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An “Off-the-Shelf” Shape Memory Hydrogel Based on the Dynamic Borax-Diol Ester Bonds

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An “off-the-shelf” hydrogel with high-efficiency shape memory property is designed on the basis of the dynamic borax-diol chemistry. The system is facilely prepared from only several unmodified commercially available components: acrylamide (AAm), bis-acrylamide (Bis), poly(vinyl alcohol) (PVA), and borax. The chemically crosslinked poly(acrylamide) network works to fix the permanent shapes of the hydrogel, while the dynamic PVA–borax boronate ester bonds serve as the reversible crosslinks to memorize the deformed temporary shapes. Retreatment of the hydrogel in acid/glucose solutions dissipates the PVA–borax ester bonds to recover its permanent shape. Because of the highly invertible nature of borax-diol chemistry, the developed hydrogel system is characterized by high shape memory/recovery ratios, continuously adjusted shape memory/recovery rates, thus having a wealth of potential applications.

1. Introduction

As one of the most significant stimuli-responsive materials, shape memory polymers (SMPs) have the property of fixing a temporary shape and recovering to its original state via the trigger of external stimuli.[1–18] In recent decades, a tremendous number of researches have been conducted on the thermal-responsive shape memory polymers, due to their great potential in biomaterials, biosensors, textile coatings, and packing materials. Nevertheless, these heat-responsive SMPs may not be suitable for some applications in the biomedical and textile fields, where large temperature change is not allowed. To this end, reversible interaction (e.g., supramolecular interactions, dynamic covalent bonds) were recently introduced into traditional SMPs to fabricate supramolecular shape memory hydrogels (SSMHs).[19–33] Due to the dynamic nature of these reversible interactions,[34–36] SSMHs are expected to perform cycled shape memory behaviors at ambient conditions and thus hold great potential applications in biosensors, smart textiles, soft robotics. Compared with the SSMH systems relying on supramolecular interactions, examples employing dynamic covalent bonds as temporary crosslinks usually suffer from long memory time and poor shape memory fixity.[37] Moreover, most of the reported dynamic covalent bond-based SSMHs are prepared by some synthetic materials.[24–26,37] Therefore, it is still a tremendous challenge to take advantage of dynamic covalent bonds to develop a robust SSMH system with satisfying shape memory performances from the commercially available and cheap starting materials.

Inspired by the work of Théato’s group,[38] we herein put forward a simple preparation method to construct a PAAm/PVA–borate hydrogel system, which employs high-efficiency borate ester bonds to realize controlled shape memory properties. As schemed in **Scheme 1**, the PAAm/PVA hydrogel was prepared by radical polymerization of AAm and the Bis crosslinker in the presence of PVA. After being deformed under external forces and treated with aqueous borax solutions, the new temporary profile will be efficiently memorized due to the formation of temporary boronate ester crosslinks. This strategy has the following strength: a) All of the raw materials are commercially available at cheap price, rather than the phenylboronic acid group-functionalized materials prepared by complicated synthetic methods in previous works;[24,26,37] b) the shape fixity ratios and efficiency can be continuously adjusted by exposing to aqueous borax solutions of different concentrations. Large density of temporary borate ester bond crosslinks can be easily produced by treating the hydrogels in high-concentration borax solutions,[38] which is favorable for high shape memory fixity; c) because of the multiresponsive nature of the boronate ester bonds,[38–40] the shape recovery process of our hydrogel could be triggered by diverse stimuli such as acid, monosaccharides, leading to multiresponsive SSMH system.

