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Ionoprinting controlled information storage of fluorescent hydrogel for hierarchical and multi-dimensional decryption

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ABSTRACT **Information storage and corresponding encryption/decryption are highly important owing to the prevalence of counterfeit activities and information leakage in the current age. Herein, we propose a novel method to store information *via* controllable ionoprinting onto fluorescent hydrogel for hierarchical and multi-dimensional decryption. Through incorporating pyrene moieties and carboxylic groups into polymeric hydrogel network, fluorescence changing and controllable shape deformation behaviors could be achieved and integrated by ionoprinting of Fe^{3+} ions. The diffusion of Fe^{3+} ions into fluorescent hydrogel can quench the fluorescence of pyrene moieties, and chelate with carboxylic groups to generate anisotropic structures for shape deformation simultaneously. Thus, fluorescence quenching-based 2D information and actuation-based 3D information could be hierarchically decrypted when exposed to UV light and being put into water, respectively. Importantly, the stored information could be erased by replacing Fe^{3+} with H^+, which allows the fluorescent hydrogel as a recyclable information storage material. This work may provide new insights in designing and fabricating novel soft devices for hierarchical and multi-dimensional information encryption, against the rising problems of counterfeiting and confidential information disclosure.**

Keywords: information storage, information decryption, hydrogel actuator, fluorescence quenching, anisotropic structures

INTRODUCTION

In the current age of artificial intelligence, information storage and subsequent encryption/decryption techniques become more and more important and thus have attracted considerable attention because of their potential applications in anti-counterfeiting, privacy protection and information security [1–3]. Actually, the encryption and decryption techniques can be traced back to early time. Given the principle of chromogenic reaction between iodine and starch, the hidden confidential information on the paper written by rice-water as ink could be observed after the addition of iodine. Another interesting example of information encryption and decryption could also be found in our daily life. Using lemon juice, vinegar or sugar solution with low ignition point as ink to write invisible information on the paper, the brown words could be observed after the carbonization of ink *via* baking the paper over the fire.

During the last decades, a variety of approaches have emerged for information encryption/decryption, ranging from security code to holographic anti-counterfeiting, as well as fluorescence recognition [4–9]. For instance, Leng *et al.* [10] have utilized shape memory epoxy within Morse code, which was preset on the surfaces of polymers *via* imprint lithography during the thermal curing process. Through programmably introducing alternating magnetic field, radiofrequency field, ultra-violet (UV) irradiation (365 nm) and direct heating, four different codes could be displayed. Xie *et al.* [11] have developed a novel photoinitibitor, which can delay and amplify the gelation process, resulting in the formation of holographic polymer dispersed liquid crystal (HPDLC), and 3D holographic images that are visible under white light have been constructed. Tan *et al.* [9] have developed an inkjet-printable hydrochromic paper, which is based on the reversible self-assembly of a diketopyrrolopyrrole dye.

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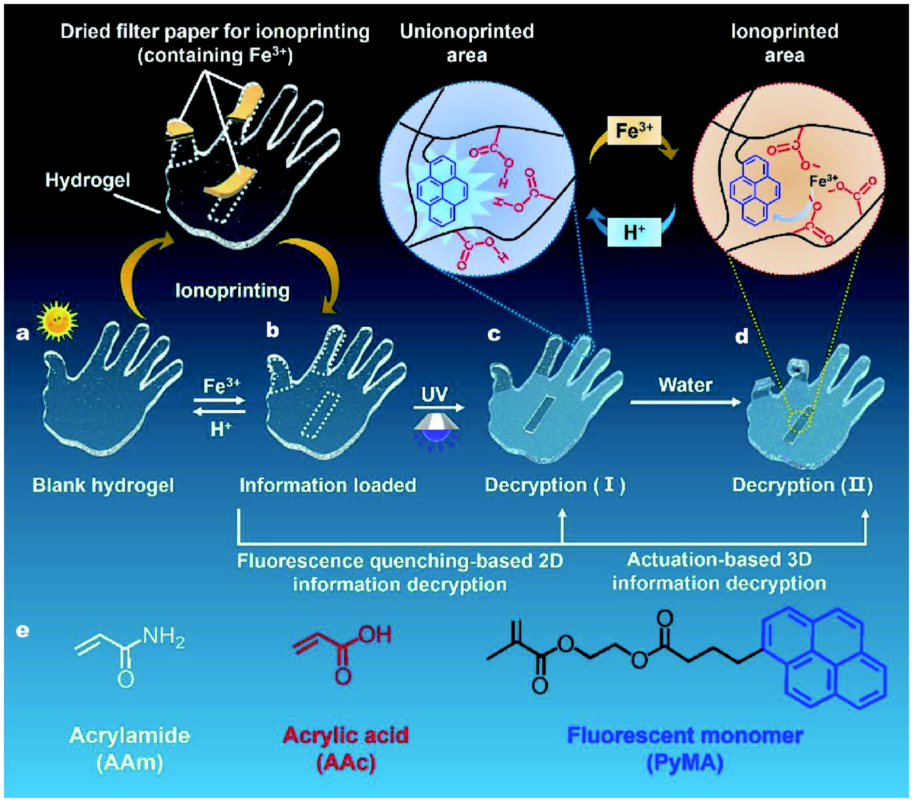

