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Article

Nanogel Crosslinking-Based Belousov–Zhabotinsky Self-Oscillating Polyacrylamide Gel with Improved Mechanical Properties and Fast Oscillatory Response

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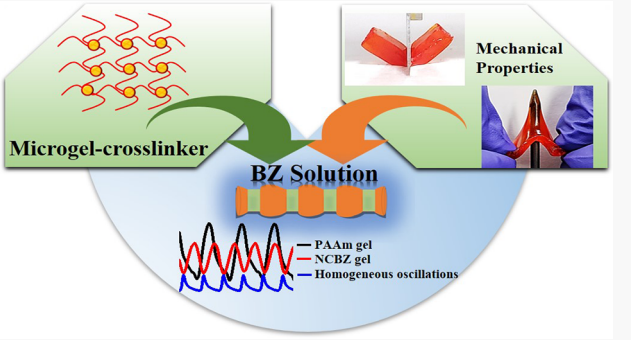
ABSTRACT: The Belousov–Zhabotinsky (BZ) self-oscillating gel is a unique actuator suited for studying the behavior of intelligent soft robots. However, the traditional BZ self-oscillating polyacrylamide (PAAm) gel is easily broken and is slow to response to stimuli, which limits its practical application. Therefore, the preparation of BZ gels with sensitive responses to external stimuli and desirable, robust mechanical properties remains a challenge. In this work, PAAm-activated nanogels with unpolymerized double bonds are used as nanocrosslinkers to synthesize a nanogel crosslinking-based BZ (NCBZ) self-oscillating PAAm gel, whose mechanical properties, for example, antipuncture, cutting, and tensile properties, are superior to those of traditional PAAm BZ-self-oscillating gels. The oscillatory period of the traditional gel is much longer than that of the corresponding homogeneous BZ system, resulting from the slow response of the gel to changes in redox potential, whereas large, interconnected pores inside the NCBZ gel provide efficient channels for rapid species transport, supporting fast response of the gel, which results in almost the same period of chemomechanical oscillations as the homogeneous system under the same conditions. Scanning electron microscopy results show that the NCBZ gel is more stable than the traditional BZ PAAm gel after 7 h of oscillation. Our results make it possible to prepare robust gel motors and provide promising application prospects for smart soft robots, actuators, sensors, tissue engineering, and other applications.



INTRODUCTION

In recent years, a great deal of work has been devoted to the design, preparation, and utilization of stimulus-responsive gels.[1] Such gels can perceive and respond to changes in external stimuli, including pH, temperature, or concentration;[2−6] they can be incorporated into various smart materials.[7] The Belousov–Zhabotinsky (BZ) self-oscillating gel, a form of active soft matter first synthesized by Yoshida,[7−9] is special among these stimuli-responsive gels in its ability to autonomously, reversibly, and repeatedly convert chemical energy to mechanical energy without external stimuli. Due to these unique self-oscillating properties, many biomimetic behaviors can be obtained that resemble heartbeat, periodic hormone secretion, and biological rhythms.[10−12] Moreover, movement driven by chemical waves has the same essential mechanism as nerve-driven muscle movement, so these gels can generate various forms of motion, such as retrograde and direct-wave locomotion,[13] photophobic and phototropic movement,[14] angular motion driven by spiral waves,[15] and accelerated motion produced through sensing the shape of a water surface,[16] which has significant potential application in the design of autonomous robots,[17] small-scale motors,[18] and drug delivery tools.[19]

Responsiveness and toughness are crucial to the adaptation and migration of stimuli-responsive gels when interacting with the surrounding environment.[20] The response indicates that the stimulus-response gel can rapidly respond to the received signal or stimulus to form deformation or rapid movement. Toughness means that the stimuli-responsive gel can ensure the integrity and stability of the structure in the complex and even harsh external environment, so that it can work normally. For the traditional BZ self-oscillating gel, slow responsiveness and week toughness in BZ reaction medium remain to be solved. First, the solution diffusion is limited due to the heterogeneity of the gel system,[21] leading to lag of gel