2. Results and Discussion

The PAAm/PVA hydrogels were obtained by the thermoinduced radical polymerization of AAm and the Bis crosslinker in the presence of PVA. On the basis of the possible modulation of the shape memory property, five hydrogel samples with

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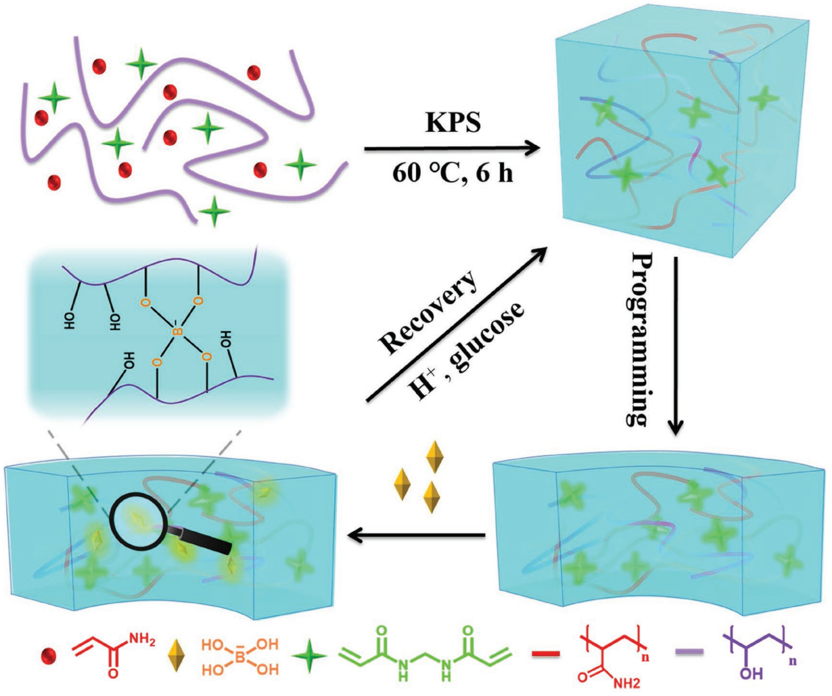

Scheme 1. Preparation of PAAm/PVA hydrogel and its shape memory mechanism based on the dynamic borax-diol chemistry.

different PVA contents were synthesized by varying the feed ratio of AAm/PVA (see **Table 1**) and named as Sample A to E, respectively.

Owing to the efficient chemical reaction between the adjacent hydroxyl groups of PVA and borax, when the PAAm/PVA hydrogel sample is deformed into a temporary shape and drenched into borax solution, the new profile will be quickly fixed. In order to investigate the influence of PVA contents on the shape memory performance of the PAAm/PVA hydrogels, these five hydrogel samples (Sample A to E) were cut into the flat and straight hydrogel stripes and treated in aqueous borax solutions of the same concentration for the same time. As shown in **Figure 1**a,b, with an increase of the PVA content, the shape fixity ratio (R_f) increases from 39.3% (Sample A) to above 95% (Sample E). When the mass ratio of AAm/PVA is fixed as 2:1 (Sample C), the R_f can reach as high as 90% or so after being immersed into 0.08 M borax solution for only 5 min. Although Sample D/E with higher PVA content has better shape memory performances, their mechanical properties decrease dramatically. Therefore, Sample C with both satisfying mechanical and shape memory properties were chosen and subject to further study.

The influence of the borax concentration on the R_f of the gels was then investigated and the results are shown in Figure 1c. As the concentration of borax solutions increases from 0.01 to 0.08 M, the R_f of Sample C increases from 41.6 to 90.4% for the same period (5 min). This finding can be easily understood because higher borax concentration will result in higher density of temporary boronate ester bond-based crosslinks. Furthermore, the effect of memorizing time on the R_f of gels was also investigated. As illustrated in Figure 1d, R_f of Sample C can reach 63.1% after being soaked in 0.08 M borax solution for just 1 min. Remarkably, the R_f can be above 90% after only 5 min, suggesting the relatively fast shape memory speed compared with the previously reported systems based on the dynamic phenylboronic-diol ester bonds between macromolecules.[37]

