed by NH₃. Therefore, in the presence of both ions, Al³⁺ would first be taken by NH₃ then Zn²⁺, which can also be proved by the changes of fluorescent emission intensity at 543 nm of hydrogels as a function of immersing time in urea solution (Figure 3 b). Compare to DEAN-H⁺ hydrogel, there was a slight lag in the decrease of fluorescence intensity for DEAN-Al³⁺ hydrogel, while the phenomenon of DEAN-Zn²⁺ hydrogel is lagging far behind.

As a proof-of-concept, the number “9”, the Chinese character “森”, the picture “the moon and stars” and the constellation “Ursa Major” were printed on fluorescent DEAN-H⁺ hydrogels by paper stamps containing corresponding ions (red for Zn²⁺ and blue for Al³⁺), in which the background is painted with fluorescent paint. As for example I, the number “9” emerges at first during the decryption period because of the deprotonation of the naphthalimide moieties in the unprinted area, then number “5” shows up due to the removal of Al³⁺ by NH₃ produced by urease in the presence of urea. When Zn²⁺ is taken away, the number “5” finally disappears (Supporting Information, Movie S5). The numbers cannot be displayed without urea, and the readers cannot recognize which number is the true message without any additional knowledge, achieving double-encrypted information with self-destruction behavior. Similarly, the information “林”, “the moon”, and “the plough” in examples II, III, and IV appear after the exhibition of information “森”, “the

