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Shape Memory Hydrogels with Simultaneously Switchable Fluorescence Behavior

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Realization of shape memory process in polymeric hydrogels at ambient condition is a significant development to shape memory materials. The sound understanding of the dynamic shape memory process is fundamentally important but limited. Here, a novel shape memory hydrogel with simultaneously switchable fluorescence behavior is developed. The hydrogel is prepared by incorporating a pH-responsive fluorescent molecule, perylene tetracarboxylic acid, into chitosan-based hydrogel, and the assembly and disassembly of chitosan chains into microcrystals upon the trigger of pH are applied as reversible crosslinks to achieve shape memory effect. Therefore, the formation and disassociation of microcrystalline chitosan, and the switchable fluorescence performance happen concurrently, which bring convenience to monitoring the shape memory process by fluorescent imaging. Moreover, the erasable fluorescence behavior also gives the hydrogel potential applications in information storage.

1. Introduction

Shape memory polymers (SMPs) are one kind of smart polymer material which can fix temporary shape and recover to permanent shape under external stimuli. They have thus aroused tremendous attention and shown promising applications in many fields such as biomedical, textiles, actuators and so on.[1–9] Classic shape memory polymers are mainly thermo-induced polymers, in which the vitrification or crystallization of switching domains are applied to stabilize the temporary shape, and shape memory effect are normally realized in bulk polymers.[1] With the development of supramolecular chemistry, reversible interactions have been applied as temporary crosslinks to realize shape memory behavior in hydrogels at ambient conditions.[10–19] Most of the current research in the fields of shape memory hydrogels is focused on the realization of shape memory effect, including the efficient fixing of a temporary shape, recovery to the original state. The investigation of the dynamic process of dissociation and recombination of molecular switches will provide more information about the mechanism of the shape memory process, and guide the molecular design of novel shape memory hydrogels for potential practical applications. However, the dynamic shape memory process is not convenient to be monitored in situ and real-timely, because they generally do not cause significant changes in physical properties compared with thermoresponsive shape memory polymers.

Recently, fluorescence-based methods have been widely used and shown great advantage in exploring the dynamic process such as self-assembly, conformational changes.[20–29] For instance, Tang and co-workers have successfully observed the entire gelation process of chitosan LiOH-urea aqueous system by aggregation-induced emission fluorescent imaging.[27] Yang et al. have tracked the process and dynamics of coordination-driven self-assembly through the fluorescence-resonance energy transfer technique.[29] The high sensitivity of fluorescence-based methods provides possibility to visualize the dynamic shape memory process.

Herein, we present a novel shape memory hydrogel system with a built-in switchable fluorescent sensor. As shown in **Scheme 1**, first of all, perylene tetracarboxylic acid (PTCA), a typical fluorescent molecule with aggregation-caused quenching (ACQ) effect,[30] was grafted onto chitosan chains, and a semi-interpenetrating polymer network hydrogel (PAAm/PTCA-CS) was prepared by free radical polymerization of acrylamide (AAm) in the presence of PTCA modified chitosan. As chitosan chains are able to self-assemble into microcrystal in alkaline condition,[19] the chitosan microcrystalline is applied as reversible crosslinks to fix the temporary shapes and render the hydrogel shape memory property. Due to the pH-responsiveness of carboxyl groups, PTCA moieties located inside the hydrogel would disaggregate upon the treatment of alkaline solution, which is evidenced by a significantly enhancement of fluorescence intensity. Since both the shape memory process and fluorescence