Enlightened by the fast shape memory speed and quite good shape fixity ratio of our hydrogel system, we try to test the possibility of fixing more complicated temporary shapes. As shown in **Figure 2**a–f, when the hydrogels were cut into 2D rectangle or butterfly shapes and changed into the 3D temporary shapes by external forces, the new 3D temporary profiles will soon be fixed after being treated by aqueous borax solution. Moreover, the dynamic PVA–borax ester bonds may also endow our hydrogels with self-healing property. As shown in Figure S1 (Supporting Information), two parts of the PAAm/PVA hydrogel, after cutting from a dumbbell-shaped sample, are able to self-heal in aqueous borax solution, as is evidenced by the tensile tests. Note that the healed Sample C has larger tensile strength than that of original Sample C, because healing the hydrogel sample in borax solution will result in the formation of the second borax-diol ester bond-crosslinked polymer network, which can serve as sacrificial bonds to effectively dissipate energy in tensile strength. The satisfying shape memory and self-healing capacities then encourage us to combine these two functionalities to fix complex and meaningful characters. For example, the abbreviated name "NIMTE" of our institute could be displayed (Figure 2g–h), in which the "N" and "M" letters are fixed via shape memory process, while the "T" and "E" letters are fixed via self-healing process. This

Table 1. Preparation formula of the PAAm/PVA hydrogel samples.

Hydrogel	AAm [g]	PVA (10% wt) [g]	Bis (10 mg mL^{-1}) [µL]	KPS (25 mg mL^{-1}) [µL]	Deionized water [mL]
Sample A	0.6	2.0	60	120	1.40
Sample B	0.5	2.0	50	100	1.00
Sample C	0.5	2.5	50	100	0.75
Sample D	0.6	4.0	60	120	0.40
Sample E	0.4	4.0	40	80	0.00