Scheme 1 The schematic illustration of ionoprinting controlled information storage of fluorescent hydrogel for hierarchical and multi-dimensional decryption. (a, b) Through ionoprinting method, dried filter paper (contains Fe^{3+}) will be contacted with hydrogel to let Fe^{3+} diffuse from paper to hydrogel, and information will be preset on the surface of the hydrogel. (c) Fe^{3+} can cause fluorescence quenching due to ICT effect, which can be used for fluorescence quenching-based 2D information decryption, like the big letter "I" under UV light. (d) The chelation between carboxylic groups and Fe^{3+} endows the hydrogel with anisotropic structure during diffusion process, which can be applied for actuation-based 3D information decryption when putting the hydrogel into water, like the gesture "OK". All in all, the whole message is "I'm OK". (e) The chemical structures of monomers used for preparing hydrogels.

The invisible printed information can be seen under UV light, playing an important role in encrypting information and anticounterfeiting. However, some inherent defects of the reported materials such as improper ink induced short storage time of information and unrewritable property limit their real applications in information encryption/decryption.

Recently, stimuli-responsive hydrogels [12–18] with the capability of undergoing reversible volume change or color switches upon the trigger by external stimuli (pH [19], ionic strength [20], temperature [21,22] or light [23,24]) have attracted tremendous attention. In addition to the rich molecular design, the property that only certain stimulus can trigger the response of stimuli-responsive hydrogels makes them promising candidates for information encryption/decryption. There was a preliminary effort made by Liu *et al.* [25] who used stimuli-responsive hydrogels for information storage and decryption. They fabricated a photoactive hydrogel, in which the chemical crosslinks can be gradient cleaved *via* UV light, and the hydrogel was then explored as 3D macro/micro-platform for printing or recording accurate information.

Herein, we propose a novel method as an alternative strategy to store information *via* controllable ionoprinting onto fluorescent hydrogel for hierarchical and multi-dimensional decryption. As shown in Scheme 1, through ionoprinting, during which dried filter papers containing Fe^{3+} were directly contacted with hydrogels, blank hydrogel (Scheme 1a) is loaded with the required information (Scheme 1b). As Fe^{3+} diffusing from paper to hydrogel, the fluorescence of the hydrogel will be quenched due to intramolecular charge transfer (ICT) between pyrene and Fe^{3+}. Under UV light, the encrypted 2D information (the capital letter "I") on the basis of fluorescence quenching would be revealed (Scheme 1c), leading to the potential application in two-dimensional (2D) information storage. Furthermore, PAAc can chelate with Fe^{3+} ions to form PAAc-Fe^{3+} temporary complexes, resulting in anisotropic structure of the whole material, and therefore the hydrogel can be actuated into complex 3D shapes when being put into water (Scheme 1d), which can be used further for 3D information storage (the gesture "OK"). As a result, both fluorescence quenching-based written messages and actuation-based shape information can be decrypted step by step, expressing the whole information "I'm OK". To the best of our knowledge, this is the first investigation to hierarchically decrypt stored information in multi-dimensions, which will enrich the storage modes for encryption and decryption of information and inspire the design and fabrication of novel materials for information encryption.