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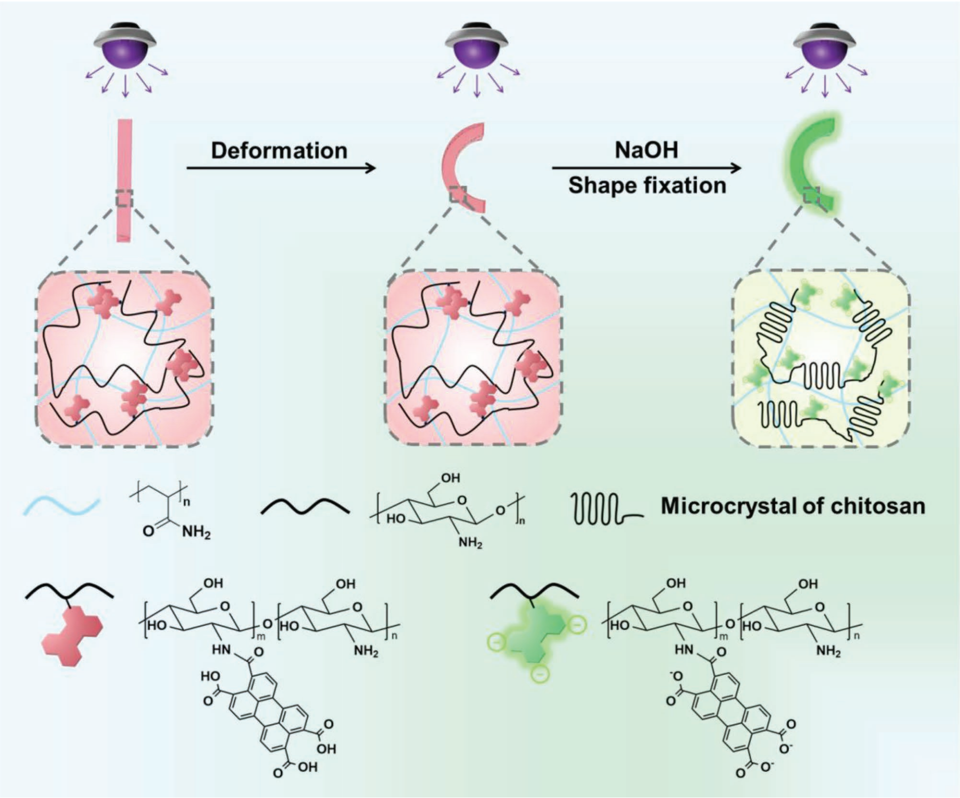

Scheme 1. The mechanisms of the shape memory hydrogels with simultaneously switchable fluorescence. Acrylamide was polymerized in the presence of PTCA modified chitosan. The reversible CS microcrystalline crosslinks endows the hydrogel with shape memory ability, the deprotonation of PTCA in alkaline solution induces the fluorescence emission of hydrogel.

performance are related to diffusion of OH^- or H^+ into the hydrogel, the in-situ and real-time formation of chitosan microcrystalline could be indicated by fluorescence imaging method. Moreover, the “on–off” switchable fluorescence behavior also endows the hydrogel with additional functionality such as erasable fluorescence-based information storage.

2. Results and Discussion

First of all, PTCA was prepared from 3,4,9,10-perylene tetracarboxylic dianhydride (Figures S1 and S2, Supporting Information), then it was grafted to chitosan following a reported procedure to obtain PTCA modified chitosan (PTCA-CS)[30] (Figure S3, Supporting Information). The attachment of PTCA onto chitosan chains is confirmed by UV–vis spectra. As shown in Figure S4 (Supporting Information), the aqueous solution of PTCA-CS shows a strong absorbance at around 400–600 nm, which is attributed to the grafted PTCA moieties.

The hydrogel (PAAm/PTCA-CS) was prepared by free radical polymerization of AAm in the presence of PTCA-CS. In visible light, the obtained hydrogel is light brown and has a superior light transmittance (Figure S6, Supporting Information). After soaking in alkaline solution, the hydrogel turns to yellow. The appearance of the hydrogel under UV irradiation (365 nm) is more prominence, the just prepared hydrogel shows no fluorescence, and a strong cyan fluorescence is observed after it was immersed into alkaline solution, and the pH-responsive fluorescence of the PAAm/PTCA-CS hydrogel is fully reversible (Figure S6, Supporting Information). Because PTCA is a typical luminogen, though it is grafted onto chitosan chains with a low grating ratio and introduced into hydrogels, the strong hydrogen bonding and π–π stacking interactions between PTCA groups still make them aggregate together,[30] therefore the fluorescence emission of the just prepared hydrogel is quenched. If the remaining carboxyl groups of PTCA groups are transformed into negatively charged carboxylate ions via NaOH aqueous solution, the hydrogen bonding of carboxyl groups will be destroyed, and the deprotonation of the carboxylic groups will bring electrostatic repulsion between PTCA moieties, which will effectively hinders them from getting together. Therefore, the fluorescence emission of the hydrogel will be greatly enhanced.