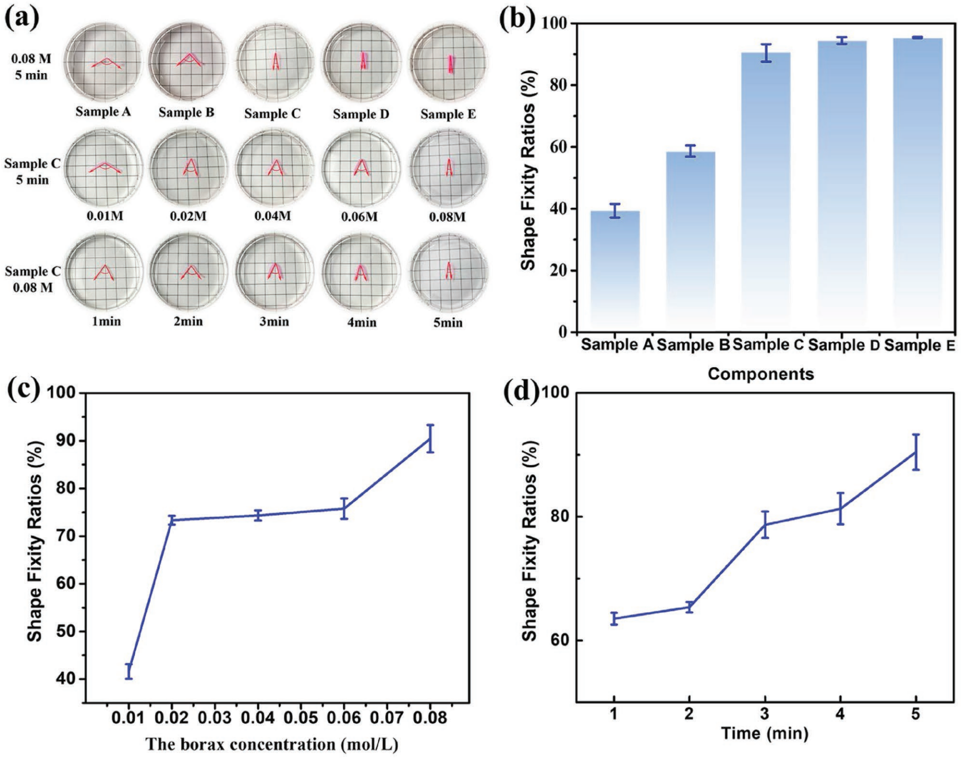

Figure 1. a) Shape memory images of five different hydrogel samples; b) shape memory ratios of five hydrogels samples obtained in the same borax solutions for the same period; c) shape memory ratios of hydrogel Sample C as a function of the borax concentrations for the same period (5 min); d) shape memory ratios of hydrogel Sample C as a function of time in the same borax solutions (0.08 M).

application is of significant interest as it may inspire the future development of novel and robust biomimic materials by combining the multi-functionalities of soft hydrogels (shape memory, self-healing, etc.)

It is well-known that the reversible PVA–borax boronate ester bonds are sensitive to many external stimuli (e.g. pH, glucose), indicating that our PAAm/PVA hydrogels may exhibit multiresponsive shape recovery performance. To assess the shape recovery behaviors, the fixed gel stripes were steeped into Na_2HPO_4-citrate buffer solutions with different pH or glucose solutions of various concentrations. As shown in Figures S2–S6 (Supporting Information), since the PVA–borax ester bonds can be destroyed when exposed to acid solutions, the memorized hydrogel stripes will gradually recover to the original straight shape. Similar results were also observed in aqueous glucose solutions (Figures S7–S11, Supporting Information). **Figure 3**a,b summarizes the shape recovery ratios as a function of time in different recovering solutions. All of these shape recovery ratios can reach nearly 100%, indicating that the dissociation of boronate ester bonds can lead to full recovery of the original state. Obviously, lower pH value or higher glucose

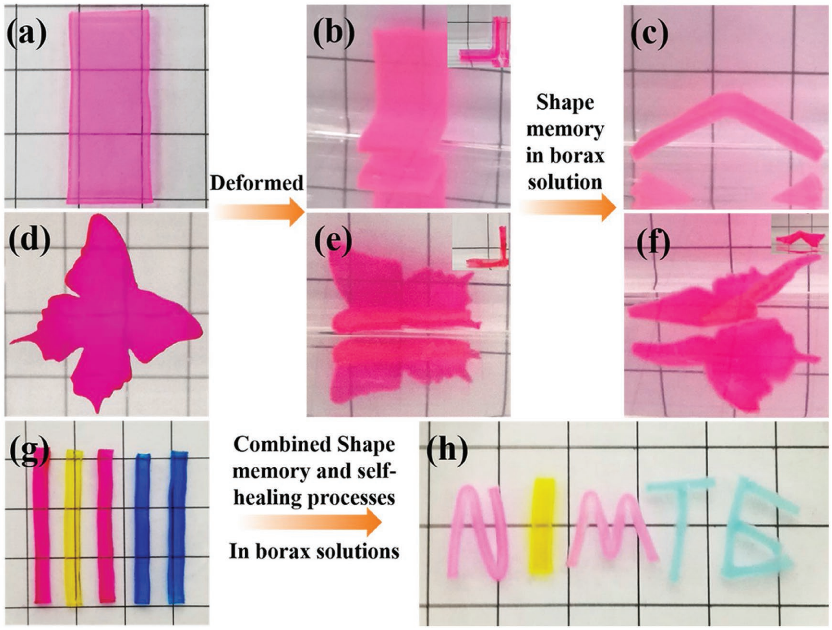

Figure 2. Shape memory images of the PAAm/PVA hydrogel Sample C: a,d) original shapes; b,e) deformed shapes; c,f) fixed temporary shapes; g) original hydrogel stripes with size of 30 mm × 3 mm × 1 mm dye tinged with red, yellow, and blue by rhodamine B, tartrazine, and erioglaucine disodium salt, respectively; h) fixed characters representing the abbreviated name “NIMTE” of our institute, in which the “N” and “M” letters are fixed via shape memory process, while the “T” and “E” letters are fixed via self-healing process. Shape memory experiments were conducted in 0.08 M borax solution for 5 min. The grid is 1 cm × 1 cm.