EXPERIMENTAL SECTION

2-hydroxyethyl methacrylate (HEMA), 1-pyrenylbutyric acid, acrylamide (AAm), ammonium persulfate (APS), *N*,*N*'-methylene bis(acrylamide) (BIS), 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), 4-dimethylaminopyridine (DMAP), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TEMED) and $FeCl_3 \cdot 6H_2O$ were commercially provided by Aladdin. Acrylic acid (AAc), HCl, CH_2Cl_2 and DMSO were purchased form Sinopharm Chemical Reagent Co., Ltd.

^{1}H NMR spectra was obtained on a Bruker AVANCE III spectrometer operating at 400 MHz for protons using $CDCl_3$ containing a small amount of tetramethylsilane (TMS) as internal standard. Steady-state fluorescence spectra were measured on a Hitachi F-4600 spectro-fluorometer at controlled conditions equipped with a Xenon (Xe) lamp (150 W). A laser cutting machine (GY-460 80W) was applied to cut the hydrogels or filter papers into various shapes. The rheological measurements were performed on a stress-controlled rheometer (Physica MCR-301) equipped with a geometry of 25 mm parallel plates.

For preparing the hydrogel, on one hand, 1.98 g AAm and 0.21 mL AAc were combined in a tube and deionized water was added till the volume to 5 mL. On the other hand, 10 mg 1-pyrenylmethyl acrylate (PyMA) was first dissolved in 5 mL DMSO, and then 47.7 mg BIS was added. After the above two solutions were mixed evenly, 70.65 mg APS and 46 μL TEMED were added step by step. After quick oscillation mixing, the mixture was transferred into home-made molds including one hollow silicone rubber sheet and two pieces of glass. After 24 h, the hydrogels were put into deionized water to remove DMSO as well as residual monomers.

RESULTS AND DISCUSSIONS

Fabrication of fluorescent hydrogel

The fluorescent monomer (PyMA) was first synthesized through the condensation reaction between HEMA and 1-pyrenylbutyric acid according to previous work (Figs S1, S2) [26]. As depicted in Scheme 1e, the hydrogel was prepared by copolymerizing fluorescent monomer (PyMA) with pH-responsive monomer (AAc) and neutral monomer (AAm) using free radical polymerization in the presence of BIS (crosslinker), APS (initiator) and TEMED (accelerator). After polymerization, the as-prepared hydrogel was soaked into water for removing residual monomers as well as replacing DMSO with H_2O. The obtained hydrogel can be arbitrarily tailored into different 2D shapes by laser cutting machine.

Creating anisotropic structures by ionoprinting

Filter papers containing different amount of Fe^{3+} were prepared by immersing blank filter papers into $FeCl_3$ solution with concentration of 25, 50, 75, 100 and 125 mmol L^{-1}, and the corresponding contents of Fe^{3+} in filter paper are expressed by 0, 25, 50, 75, 100 and 125, respectively (Fig. S4). Then the wet papers were dried in an oven (60°C) and cut into various shapes as needed. For ionoprinting, various tailored papers were in contact with hydrogels. It is worth mentioning that the hydrogels still have good light transmittance when Fe^{3+} was introduced into the hydrogel systems (Fig. S5), though the colors of hydrogels became light yellow, which suggests that Fe^{3+} diffused into them.

The morphology of the fabricated hydrogels was investigated by scanning electronic microscopy (SEM). Fig. S6a shows typical porous structure of the original hydrogel, indicating the uniformity of hydrogel networks. After introducing Fe^{3+} by ionoprinting, the hydrogel exhibits anisotropic structure, where AAc-Fe^{3+} crosslinks induce the reducing of pore size (Fig. S6b). With the increase of contact time, Fe^{3+} diffuses deeper into the hydrogel network, resulting in the augment of cross-linking density of the whole hydrogel, which becomes isotropic again (Fig. S6c).