Because the fluorescence of the hydrogel is determined by the deprotonation of PTCA groups, which is related to the diffusion of NaOH into hydrogels, therefore the fluorescence of the hydrogel is affected by the immersing time and the concentration of the NaOH aqueous solution. As illustrated in **Figure 1**a, with the increase of soaking time into NaOH aqueous solution, the cyan fluorescence gradually diffused from the edge of the hydrogel sheet to the center, indicating OH^- entering into the hydrogel and causing the disaggregation of the PTCA moieties. In addition, the relation between the fluorescence intensity and concentration of NaOH was investigated. A series of

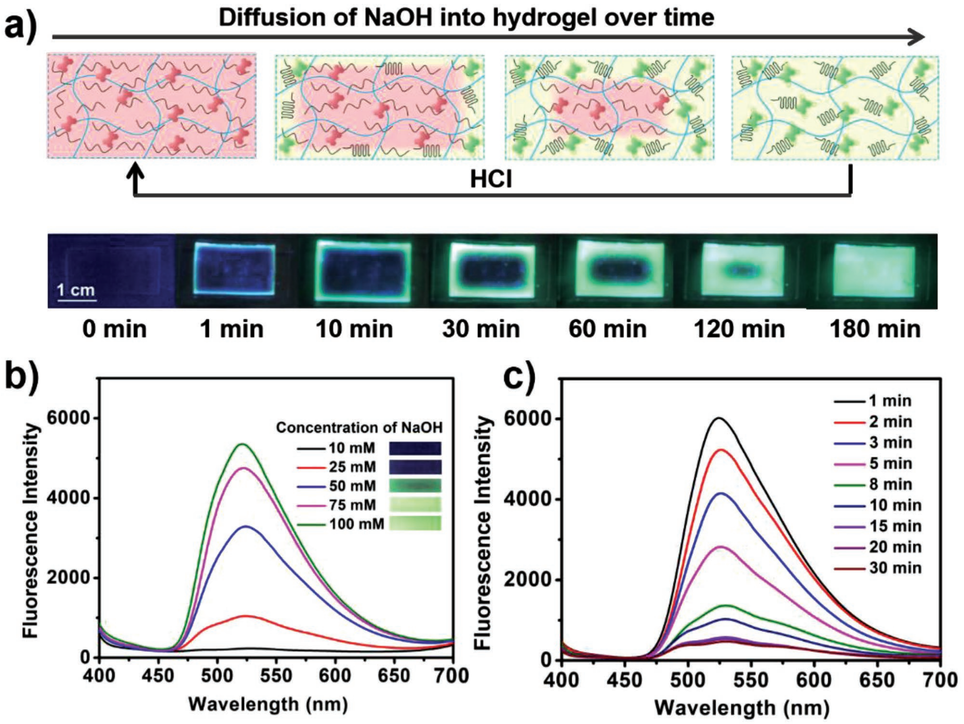

Figure 1. a) Illustration and images showing the time-dependent fluorescence of PAAm/PTCA-CS hydrogel in NaOH aqueous solution (0.1 M). (Photos were taken under 365 nm UV light). b) Fluorescence spectra and images of PAAm/PTCA-CS hydrogels upon treatment with NaOH aqueous solutions with different concentrations for 30 min. c) Fluorescence spectra and images of PAAm/PTCA-CS hydrogels upon treatment with HCl aqueous solutions (0.1 M) for different times.

hydrogel strips with the same size were immersed into NaOH aqueous solutions of different concentration (ranging from 0.01 to 0.1 M) for 30 min, the fluorescence color of the hydrogel would change from dark to bright cyan under UV irradiation with the increment of NaOH solution, accompanied by the significant enhancement of the fluorescence intensity (Figure 1b). This remarkable fluorescence color change is due to the reduced ACQ effect between PTCA groups at alkaline condition. If the hydrogel is then immersed in acidic condition, the PTCA moieties would aggregated again because of the protonation of carboxyl groups, and the fluorescence intensities would decrease. As shown in Figure 1c, the fluorescence intensities decrease with increase immersing time in HCl solution, which indicates the increment of ACQ effect between PTCA groups at acidic condition. Because of the pH dependent fluorescence behavior of PTCA groups, the diffusion process of OH^- into hydrogel can be clearly visualized by naked eyes under UV irradiation, which would bring convenience for investigating the shape memory process.