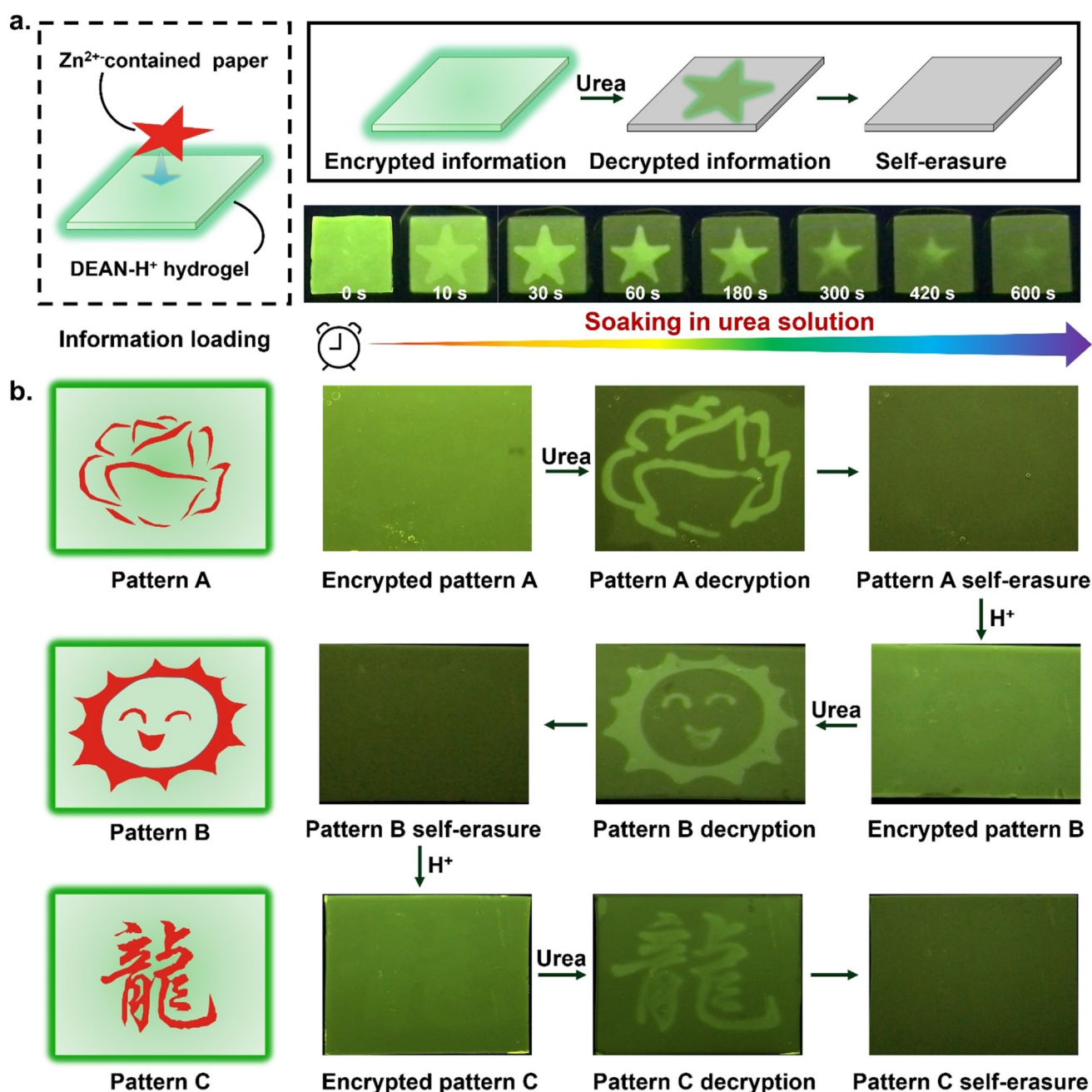


Figure 2. a) Schematic illustration of information loading through ionprinting technique and corresponding encryption, decryption, and self-erasure of information. For example, a star pattern ionprinted by Zn²⁺ on DEAN-H⁺ hydrogel, which can firstly emit fluorescence and subsequently be erased during the urease–urea reaction in 10 min. b) Photos showing the “ionprinting–erasing” cycles. The ionprinted pattern A (the rose) can be facily shined and self-erase in urea solution (0.1 M) and rewritten as pattern B (the sun) as well as pattern C (“龍”, Chinese character) by Zn²⁺ solution (0.1 M) after treatment with acetic acid buffer solutions, all the photos were taken under 365 nm UV light.

moon and stars” and “Ursa Major”, which all disappeared eventually (Supporting Information, Movies S6–S8).

Furthermore, through polymerization of our hydrogel on the basis of paper, mysterious code paper can be fabricated (Supporting Information, Figure S15a), which is more convenient for storage as well as broadening the approaches for information loading (writing, printing etc.). In addition, taking advantages of the paper, which is easy to be cut, folded, and deformed, various recoverable shapes (spiral staircase, cube etc.) were obtained (Supporting Information,

Figure S15b) at the dry state. As shown in Figure S15c in the Supporting Information, Mode I with spiral staircase shape can recover to the flat forms in urea solution due to the softening of papers as well as the transition from xerogels to hydrogels. At the same time, the stored information (“福”), taking Zn²⁺ as ink, first appears and then disappears due to the NH₃ produced by urease-catalyzed reaction for taking the place of H⁺ and Zn²⁺ step by step. Similarly, cube-shaped code paper opens up to show loaded information “hydrogel”