Controllable fluorescence quenching and fluorescence quenching-based 2D information storage

It should be noted that under irradiation (341 nm), pyrene groups with limited aggregation will emit blue light [27]. However, with the presence of transition metal

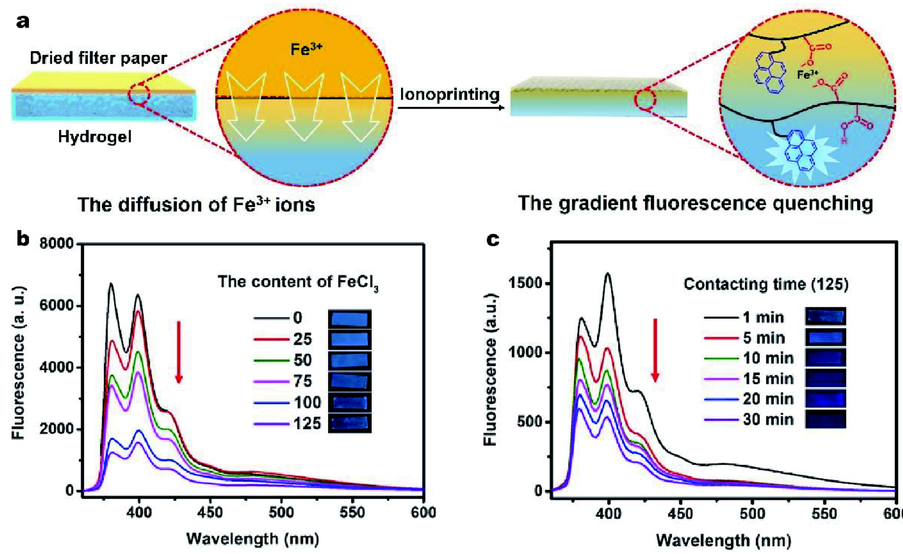

Figure 1 (a) The mechanism of fluorescence quenching: when encountering with Fe^{3+} ions, fluorescence quenching of pyrene moieties occurs because of ICT effect. (b) Fluorescence spectra of hydrogels upon treatment with dried filter papers containing different content of Fe^{3+}. (c) Fluorescence spectra of hydrogels upon treatment with dried filter paper with different contacting time.

ions (the electron acceptor), especially those with strong oxidation ability such as Fe^{3+} ions, the fluorescence of PyMA (the electron donor) is easy to be quenched because of the ICT effect. As shown in Fig. 1a, with the diffusion of Fe^{3+}, the fluorescence intensity of hydrogel reduces remarkably at the contact interface. The fluorescence quenching can be affected by the content of Fe^{3+} in filter paper as well as the contacting time. Proved by fluorescence spectra, the emission intensities around 380 nm fall rapidly through increasing the content of Fe^{3+}, while keeping the contacting time for 1 min (Fig. 1b). When the contacting time is prolonged from 1 to 30 min, the fluorescence intensities declines gradually as well (Fig. 1c).

Due to the excellent fluorescence quenching performance, information storage in the plane (2D information storage) has been achieved. As shown in Fig. 2a, through ionoprinting method, English letters “UCAS” and Chinese characters “中科院” were imprinted onto the surface of hydrogels *via* contacting with filter papers containing Fe^{3+}. Through the similar way, flower images (assisted by small seals) were recorded on the surface of hydrogel (Fig. 2b). Furthermore, high-precision Quick Response Codes (QR codes) have also been printed on the hydrogel, which can be scanned by a smartphone linked to corresponding words. Here, words “smart” and “hydrogel” were acquired by scanning QR code I and QR code II, respectively (Fig. 2c, Movie S1, Movie S2). The above information can be only displayed upon exposure to UV light, which is effective for preventing information leakage.