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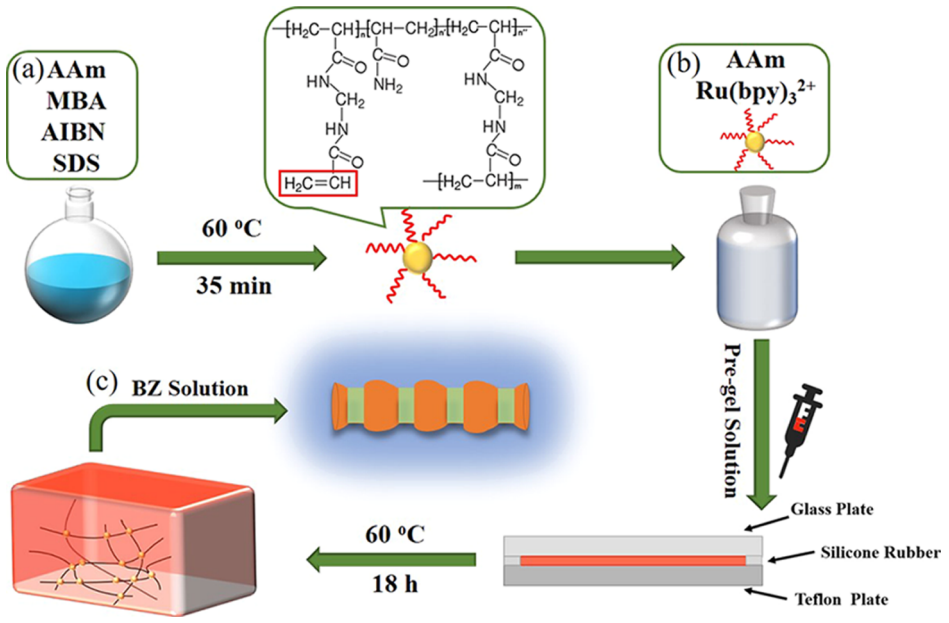

Figure 1. Schematic diagram of the synthesis and spatiotemporal dynamics of the NCBZ gel. (a) Reactants for fabrication of the activated PAAm nanogel. (b) Reactants for preparation of the NCBZ gel. (c) Spatiotemporal dynamics of the NCBZ gel. Gel swells at Ru (II) (orange part) and deswells at Ru (III) (green part).

responsiveness[22] and longer oscillatory period of the traditional BZ gel than that of the corresponding homogeneous system under the same condition. Second, the spatial structure of the traditional BZ self-oscillating gel is easy to degrade and destroy in acidic BZ reacting solution. These two shortcomings are caused by ingredients and geometric structure of the gel, including monomer stability, crosslinking distribution, size, deepness and connection of pores, and so on.

Suzuki et al.[23,24] synthesized a series of BZ microgels that can be oscillated at high frequencies without diffusive delay. However, the synthesized macrogel was too brittle, that is,[24] leading to low mechanical stability, because the traditional BZ gel has relatively weak mechanical properties (i.e., low tensile strength and low Young modulus).[25] In addition, the gel will slowly degrade and rupture in alternate swelling and deswelling of BZ reacting solution. Therefore, improving the toughness of the BZ macrogel is the key to practical application. Three types of tough gels have been prepared: double network structure gels,[26] topological gels,[27] and nanocomposite gels.[28−30] However, only toughness is not enough for the BZ self-oscillating gel, and high responsiveness is also important to retain its activities. A mechanically enhanced gel prepared with an activated nanogel[30] as the crosslinking agent does not introduce other components into the system, thereby ensuring that the pore structure in gel is relatively uniform with rapid response and high mechanical properties.

In this study, we synthesize a nanogel crosslinking-based BZ (NCBZ) self-oscillating gel with swelling−deswelling properties based on the strategy of using an activated polyacrylamide (PAAm) nanogel as a crosslinker, where the first key step is to synthesize the activated nanogel. The second process involves the use of a polyacrylamide (PAAm) BZ self-oscillating gel prepared by thermally initiating crosslinking of the activated nanogel, acrylamide monomers, and the BZ reaction catalyst, $Ru(bpy)_3^{2+}$. We investigate the structural and mechanical properties as well as the nonlinear spatiotemporal dynamics of the synthesized gels. Compared with the traditional PAAm BZ self-oscillating gel,[31] the NCBZ gel used here exhibits improved mechanical properties and an oscillatory frequency closer to that of a homogeneous system.

