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Capillarity-Induced Propagation Reversal of Chemical Waves in a Self-oscillating Gel

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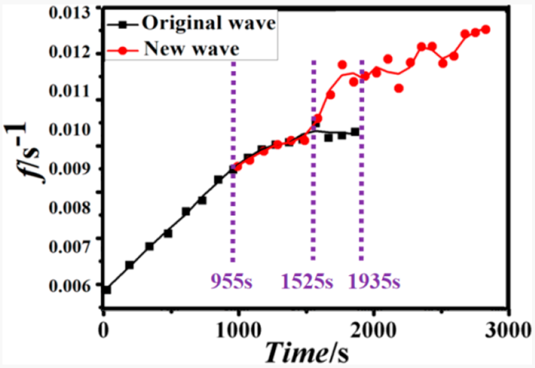
ABSTRACT: In a self-oscillating gel, unidirectional chemical waves generated by the Belousov−Zhabotinsky reaction can drive locomotion, which results from the difference between the push and pull forces in the wavefront and waveback, respectively. In a narrow tube, such a gel is subject not only to the asymmetric force engendered by the propagation of the chemical waves but also to additional forces originating from the capillary effect in the polymer skeleton. The ends of a self-oscillating gel in a tube are squeezed unequally during unidirectional motion, causing new waves of higher frequency and ultimately giving rise to reversal of the direction of chemical wave propagation. This peculiar phenomenon of a self-oscillating gel in a narrow glass tube results in a nonmonotonic evolution of the gel locomotion velocity.



INTRODUCTION

In living organisms, motility typically relies on the transduction of chemical to mechanical energy. In recent years, the design of artificial actuators has been extensively studied to establish how mechanical work[1] may be obtained from other forms of energy. A typical material used in artificial actuators is a polymer gel, due to the fact that such substances can undergo the changes in shape and volume that are inherent to movement. A polymer gel covalently bonding the metal catalyst for the oscillatory Belousov−Zhabotinsky (BZ) reaction[2] can swell and shrink as a result of the periodic changes in the redox state of the ruthenium catalyst to realize this form of energy conversion.[3] A biomimetic walking actuator has been constructed, for example, from a poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gel that exhibits spontaneous oscillations in a BZ solution without requiring any on−off switching of external stimuli.[4] Further investigations demonstrated that this system can undergo photosensitive locomotion (phototaxis) under heterogeneous illumination.[5−7]

Chemical waves in BZ gels have been widely studied in recent decades.[8−11] It was found that these waves can be regulated via asymmetry,[12] and chemical oscillations in heterogeneous BZ gels can be controlled via mechanical strain.[13] In addition, BZ gels can sense external mechanical forces to trigger chemical waves.[14]

In other words, BZ gels can not only convert chemical energy into mechanical movement, but also *vice versa*. In this work, we examine how the locomotion of a BZ self-oscillating gel can cause reversal in the direction of propagation of chemical waves in that gel. We initiate chemical waves in a BZ self-oscillating gel in a capillary open at both ends and immersed in a BZ solution. We find that the chemical waves in the gel spontaneously reverse their propagation direction as the result of capillary forces, and we study how the time needed for reversal depends on the reactant concentrations.

EXPERIMENTAL SECTION

Materials. All chemicals (*N*-isopropylacrylamide (Tokyo Chemical Industry Co Ltd.), *N*,*N*-methylenebis(acrylamide) (Sinopharm Chemical Reagent Co Ltd.), azodiisobutyronitrile (Sinopharm Chemical Reagent Co Ltd.), 2-acrylamide-2-methylpropanesulfonic acid (Sinopharm Chemical Reagent Co Ltd.), malonic acid (Sigma-Aldrich), sodium bromate (Sinopharm Chemical Reagent Co Ltd.), and nitric acid (Sinopharm Chemical Reagent Co Ltd.)) were used without further purification. (Ru(bpy)$_2$(4-acryloylmethyl-4′-methyl-bpy)$^{2+}$ was synthesized according to the literature,[15] and the details are shown in the Supporting Information. All stock solutions were prepared with distilled water having a resistivity of 18.2 MΩ cm obtained from a Milli-Q purification system.