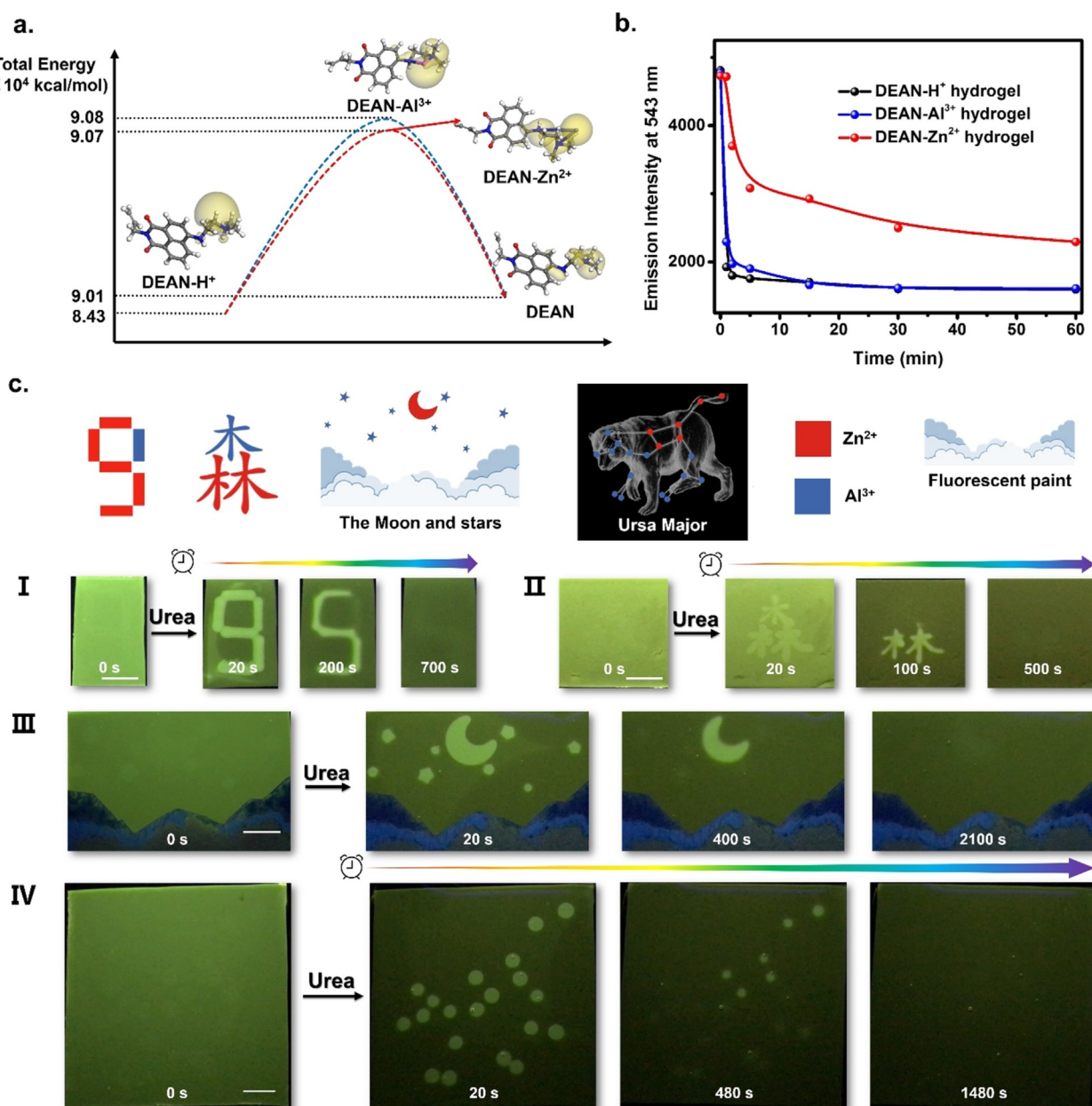


Figure 3. a) The total energy of optimized geometries of DEAN, protonated DEAN, and DEAN coordinated with Al³⁺, Zn²⁺. b) Changes of the fluorescence peak intensities at 543 nm of DEAN-H⁺, DEAN-Zn²⁺, and DEAN-Al³⁺ hydrogels as a function of immersing time in urea solution. c) Various patterns for ionoprinting, in which red represents Zn²⁺, blue stands for Al³⁺, and background was painted with commercially available fluorescent paint. I–IV) Ionoprinted hydrogels were immersed in urea solution (0.1 M) in order to present encrypted information at different times. Scale bar: 1 cm.

when being put into urea solution, which can also self-erase gradually (Supporting Information, Figure S15 d).

Conclusion

In conclusion, we presented an enzyme involved fluorescent hydrogel for transient information storage. The hydrogel was prepared by copolymerization of acrylamide and an ingenious designed fluorescent monomer 4-(N,N-dimethylaminoethylene)amino-N-allyl-1,8 naphthalimide in the presence of urease. Since urease can catalyze the decomposition

of urea to produce NH₃, and naphthalimide moieties could thus be deprotonated, leading to the fluorescence on–off performance, and the fluorescence can be restored in citric acid buffer solution (pH 6). Moreover, the introduction of metal ions, such as Zn²⁺ and Al³⁺, could also enhance the fluorescence of hydrogel, and the metal ions could be sequentially removed by NH₃. Therefore, the hidden information printed by metal ions could be displayed in sequence in urea solution, and finally disappear, ending the hydrogel with programmable information decryption capacity. In view of reusability of enzyme and reversibility of fluorescent performance, this kind of hydrogel can endure repeated cycles

of “encryption–decryption–self erasure”. In addition, the hydrogel could be loaded on papers to fabricate code papers that are capable of long-term storage and convenient delivery. By integrating origami and kirigami techniques, multistage information storage can also be achieved. In a word, our strategy may provide new ideas for designing and manufacturing novel information storage materials and has a broad promising application prospect in information anti-counterfeiting fields.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anti-counterfeiting · enzyme catalysis · fluorescent hydrogel · information decryption · information storage

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