EXPERIMENTAL SECTION

Materials. Acrylamide (AAm, purity 99.9%) (Aladdin Biochemical Technology Co. Ltd., Shanghai, China), N,N′-methylenebis(acrylamide) (MBAA), sodium dodecyl sulfonate (SDS), azobisisobutyronitrile (AIBN), dimethyl sulfoxide (DMSO), malonic acid (MA), sodium bromate ($NaBrO_3$), and nitric acid (HNO_3) were all purchased from Sinopharm Chemical Reagent Co., Ltd., China and used without further purification. Ruthenium (4-vinyl-4′-methyl-2,2′-bipyridine) bis(2,2′-bipyridine) bis(hexafluorophosphate) ($Ru(bpy)_3^{2+}$) was synthesized according to the literature,[32] and Milli-Q water (18.2 MΩ) was used in all experiments.

Synthesis of PAAm-Activated Nanogels. The PAAm-activated nanogel was synthesized according to the method of Xia et al.,[30] changing the monomer to AAm and the initiator to AIBN. A schematic diagram of the synthesis of the NCBZ self-oscillating PAAm gel in this study is shown in Figure 1. First, AAm and MBAA were added to 50 mL of deaerated water at room temperature ([AAm] = 0.2 mmol/mL and [MBAA] = 0.008 mmol/mL). After stirring and dissolving the above-mentioned mixture, 1 ml of methanol solution containing 0.1 mmol AIBN was added, followed by 1 mmol surfactant SDS. When the solution was uniform, the water bath was heated to 60 °C, and the activated nanogel with unsaturated bonds was obtained after 35 min. The activated nanogel was stored at 0 °C.

Synthesis of NCBZ Self-Oscillating PAAm Gels. Compared with the traditional method of synthesizing a PAAm gel, the method used for synthesizing NCBZ PAAm gels employed here is simpler and faster. In the first step, AAm (2 mmol) and $Ru(bpy)_3^{2+}$ (0.013 mmol) were dissolved in DMSO. After the solid was completely dissolved using ultrasound, the activated nanogel solution was slowly added

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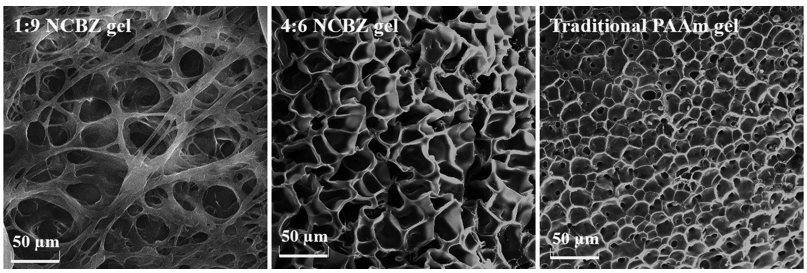

Figure 2. SEM micrographs of an NCBZ gel and a traditional PAAm gel before BZ reaction. The magnification is 500×.

to the solution (the volume ratios for DMSO: activated nanogel were 1:9, 2:8, 3:7, 4:6, 5:5, and 6:4). In the second step, the mixed solution was rapidly injected into a glass tube with a diameter of 1.0 mm, the ends of the tube were sealed, and then, the solution was polymerized at 60 °C for 18 h. After gelation, the resulting NCBZ gel was soaked in methanol to remove unreacted reagents and then stored in pure water. We also synthesized gels with a thickness of 2.5 mm for rheological measurements and antipuncture tests.

To compare the mechanical properties between the NCBZ and traditional PAAm gels, we synthesized PAAm gels (MBAA = 0.025 mmol/mL) according to the method of Yuan et al.[31]

Tensile Test. Uniaxial tensile tests of hydrogels were carried out on a universal material testing machine UTM4202XS (SANS). The sample was cut into a rectangular shape (length is approximately 30.0 mm, width is approximately 13.0 mm, and thickness is approximately 2.5 mm). A Vernier caliper is used to measure the actual size of the hydrogel, and both ends of the sample were connected to the fixture, where the lower clamp is fixed. The force−displacement curve is obtained by pulling the upper clamp at a constant speed of 3 mm/min at room temperature. The stress−strain curves for the NCBZ gel and traditional BZ gel are obtained from the force-displacement determination.