Synthesis and Characterization of Capillary BZ Gels. In this work, we synthesized a photosensitive gel, poly(NIPAAm-*co*-Ru(bpy)$_3$-AMPS), inside a narrow glass tube. Poly(NIPAAm-*co*-Ru(bpy)$_3$-*co*-AMPS) gels were prepared as follows. (Synthesis and characterization can be found in part 1

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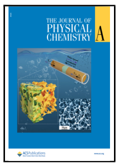

of the Supporting Information.) For the monomer solution, NIPAAm (1525 mg), (Ru(bpy)$_2$(4- acryloylmethyl-4′-methylbpy))(PF$_6$)$_2$ (125.0 mg), *N*,*N*′-methylenebis(acrylamide) (MBAAm, 11.0 mg), and 2,2′-azobis (isobutyronitrile) (AIBN, 23.0 mg) were dissolved in methanol (5.0 mL), and 2-acrylamido-2-methylpropanesulfonic acid (AMPS, 51.0 mg) was dissolved in water (5.0 mL).[16] The water and methanol solutions were mixed to give the monomer solution. The monomer solution was then injected into a glass tube of diameter 1.0 mm, and the tubes end was sealed. The tube were heated at 60 °C for 24 h. The gels were cut into several segments of 5−6 mm, then soaked in distilled water. The water was replaced several times until it was colorless. SEM (scanning electron micrograph) pictures of this pseudo-one-dimensional gel were taken after lyophilization and metal spraying of the BZ-gel.

Methods and Instrumentation. The experiments were carried out in a reaction cell connected to a refrigerated circulating bath (SD7LR-20A12Y, Polyscience, America) at 22.0 ± 0.005 °C. The gel was monitored with a refrigerated CCD Camera (TCH-1.4CICE, Fuzhou Xintu Photoelectric Corporation). Gray levels were extracted from the RGB image with MatLab software. The volume of the BZ solution was 5 mL, and the diameter of the reaction cell was 26 mm.

RESULTS AND DISCUSSION

SEM Structure of Gel. SEM micrographs of the synthesized photosensitive gel (poly(NIPAAm-co -Ru(bpy)$_3$-AMPS)) inside a glass tube are shown in Figure 1. The honeycomb-like microstructure provides a locally open reaction−diffusion medium that is free from convection effects, allowing us to investigate the propagation of convection-free chemical waves and gel locomotion.

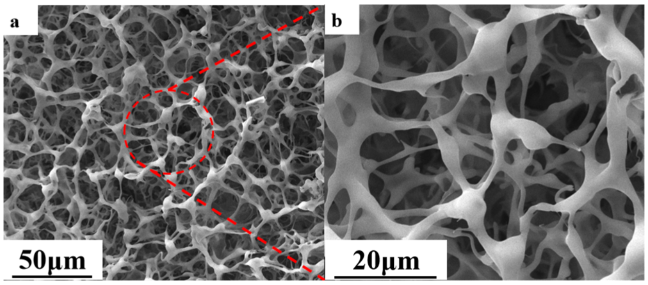

Figure 1. SEM micrographs of BZ gel. (a) The magnification is 1500×. (b) Enlargement of area in red dotted circle in part a. The magnification is 5000×.