concentration is favorable for the faster shape recovery process because of the faster dissociation rate of the PVA–borax ester bonds. It is worth noting that the recovered time of our shape memory hydrogel systems could be continuously adjusted from several minutes to tens of minutes by different stimuli, suggesting their many potential applications. In addition, this “shape deformation-to-memory-to-recovery” cycle could be repeated at least three times (Figure S12, Supporting Information). Moreover, since the shape memory process was conducted in aqueous solution, the influence of the swelling behavior of hydrogels on their shape memory process was also investigated. As shown in Figure S13 (Supporting Information), both the mass and volume of the hydrogel Sample C increase by about six and four times after being treated in 0.08 M borax solution and deionized water for more than 10 h, respectively. However, only slight volume/mass increase is observed after 5–10 min, which is sufficient to complete the shape memory experiment. Therefore, we think it is reasonable to conclude that the shape memory process should not be influenced by the swell of hydrogels.

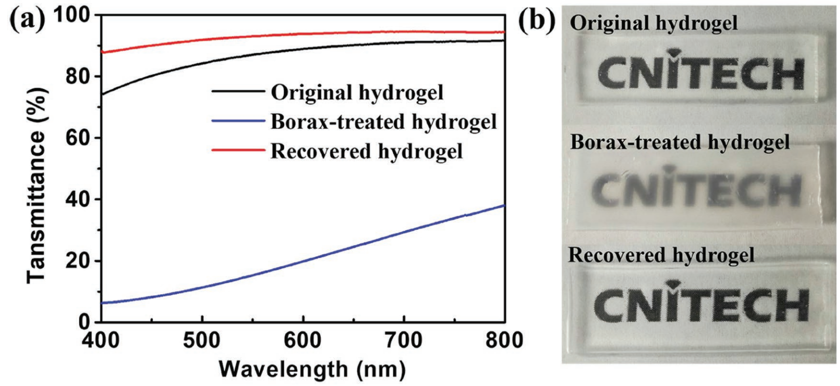

Figure 4. a) Transmittance curves and b) optical images of the original PAAm/PVA hydrogel (Sample C), as well as samples treated in aqueous 0.08 M borax solution for 5 min and retreated in Na_2HPO_4-citrate buffer solutions (pH = 2.2) for 7 min.