RESULTS AND DISCUSSION

SEM Structure of the NCBZ Gels. The gold film was sprayed on freeze-dried samples, and the microstructure of the NCBZ self-oscillating PAAm gel was observed by scanning electron microscopy (SEM). Figure 2 shows that the NCBZ self-oscillating PAAm gel has an obvious three-dimensional net structure that is composed of pores and walls, which is conducive to diffusion of solution and stability of the mechanical properties. Because the nanogels contain unpolymerized double bonds, which act as cross-linkers during the gel synthesis process. Therefore, high cross-link density (i.e., low volume ratio of DMSO to nanogel) causes low porosity and high density of walls. When the content of the activated nanogel was decreased, the cross-linking structure of the NCBZ gel gradually became soft and cottony after water absorption, leading to lowered mechanical strength of the gel. Compared with the NCBZ gel, the traditional PAAm gel has the disadvantage of smaller pores with no obvious interconnected structure, resulting in poor mechanical properties of the gel unfavorable to the diffusion and transport at of solution through the network.

Mechanical Properties of the NCBZ Gels. *Macroscopic Visualization of Mechanical Properties.* Using an activated nanogel as a crosslinking agent contributes to the homogenization of our NCBZ gel network structure that dissipate the external load evenly, thereby resulting in the enhanced mechanical strength and toughness. In the following experiments, we chose a gel sample with a volume ratio (DMSO/activated nanogel) of 1:9 for testing. This gel showed high elasticity and deformability. The gel can withstand large mechanical deformation, including tensile strain and distortion, without damaging its structure (Figure 3a,b).

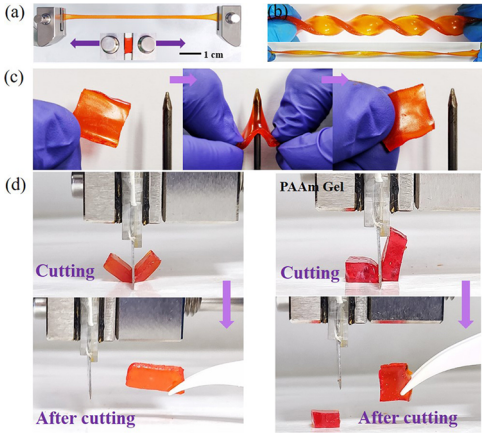

Figure 3. NCBZ gels can be significantly deformed in various ways: (a) Linear stretching. (b) Twist stretching without rupture. (c) Antipuncture. (d) Anticutting, under the same conditions. The righthand panels show that the traditional PAAm gel is directly cut into two parts.

As shown in Figure 3c, when the gel (20 mm × 20 mm × 2.5 mm) was punctured, it became thin and transparent without penetration.[33] After this test, the gel maintained its integrity. Under the same conditions, the traditional PAAm gel was easily fractured under small pressure (Figure S1 in Supporting Information). The NCBZ gel also exhibited excellent mechanical properties under extreme conditions. When the sharp blade moved downward slowly into a gel for 2.5 mm, the NCBZ gel withstood cutting without breaking, as shown in the left column of Figures 3d and S2 in the Supporting Information. However, under the same conditions, the traditional PAAm gel was easily divided into two parts by the blade (right column of Figure 3d). The abovementioned macroscopic visualization of mechanical properties shows that the activated nanogel as a crosslinking agent can significantly improve the toughness of NCBZ gels, enabling soft robots made from such gels to perform in harsh and complex environments.

Tensile Properties of the NCBZ Gel. Generally, the mechanical properties of BZ gels are determined and regulated by the amount of the crosslinking agent. However, a higher MBAA content also leads to brittleness of the traditional PAAm BZ gel, resulting in relatively low toughness. The origin

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of the improved mechanical properties of the NCBZ gel lies in the microstructure of the activated nanogel: there is a longer PAAm chain between activated nanogels, which can change the conformation of the activated nanogel and bear greater stress.[30] Figure 4 shows the tensile stress−strain curves of

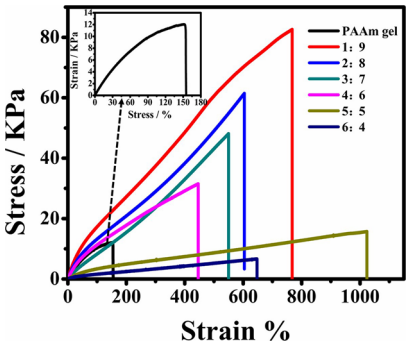

Figure 4. Tensile stress−strain curves of NCBZ gels for different volume ratios of DMSO and activated nanogel. The inset is an enlarged curve for the traditional PAAm gel.