Propagation Reversal of Chemical Waves and Its Effect on Gel Locomotion. The responsive gel in a glass tube open at both ends was soaked in a 5.0 mL mixture of catalyst-free BZ solution containing malonic acid (MA), nitric acid (HNO$_3$) and sodium bromate (NaBrO$_3$). The temperature was maintained at 22.0 ± 0.005 °C. The gel was homogeneously illuminated by an LED source. As shown in Figure 2a, at first chemical waves originated spontaneously at the left end and propagated toward the right end, which resulted in gel movement toward the left, i.e., retrograde locomotion.[17,18] About 1200 s later, new chemical waves originated at the right end (see Movie S1 in Supporting Information). The initial rightward moving waves collided with the new leftward moving waves and annihilated (see Movie S1 in Supporting Information), after which the rightward moving chemical pulse wave was suppressed. Finally (after $T = 1945$ s, as shown in panels 7−9 of Figure 2a), only waves originating spontaneously at the right end and propagating toward the left end remained.

Examination of Figure 2a and Movie S1 shows the frequency evolution of the chemical waves emanating from the left and right boundaries over time in this particular experiment (Figure 2b). Whether the initial wave starts at the right or the left boundary of the gel in a given experiment is random. There are four wave regions in Figure 2b. They display only waves emanating from the left boundary (panels 1−3, $T < 955$ s), mutual inhibition after wave collision (panels 4−6, 955−1525 s), waves from the left boundary suppressed by that from the right boundary after collision (1525−1935 s), and only waves from the right boundary (panels 7−9, $T > 1935$ s), respectively. The above phenomena result from the fact that the highest frequency wave determines the ultimate direction of wave travel when there are regions of different oscillatory frequencies.[17−19]

In order to clarify the effect of the chemical waves on the gel movement, we analyzed the spatiotemporal dynamics in detail. In Figure 3a, we show the time dependence of the positions of the ends and the center of the gel. The plot is divided into two regions: (I) pretransition and (II) post-transition. The duration of the pretransition region is defined as T_t (in replicate experiments, the reproducibility of T_t was ±2%). The curves in Figure 3b correspond to the velocity of the gel, i.e., the slopes of the curves in Figure 3a. The velocity of the right boundary of the gel is significantly larger than that of the left boundary, so the gel shrinks, and the material at the right end of the gel is compressed relative to that at the left end. Thus, the local Ru-catalyst concentration near the right boundary of the gel increases, resulting in new chemical waves originating at the right end (from $T = 955$ s, see Movie S1 and Figure 2b). At the frequency peak of the original wave in Figure 2b ($T = 1500$ s), the gel begins to accelerate (from $T = 1500$ s to $T = 1935$ s in Figure 3b). At $T = 1935$ s, the locomotion of the gel decelerates sharply as the original wave, which was responsible for the rightward motion of the gel, is annihilated by the new waves (see Figure 3a).

Mechanical Analysis and Effects of Species Concentration on Wave Reversal. On the basis of our experimental results, we discuss the mechanism of the reversal of chemical wave propagation in the self-oscillating gel as summarized in Figure 4, where the direction of chemical wave propagation is denoted by blue arrows. The capillary additional forces at the ends of the gel in solution are labeled F_C and are indicated by black arrows. Since the mesoporous polymer framework of the gel has hydrophilic groups such as −CONH−, Ru(II), and −COO−, the capillary force, F_C, is generated from the concave surface of water along the mesopores when BZ wave fronts with high [Ru(III)] reach the boundary of the gel, as shown in the enlarged view in Figure 4. The driving force produced by the chemical pulse waves at the boundaries of the gel is defined as F_w as indicated by red arrows. Under our experimental conditions, the propagation of the chemical waves is opposite to that of the active gel.[20,21]

In Figure 4a, the net force near the left boundary of the gel is $F_w - F_C$, while the net force near the right boundary is $F_w + F_C$. In the middle portion of gel, the gel locomotion is driven only by pulse waves. Thus, the gel actuates directionally with decreasing velocity from right to left, resulting in an asymmetric compression that generates a higher Ru-catalyst