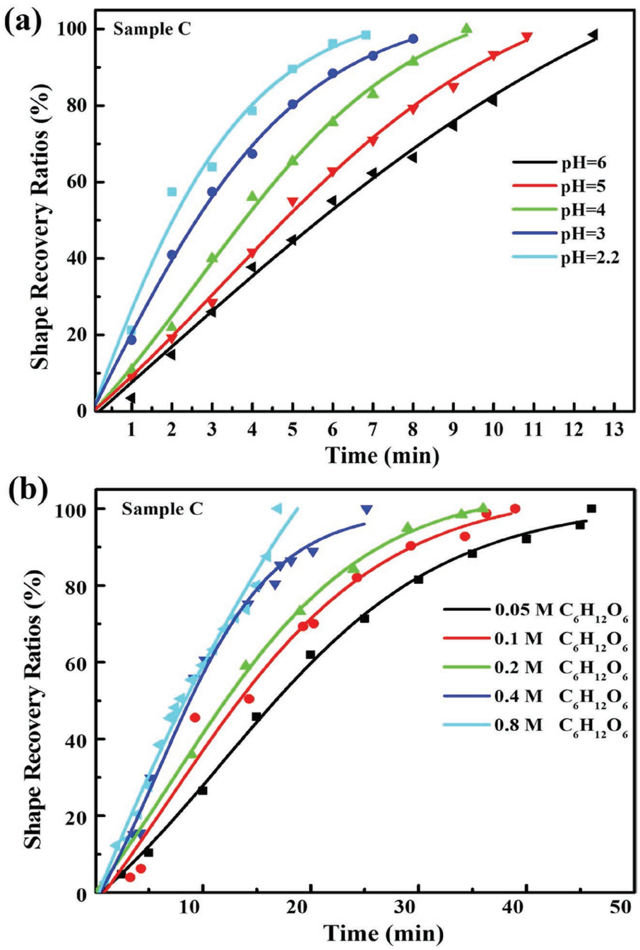

Figure 3. Recovery behaviors of the PAAm/PVA hydrogel C programmed in 0.08 M borax solution for 5 min a) in Na_2HPO_4-citrate buffer with different pH (pH = 2.2, 3, 4, 5, 6) and b) glucose solution with different concentration (0.05, 0.1, 0.2, 0.4, 0.8 M).

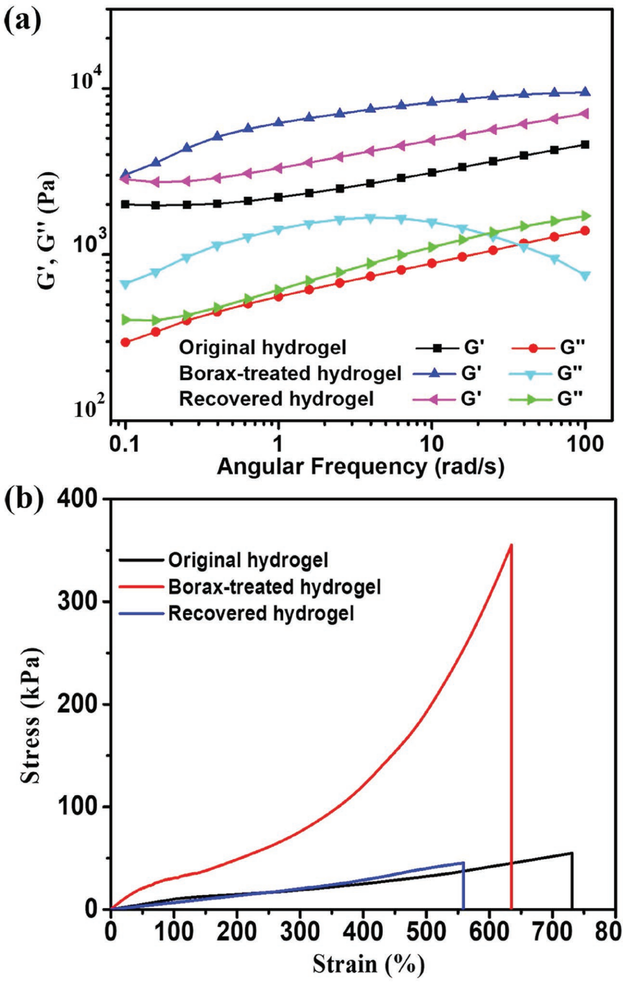

Figure 5. a) Rheology analysis and b) tensile stress–strain curves of the original PAAm/PVA hydrogel (Sample C), as well as samples treated in aqueous 0.08 M borax solution for 5 min and retreated in Na_2HPO_4-citrate buffer solutions (pH = 2.2) for 7 min.