Controllable shape deformations and actuation-based hierarchical and multi-dimensional information decryption

Because of the diffusion of Fe^{3+} into hydrogel, anisotropic structure is created (Fig. 3b). As illustrated in Fig. 3a, when Fe^{3+} enters into the hydrogel, it could chelate with AAc to form temporary crosslinks [28–30] that reduces the swelling rate of one side. When putting the hydrogels into water, the rearrangement of Fe^{3+} leads to the formation of tridentates between Fe^{3+} and AAc, thus causing the bending behavior of hydrogel [31]. By increasing the content of Fe^{3+} from 0 to 125, the bending angles increase from 0° to more than 350°, indicating the anisotropic structure becomes more obvious due to the formation of more Fe^{3+}-AAc crosslinks, and thus leads to stronger bending force (Fig. 3c). Furthermore, fixing the content of Fe^{3+} as 125 and increasing the contacting time from 1 to 30 min, Fe^{3+} would diffuse deeper and deeper into the hydrogel. As a result, the bending angles first increase and then decrease due to the gradual loss of anisotropic structure (Fig. S7).

Though the degree of shape deformation only has small change by tuning the contact time between hydrogel and paper, the toughness of hydrogel makes a big difference (Fig. S8). With the elongation of contact time, the storage modulus increases at first and then decreases, which

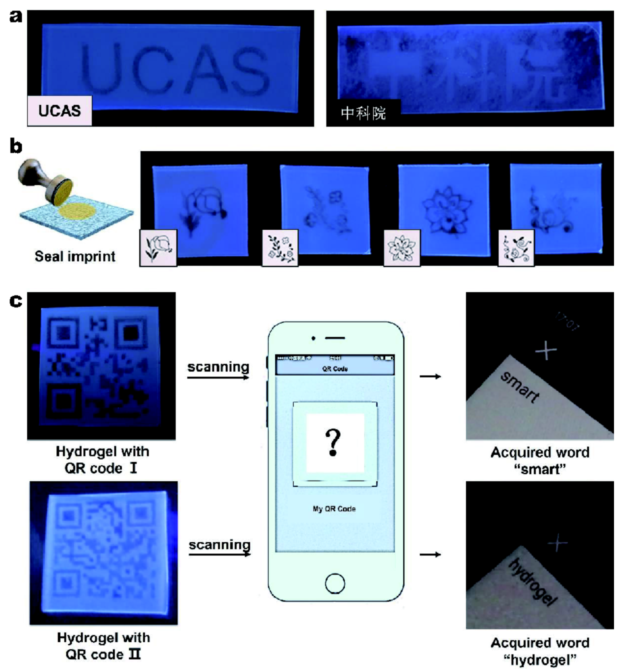

Figure 2 Fluorescence quenching-based 2D information storage, hidden messages are visible only upon exposure to UV light. (a) Applying Fe^{3+}-containing dried filter papers for ionoprinting, English lettters "UCAS" and Chinese characters "中科院" were visible under UV light. (b) Flower images (1 cm×1 cm) were obtained *via* imprinting on the surface of hydrogels by four different seals containing Fe^{3+}. (c) The QR codes were ionoprinted onto the surface of hydrogels, which can be scanned and accessing to the words "smart" and "hydrogel", respectively.