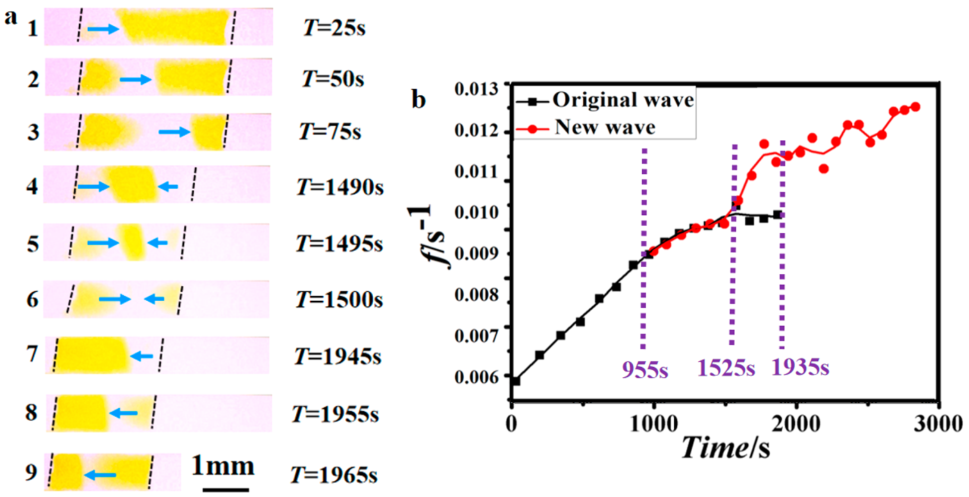

Figure 2. Spontaneous reversal of chemical waves in a self-oscillating gel. (a) Snapshots of an experimental system (top view). Blue arrows show the direction of propagation of chemical waves. Yellow color corresponds to reduced catalyst (waveback). Black dashed lines denote the boundaries of the self-oscillating gel. (b) Frequency of local oscillations at tube ends vs. time. Experimental conditions: $[\mathrm{MA}]_0 = 70$ mM, $[\mathrm{HNO_3}]_0 = 700$ mM, and $[\mathrm{NaBrO_3}]_0 = 140$ mM. Temperature was maintained at 22 °C. $I = 75.8$ μw/cm^2.

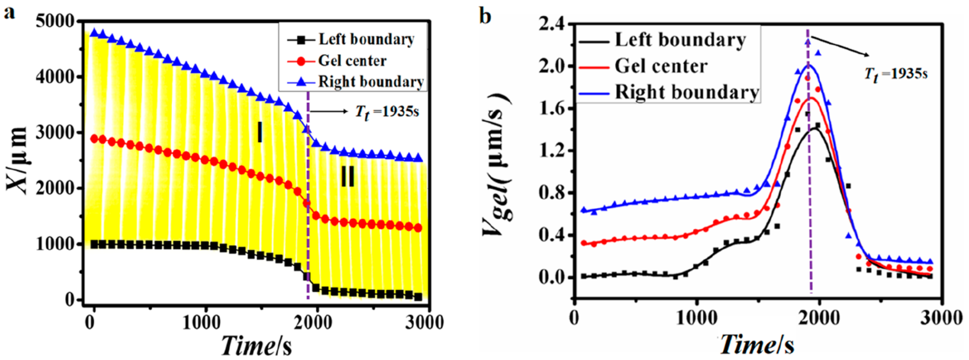

Figure 3. Spatiotemporal diagram and velocity evolution of gel locomotion. (a) Position of left boundary, center and right boundary of the gel vs. time. (b) Velocity of the gel vs. time. Experimental conditions: $[\mathrm{MA}]_0 = 70$ mM, $[\mathrm{HNO_3}]_0 = 700$ mM, and $[\mathrm{NaBrO_3}]_0 = 140$ mM. Temperature was maintained at 22 °C, $I = 75.8$ μw/cm^2.