It has been reported that the amino groups on chitosan chains will deprotonated and form microcrystalline in alkaline solution,[31] and the microcrystalline are expected to function as temporary crosslinks and endow the PAAm/PTCA-CS hydrogel shape memory property. As shown in **Figure 2**a, a straight strip sample was bent into a “U” shape and immersed in NaOH solution, the temporary shape with a bright fluorescence can be fixed within 5 min due to the crystallization of chitosan chains and the deprotonation of PTCA groups. When the hydrogel was transferred into HCl solution, the microcrystalline will be destroyed and the fluorescence of the PTCA moieties will be quenched because of the protonation, the hydrogel quickly recovers to the original straight shape with no fluorescence emission. Since the shape memory effect of the PAAm/PTCA-CS hydrogel is caused by the diffusion of OH^-, it can infer that the shape memory ratio of the hydrogel is determined by the concentration of NaOH.[31] As shown in Figure 2b, with the concentration of NaOH solution raises from 0.01 to 0.1 M, the shape fixity ratio of the hydrogel increases from 30% to almost 70%, which indicates that higher concentration of NaOH aqueous solution tends to induce more crystallization of chitosan chains in a certain period of time, and the shape fixity ratio will be improved because of the increment of temporary crosslinks. When the hydrogel with a deformed temporary shape is immersed into HCl aqueous solution, a fast shape recovery process could be observed (Figure 2c; Movie S1, Supporting Information), which suggests the disassociation of the chitosan chain microcrystal crosslink can lead to the recovery of the original state. The good shape memory effect of the PAAm/PTCA-CS hydrogel encourages us to explore the ability to fix and recover more complicated temporary shapes. As shown in Figure 2a, three straight samples were deformed to “C,”“∧,” and “S,” and the temporary shapes could be fixed in alkaline solutions and recovered to the original straight shape in acid condition. In addition, more complicated temporary shapes like “table” and “flower” could also be stabilized by the treatment of NaOH and recovered to the original flat shapes under the trigger of HCl (Movie S2, Supporting Information). More evidence for the formation and disassociation of microcrystalline

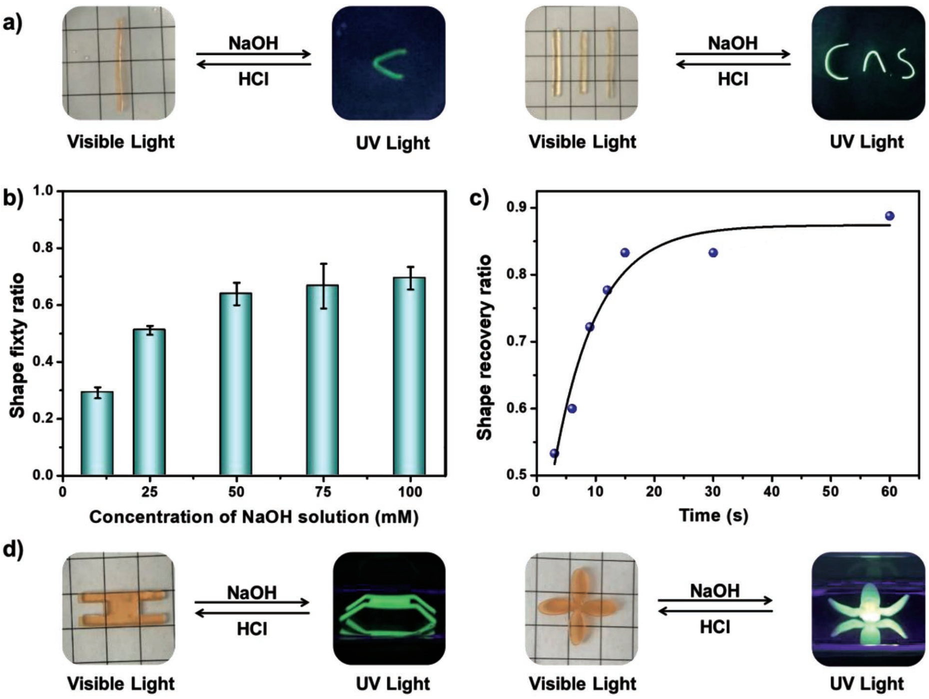

Figure 2. a) The shape memory behavior based on chitosan microcrystalline crosslink. b) Variation of the shape fixity ratios of the PAAm/PTCA-CS hydrogels as a function of concentration of NaOH solution with a shape fixity time of 5 min. c) Variation of the shape fixity ratios as a function of recovery time in HCl solution (0.5 M). d) Images of the more complex temporary shapes of PAAm/PTCA-CS hydrogel fixed by NaOH (0.1 M).

can be obtained from rheological and tensile experiments. As shown in Figure S7 (Supporting Information), the *G′* and *G″* values of the PTCA-CS/PAAm hydrogel increase when soaking in NaOH aqueous solution (0.1 M) and the recover after being treated in HCl aqueous solution (0.1 M), which indicates the crystallization of chitosan chains enhances the mechanical properties of our hydrogels. This explanation is further supported by the tensile experiment (Figure S8, Supporting Information), the tensile stress of the NaOH treated hydrogel is much higher than that of the original hydrogel, which is ascribed to the formation of rigid chitosan network.