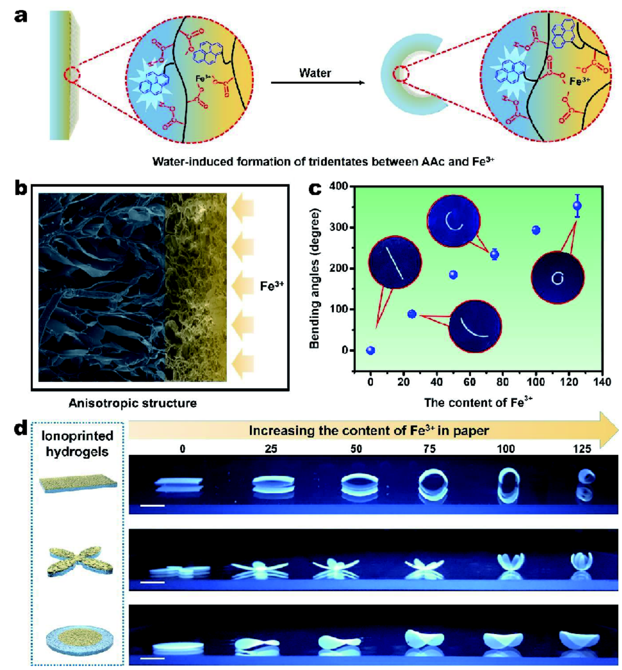

Figure 3 Controllable 2D/3D shape deformations. (a) The schematic illustration of the bending of hydrogel in water due to the formation of tridentates between AAc and Fe^{3+}. (b) SEM image of anisotropic structure induced by Fe^{3+} diffusion (125, 1 min). (c) 2D shape deformations: through changing the filter papers (containing different content of Fe^{3+}) and keeping the contacting time fixed at 1 min, the bending angles change from 0° to about 350°. (d) 3D shape deformations: the degree of deformations can be tuned by using the filter papers with different content of Fe^{3+}. Rectangle hydrogel film can arch with varying degrees of curvature. The flower-shaped hydrogel can bloom with different degrees. The disk-shaped hydrogel can change into diverse saddle shapes by contacting with a smaller disk filter paper. Scale bar: 1 cm.

means that suitable amount of Fe^{3+} ions can enhance the stiffness of hydrogel due to the formation of tridentates between Fe^{3+} and AAc. However, excess Fe^{3+} will lead to the chelation of AAc and Fe^{3+} in the form of mono-, bidentates, which would reduce the amount of effective crosslinks [32,33]. On the basis of the good mechanical properties, a hydrogel gripper was designed for grabbing sponge containing conductive sheet, which was 7 times higher than hydrogel's weight (Fig. S9, Movie S3).

Through adjusting the contacting area with filter papers owning different amount of Fe^{3+} ions, planar hydrogels with different simple 2D shapes can turn into complex 3D shapes through ionoprinting treatment and actuating in water. As shown in Fig. 3d, rectangle hydrogel film can arch with varying degrees of curvature *via* contacting with filter papers (0, 25, 50, 75, 100, 125) for 1 min. Similarly, the flower-shaped hydrogel can bloom with different degrees, and the disk-shaped hydrogel can change into diverse saddle shapes by contacting with a smaller disk filter paper. Therefore, controllable complex shape deformations can be realized by changing the filter papers with different content of Fe^{3+}, with maintaining the contact time.

In view of fabulous morphology changing behaviors, the hydrogels were considered in actuation-based information storage and decryption. By tuning contacting position and directions with filter paper (125), original straight strip hydrogels were preprocessed. After putting hydrogels into water, hidden capital letters "U" "C" "Λ" "S" (Fig. 4a), which is the abbreviation of the University of Chinese Academy of Sciences (UCAS), are emerging. Different from common 2D written information storage, our hydrogel exhibits actuation-based information storage (Fig. 4b–d). Through introducing two stimuli (UV light and water) separately, hierarchical and multi-dimensional information decryption can be realized. As demonstrated in Fig. 4b, there is no difference among the