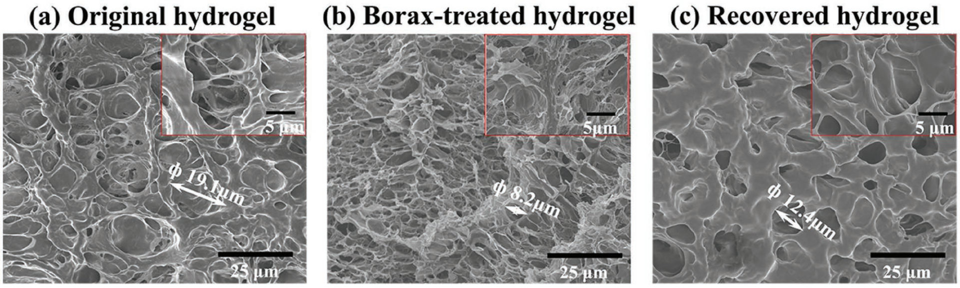

Figure 6. SEM images of the original PAAm/PVA hydrogel (Sample C), as well as samples treated in aqueous 0.08 M $Na_2B_4O_7$ solution for 5 min and retreated in Na_2HPO_4-citrate buffer solutions (pH = 2.2) for 7 min.

As mentioned above, the dynamic PVA–borax boronate ester bond was selected as the temporary switch and introduced into the chemically crosslinked PAAm network (permanent segment) to produce the PAAm/PVA shape memory hydrogel system. The shape memory mechanism was illustrated in Scheme 1. When the PAAm/PVA hydrogel is exposed to the aqueous borax solutions, the adjacent hydroxyl groups of PVA will immediately react with borax to form boronate ester bonds, resulting in a significant rise in the crosslinking density. The borax-treated hydrogel sample is thus expected to undergo large transmittance decrease, which is in good agreement with the experimental result. As shown in **Figure 4**, the transmittance value of the hydrogel at 550 nm falls from nearly 90% to less than 20% after being treated in aqueous borax solutions. The transparency change is obvious enough to be observed by naked eyes only. Remarkably, further treatment in acid solutions will recover the hydrogel transparency. It should be noted that the recovered transmittance value is virtually the same as that of the original hydrogel within experimental error. These results indicate that the temporary crosslinks have high density and can be totally destroyed, which is the reason why our hydrogel system has quite good shape memory/recovery properties.

More evidences for the formation and dissociation of temporary PVA–borax ester bond-based crosslinks come from the rheology, tensile, and scanning electron microscopy (SEM) characterizations. As illustrated in **Figure 5**a, the G′ and G″ values of the PAAm/PVA hydrogel sample increase when soaking in aqueous borax solutions and then recover after being treated in Na_2HPO_4-citrate buffer solutions (pH = 2.2). The underlying reason is that the PAAm/PVA hydrogel is strengthened by the formation of the temporary PVA–borax crosslinked second network during shape memory process. The significantly improved mechanical strength of the borax-treated hydrogel sample further demonstrates the formation of the temporary PVA–borax crosslinked second network, because the dynamic network can serves as a sacrificial network to dissipate stress generated during the deformation.[24] Additional SEM imaging measurements of the freeze-dried hydrogel samples give more direct evidence for the formation of the temporary second network. As shown in **Figure 6**a, a loosely porous crosslinked network is observed for the original PAAm/PVA hydrogel, while relatively small pores are observed for the temporary shape (Figure 6b), demonstrating soft matrices with high-density crosslinks. Further retreatment of the hydrogel in Na_2HPO_4-citrate buffer solutions (pH = 2.2) will recover the microscopic morphology (Figure 6c).

3. Conclusions

In summary, we have reported an utterly simple off-the-shelf shape memory hydrogel, produced from only several unmodified commercially available and cheap materials. Its design takes advantage of the highly reversible PVA–borax boronate ester bonds as temporary crosslinks, while the chemically crosslinked PAAm network is employed to fix the permanent shape. Due to the facile formation of high-density PVA–borax crosslinks in the PAAm–PVA hydrogel system, the proposed system is endowed with quite good shape memory ratios/rates. Especially, the shape memory/recovery time of our hydrogel system could be continuously adjusted from several minutes to tens of minutes by different stimuli, suggesting its many potential applications.

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

double network hydrogels, dynamic covalent bonds, facile shape memory, multiresponsive

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