the NCBZ gels prepared with different solvent/nanogel volume ratios. For comparison, the tensile stress−strain curve for a traditional PAAm gel is also included in Figure 4. When the volume ratio of the activated nanogel was decreased from 90 to 40%, the tensile strength of the gel decreased from 84 to 9 kPa, suggesting that a lower proportion of the activated nanogel leads to less desirable mechanical properties. Increasing the volume ratio of activated nanogels is equivalent to increasing the molecular chain density, while reducing the porosity of hydrogels, both of which increase fracture resistance and toughness.

The elongation at break first decreases and then reaches a maximum of 1040% when the volume ratio is 5:5, due to the optimal three-dimensional crosslinking structural integrity. The traditional PAAm gel had a lower tensile strength and elongation length (11.9 kPa, 153%). In summary, the mechanical properties of the BZ gel were significantly improved by using an activated nanogel as the crosslinking agent.

The rheological measurements in Figure S3 in Part 3 of the Supporting Information show that when the dynamic storage modulus (G') was approximately the same ($G'_{\text{NCBZ gel(DMSO/activated nanogel = 1:9)}}$ = 780 Pa, $G'_{\text{PAAm gel}}$ = 676 Pa), the amount of MBAA used in the traditional PAAm gel was approximately 3.4 times that in the NCBZ gel.

Stimulus Responsiveness, Pulse Waves, and Local Oscillations in an NCBZ Self-Oscillating PAAm Gel. We measured the swelling−deswelling properties of an NCBZ self-oscillating PAAm because these constitute the basis for the functionality of the BZ gel. PAAm gels are acidity-responsive due to ionizable groups in polymer chains.[34] In the following, we used an NCBZ gel fabricated with a 4:6 volume ratio of DMSO to activated nanogel to optimize stimulus-responsiveness and gel strength. According to the criterion of NCBZ gels for spatiotemporal swelling−deswelling oscillations, both excellent toughness, that is, the ability for adsorbing energy