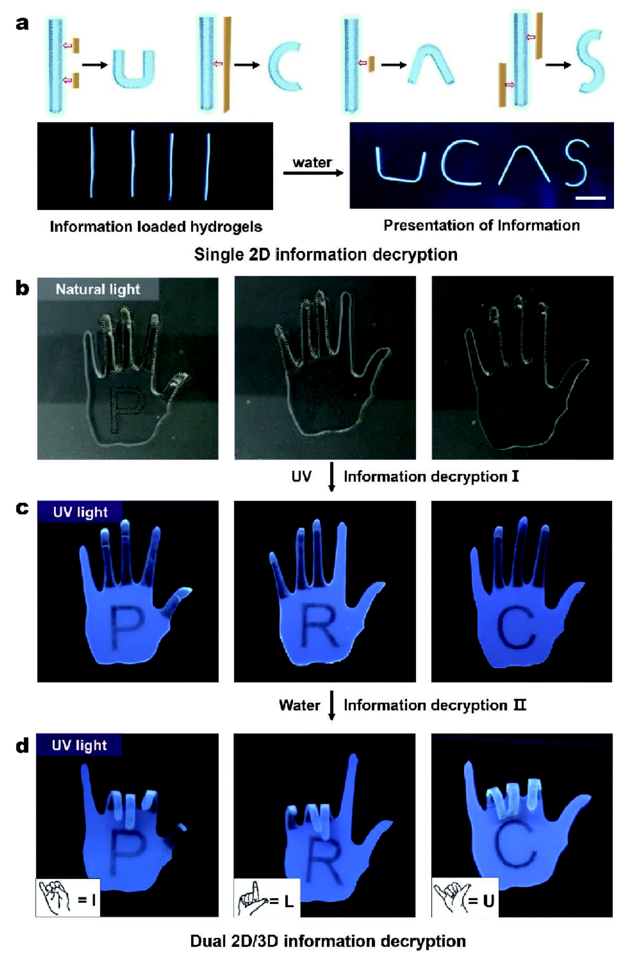

Figure 4 Hierarchical and multi-dimensional information decryption. (a) 2D information decryption on the basis of shape deformation performance: by changing the contact areas of straight hydrogels and filter papers, and putting the hydrogels into water, different capital letters "U", "C", "Λ", "S" (UCAS is the abbreviation of University of Chinese Academy of Sciences) can be achieved. (b–d) Hierarchical information decryption: after being pre-treated *via* ionoprinting, the first level of information-the letters "P" "R" "C" (PRC is the abbreviation of the People's Republic of China) can be seen under UV light. After actuating in water, the second level of information-American Sign Language corresponding to "I" "L" "U" show up, which means I LOVE YOU. As a result, the whole emerging message is "I love you, China".

three hands carrying different information under natural light. However, once putting the hydrogels under UV light (365 nm), three hidden letters ("P" "R" "C") appear, forming the abbreviation of the People's Republic of China (Fig. 4c). Immersing the above hydrogels into water, various gestures are generated, which respectively correspond to the letters of "I" "L" "U" in American Sign Language with the meaning of "I LOVE YOU" (Fig. 4d). As a result, by introducing stimuli of UV and water step by step, the whole hidden message "I Love You, China" can be read.

The erasure of stored information

In order to prevent environmental problems caused by paper or inks, various rewritable papers have been developed [34–39]. Like other rewritable papers, our hydrogels can also be recycled *via* simply immersing in HCl solution, during which H^+ would replace Fe^{3+}. As Fe^{3+} quenches the fluorescence of hydrogel, the ionoprinted area becomes darker under UV light (365 nm), which will be brighter again after treating with HCl solution (Fig. 5a). Especially, the paper with pattern of cross stripes with width of 3 mm can be easily fabricated with laser cutting machine and firstly transferred to hydrogels through ionoprinting (Fig. 5b, Fig. S10). The patterned hydrogels not only show fluorescence quenching on the contact areas but also can be actuated into a 3D shape I (quadrangular shape). When the hydrogel with actuated shape is transferred into HCl solution (0.2 mol L^{-1}), the hydrogel with sophisticated 3D shape can gradually return to original 2D flat ones (Fig. S11a, Movie S4), which is ascribed to the cleavage of the AAc-Fe^{3+} crosslinks [40,41]. As H^+ replaces Fe^{3+}, the intramolecular charge transfer between Fe^{3+} and pyrene will be interrupted. Therefore, the fluorescence reappears at the same time of shape recovery (Fig. S12). Then the patterns of diagonal stripes (Fig. S11b) and cross shape (Fig. S11c) are separately imprinted onto the hydrogel, which corresponds to dumpling shape and aircraft shape after being put into deionized water (Movie S5, S6). The cycling performance further indicates that the hydrogel has great potential to be applied in the field of information storage.

CONCLUSIONS

In summary, we have developed a novel strategy for information storage on the basis of fluorescent hydrogel *via* ionoprinting technique, which can achieve hierarchical and multi-dimensional decryption. After ionoprinting, the introduced Fe^{3+} ions can induce the fluorescence quenching of pyrene groups and coordinate with carboxylic groups, leading to anisotropic structure of hydrogel for shape deformation. By combining fluorescence quenching with shape deformation behaviors, 2D written message and 3D deformation information can be respectively decrypted under UV light and in the water step by step. In addition, both shape deformation and fluorescence quenching behaviors can be erased at the same time by replacing Fe^{3+} with H^+. We believe that the present work can provide new insights in the design and