The reversible pH-responsive fluorescence behavior of PAAm/PTCA-CS hydrogel was applied to construct fluorescent color codes. As shown in **Figure 3**, nonfluorescent PAAm/CS hydrogel blocks were prepared to assembly with PAAm/PTCA-CS hydrogel domains. In neutral condition, the code carried by the hydrogel pattern could not be observed, because there is no fluorescence under UV irradiation. After treating with NaOH, the fluorescence of the PAAm/PTCA-CS hydrogel domains is greatly enhanced, and code A could be recognized. The encoded information could be transformed by rearrange the hydrogel blocks. For example, if the position of two blocks at the last line is changed, and code B is read out. The information within the hydrogel pattern could be erased by HCl because of the pH-responsiveness fluorescence performance of PAAm/PTCA-CS hydrogel. The illustrated approach will inspire the design and fabrication of novel smart fluorescence-based information storage materials.

3. Conclusion

In conclusion, a novel shape memory hydrogel with simultaneously on–off switchable fluorescence behavior has been successfully developed, the hydrogel was fabricated by polymerizing acrylamide in the presence of PTCA modified chitosan, the pH-responsive chitosan microcrystalline could act as temporary crosslinks to stabilize the deformed shape of the hydrogel, which is accompanied by the disaggregation of PTCA moieties and endow the hydrogel with on–off switchable fluorescence performance upon UV irradiation, therefore the hydrogel shows simultaneously shape memory and

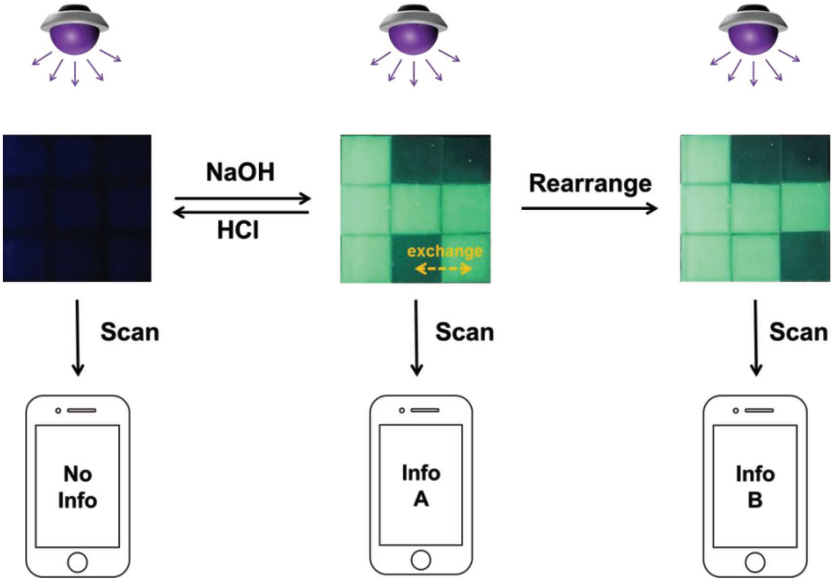

Figure 3. Fluorescent color code generated by the PAAm/PTCA-CS hydrogel and PAAm/CS hydrogel. In neutral condition, there is no information. Information A could be recognized by treating with alkaline condition, and information B could be read out by reassembly of individual domains. Photos were taken under 365 nm UV light. The size of the hydrogel blocks is 1.0 cm × 1.0 cm.

switchable fluorescence behaviors under alkaline condition. The fluorescence allows one to monitor the diffusion of OH^- into the hydrogel, and provides a feasible method for further study the mechanism of the obtained shape memory hydrogels. In addition, erasable fluorescent color codes have also been constructed by assemble the fluorescent hydrogel domains with nonfluorescent hydrogel domains. The present strategy, which including two pH-responsive properties within one system, is expected to points the way for the design and fabrication of novel and powerful shape memory systems with versatile functions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chitosan, microcrystals, pH-responsive, shape memory hydrogels, switchable fluorescence

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