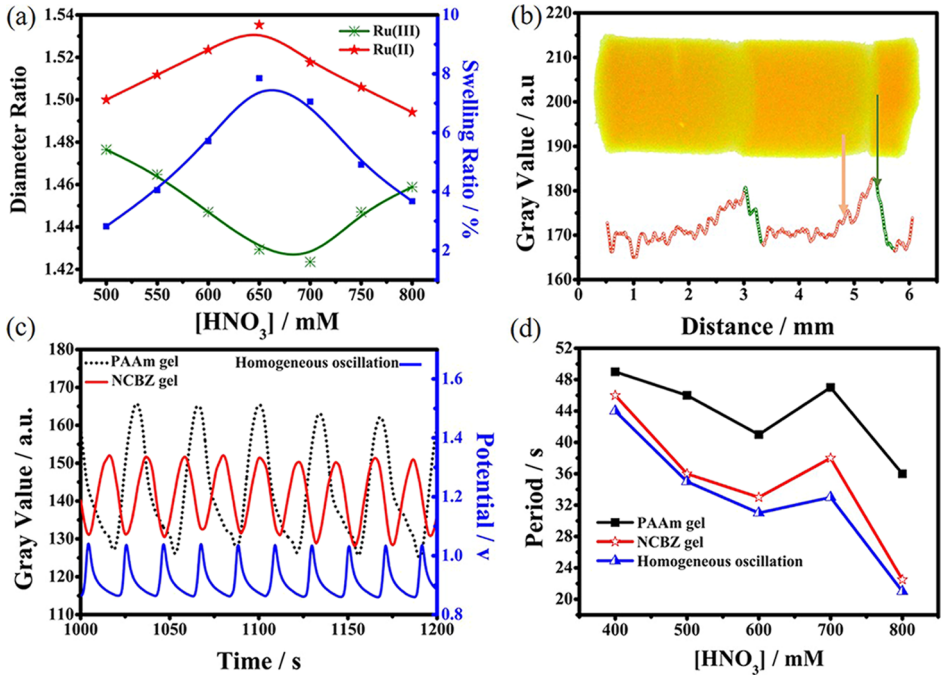

Figure 5. Stimulus responsiveness, pulse waves, and local oscillations for an NCBZ gel. (a) Effect of $[HNO_3]$ on the responsiveness of the NCBZ gel (volume ratio of DMSO to activated nanogel is 4:6). The red, green, and blue lines denote R_{red}/R_{ori}, R_{oxd}/R_{ori} and $[(R_{red} - R_{oxd})/R_{ori}] \times 100\%$. Experimental conditions: $[Ce_2(SO_4)_3]$ = 0.001 M, $[Ce(SO_4)_2]$ = 0.001 M. (b) Snapshot and gray-value spatial curve of pulse waves in a cylindrical NCBZ gel. Gray values are proportional to the concentration of the oxidized form of the Ru(II) catalyst. (c) Time series of the local gray value and potential in the traditional BZ self-oscillating PAAm gel (black dotted line), NCBZ gel (red solid line), and homogeneous BZ system (blue solid line). Gray value and potential are proportional to the catalyst concentration of the reduced and oxidized form, respectively. (d) Oscillatory period vs $[HNO_3]$ in traditional BZ self-oscillating PAAm gel [black, ($[Ru]^{2+/3+}$ = 0.01 M)], NCBZ gel (red), and homogeneous solution (blue). Experimental conditions: gel length = 5 mm; $D_{\text{traditional PAAm gel}}$ = 1.2 mm, $D_{\text{NCBZ gel}}$ = 1.8 mm; $[MA]_0$ = 0.2 M; $[NaBrO_3]_0$ = 0.2 M; I = 34.2 μW/cm^2 (LED white light); T = 22.0 ± 0.1 °C.

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per unit volume (i.e., increasing the loaded stress) before breaking, and good swelling−deswelling property are important. A high crosslinking density results in a decrease in the swelling−deswelling properties, that is, if the volume ratio of DMSO to activated nanogel is too low, the gel shows unobvious volume oscillations; and too high a volume ratio of DMSO to activated nanogel leads to low tensile stress (brown and deep-blue lines in Figure 4), that is, weak toughness. There is an important distinction between the mechanical response of the PAAm-based and PNIPAAm-based BZ gels to the change in the oxidation state of the ruthenium catalyst, caused by different mechanisms analyzed in detail by Yuan et al.[31] For NCBZ self-oscillating PAAm gels, the change in the oxidation state of Ru centers mediates intra-/interchain segmental interactions, so that additional crosslinks are formed upon Ru oxidation, leading to removal of water out of the gel matrix and shrinking of the gel. The gel swells when the reversible additional crosslinking is destroyed in the reduced state to restore the original low crosslink density. For PNIPAAm gels reported by Yoshida et al.,[7] the osmotic forces due to the difference of the solvation of Ru(III/II) centers result in a higher degree of swelling when Ru is oxidized. For NCBZ self-oscillating PAAm gels, the change in the oxidation state of Ru centers mediates intra-/interchain segmental interactions, so that additional crosslinks are formed up Ru(II) oxidation, leading to removal of water out of the gel matrix and shrinking of the gel. The gel gets swelling when the reversible crosslinking is destroyed in the reduced state to restore the original low crosslink density. For PNIPAAm gels reported by Yoshida et al.,[7] the osmotic forces due to the difference of the solvation of Ru(III/II) centers result in a higher degree of swelling when Ru is oxidized. The swelling−deswelling ratio for gels containing Ru(III)/(II) under different acidity conditions is shown in Figure 5a. In the reduced state, the swelling ratio of the gel first increases and then decreases with increasing acidity, while in the oxidized state, it first falls and then rises. To characterize the difference in the swelling−deswelling ratio of the gels in the two oxidation states, we introduce the concept of a swelling ratio (R)

$$R = [(R_{red} - R_{oxd})/R_{ori}] \times 100\% \quad (1)$$

In eq 1, where R_{red}, R_{oxd}, and R_{ori} are the diameters of NCBZ-Ru(II) gel in acidic solution, NCBZ-Ru(III) gel in acidic solution, and NCBZ-Ru(II) gel in Milli-Q pure water (R_{ori} = 1.8 mm), respectively. Both R_{red}/R_{ori} and R_{oxd}/R_{ori} are bigger than one because the NCBZ-Ru(III)/(II) gel swells in acidic solution. The difference between the two diameter curves reaches a maximum of 10.7% at an acidity of 0.65 M. Even though the swelling ratio of the NCBZ gel is slightly lower than that of the traditional PAAm gel at the same acidity shown in Figure S4 in the Supporting Information (11.6%), the NCBZ gel still maintains good stimulus responsiveness.