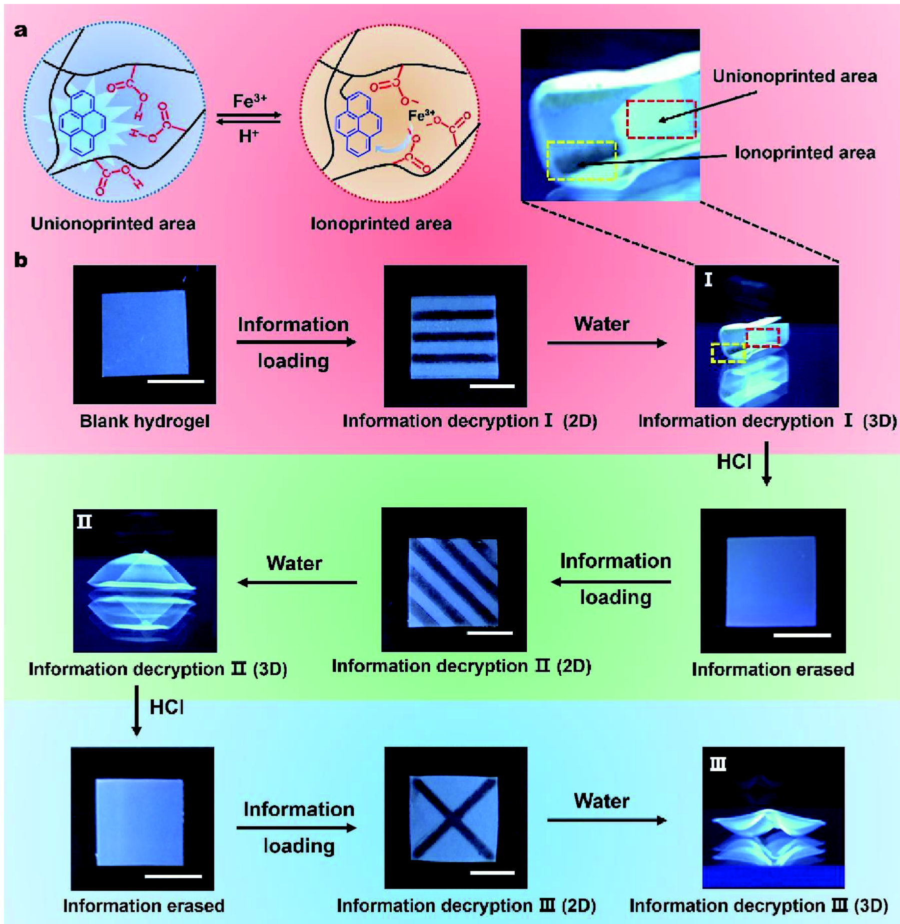

Figure 5 The recycle use of hydrogel. (a) The schematic diagram of reversible cycle between ionoprinting procedure and the erasing procedure. (b) A square hydrogel was first ionoprinted with pattern of cross stripes, which can be actuated into 3D complex shape I. After erasing the deformed shape and recovering fluorescence in HCl solution, pattern of diagonal stripes was imprinted, leading to 3D complex shape II by actuating in water. At last, cross shape was ionoprinted on the erased surface of hydrogel, and 3D complex shape III can be achieved. Scale bar: 1 cm.

fabrication of novel intelligent materials for information storage and hierarchical and multi-dimensional decryption, and has promising applications in anti-counterfeiting.

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Author contributions Chen T and Zhang J initiated and guided the work. All authors contributed to the discussion and preparation of the manuscript.

Conflict of interest The authors declare no conflict of interest.

Supplementary Information Supporting data are available in the online version of the paper.

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离子印染可控的荧光水凝胶用于多维度信息存储

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摘要 本文通过离子印染的方式,赋予荧光水凝胶信息,并将其用于逐级、多维度信息存储. 通过铁离子的引入,荧光水凝胶中的芘基团会发生荧光淬灭,在紫外灯下可用于二维平面的信息存储;同时,铁离子的扩散会赋予水凝胶各向异性的结构,使得其在水中驱动得到三维的信息. 并且,储存的二维、三维信息可以通过氢离子取代铁离子进行擦除,这使得材料具有很好的可重复利用性. 总之,本文为新型柔性信息存储装置的设计和制备提供了新的思路.