A cylindrical traditional gel and an NCBZ gel were immersed in a 15 mL solution containing MA, HNO_3, and $NaBrO_3$ without the catalyst. When the BZ solution was gradually diffused into the gel system, the gels produced stable pulse waves (Figure 5b). Figure 5c shows the oscillations of the local gray value in the traditional BZ PAAm gel and the NCBZ gel and potential oscillations of the homogeneous system under the same BZ reagent concentrations. Experimental details of image collection, local oscillations, and homogeneous oscillations are shown in part 5 of the Supporting Information. Swelling and deswelling curves of the NCBZ gel and traditional PAAm gel are shown in Figure S5 in part 6 of Supporting Information. By comparing the diameter evolutions between the NCBZ gel and traditional PAAm gel from Ru (II) to Ru(III), the deswelling time $t_{Ru(II)/(III)}$ of the PAAm gel is about twice of that of the NCBZ gel, that is, the response of the NCBZ gel is fast. In Figure 5d, we can also observe that the oscillation period of the NCBZ gel is almost the same as that of the homogeneous system and significantly shorter than that of the traditional BZ PAAm gel, indicating that the NCBZ gel displays a faster response, resulting from the larger and deeper pores in the NCBZ gel than in the traditional BZ PAAm gel, which provide efficient channels for rapid species transportation.

Comparison of BZ Oscillation-Induced Microstructure Degradation of Traditional Gel and NCBZ Gel. Traditional PAAm and NCBZ gels were reacted in BZ solution (without catalyst) for 7 h and then purified in pure water for 3 h to replace the BZ solution in the gel before being freeze-dried for SEM characterization. By comparing the micrographs before and after oscillations, after 7 h of the BZ reaction (Figure 6), the network structure of the traditional hydrogel is seen to be seriously damaged and largely collapsed. However, for the NCBZ hydrogel, the spatial structure of the gel is only partially damaged after oscillation, but the overall gel spatial framework remains intact. Thus, activated nanogels as crosslinking agents strongly enhance the structural robustness of BZ self-oscillating gels.

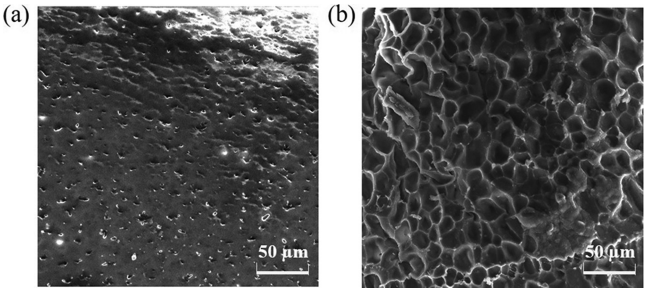

Figure 6. SEM micrographs of the BZ gel after 7 h oscillations. (a)Traditional PAAm gel. (b) NCBZ gel. The magnification is 500×. Experimental conditions: $[MA]_0$ = 0.2 M, $[HNO_3]_0$ = 0.8 M, $[NaBrO_3]_0$ = 0.2 M, T = 22.0 ± 0.1 °C.

CONCLUSIONS

In this paper, we report an activated NCBZ self-oscillating PAAm gel with excellent, robust mechanical properties, and fast response. This work demonstrates the rapid transport of species in a three-dimensional gel, leading to a small difference in the oscillatory period between our NCBZ gel and a homogeneous BZ system. Tensile properties, antipuncture and anticutting behavior, and resistance to BZ oscillation-induced microstructure degradation indicate that significantly enhanced mechanical properties result from the more homogeneous network in this novel hydrogel. Such self-oscillating stimuli-responsive gels with fast response and improved mechanical properties are excellent candidates for use in more adaptable soft robots, their miniaturization, and collective behavior.[18,35−38]

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.1c07996.

Antipuncture test of the gel, anticutting property of the gel, rheological measurement, swelling−deswelling ratio of the PAAm gel, experimental details for spatiotemporal dynamics, and comparison of stimulus-responsive evolution between NCBZ and traditional BZ self-oscillating PAAm gel (PDF)

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Notes

The authors declare no competing financial interest.

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