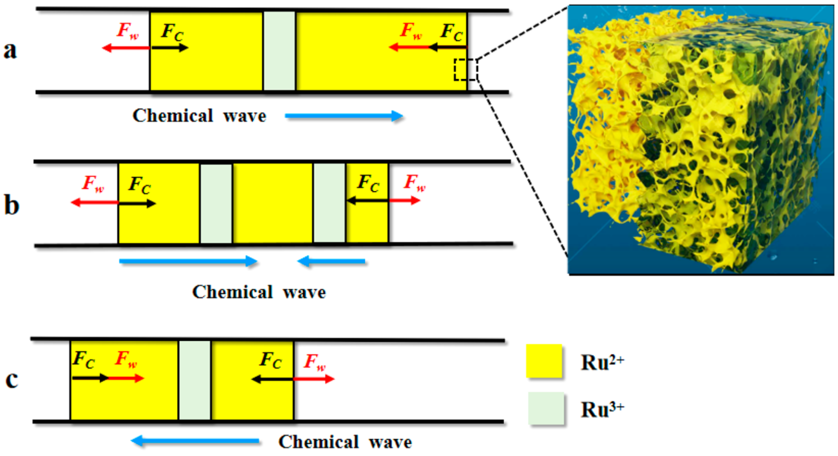

Figure 4. Schematic of the capillarity-induced reversal of propagation of the chemical waves. The black square frame on the left is an enlarged view of the gel meso-structure in part a.

concentration at the right boundary of the gel. After a while, a series of new chemical waves originates at the right boundary as shown in Figure 4b. During the transition period from two coexisting waves to only the newly generated pulse wave, the frequency of the original wave increases gradually, as shown in Figure 2b, causing the increased velocity of gel locomotion shown in Figure 3b ($T = 955-1935$ s). Finally, when only the new pulse wave of higher frequency is left, the velocity of gel locomotion decreases dramatically as the result of the opposite net driving force of the new pulse wave (Figure 4c). We were

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unable to observe complete reversal of the gel motion, because the opposing net force is not sufficient to reorient the gel locomotion before degradation and shrinkage of the gel cause cessation of oscillations.

We performed further experiments to investigate the effects of $[MA]_0$ and $[NaBrO_3]_0$. The results are shown in Figure 5. T_t indicates the duration of the pretransition region defined in Figure 3a. We see that T_t decreases with increasing $[MA]_0$ and $[NaBrO_3]_0$. These observations can be understood by considering the FKN mechanism,[22] in which the BZ reaction is divided into three main processes: consumption of bromide (process A), autocatalytic reaction of bromous acid ($HBrO_2$) with the oxidization of the catalyst (process B), and organic reaction with the reduction of the catalyst (process C).

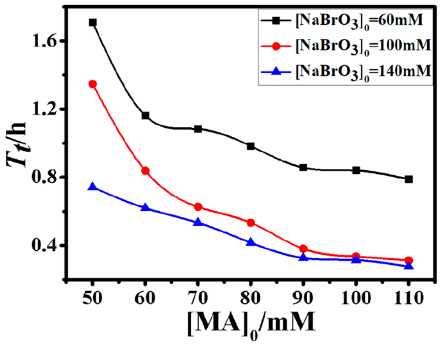

Figure 5. Effect of $[MA]_0$ and $[NaBrO_3]_0$ on transition time (T_t) of chemical waves in the capillary gel. Experimental conditions: $[HNO_3]_0 = 700$ mM, $T = 22$ °C. The reproducibility of T_t was ±2%.

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \tag{A1}$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \tag{A2}$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{A3}$$

$$BrO_3^- + HBrO_2 + 2Ru(II) + 3H^+ \rightarrow 2HBrO_2 + 2Ru(III) + H_2O \tag{B1}$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \tag{B2}$$

$$2Ru(III) + MA + BrMA \rightarrow fBr^- + 2Ru(II) + \text{other products} \tag{C}$$

The transition time depends primarily on the velocity of the initial left-to-right wave, which results in initiation of the compression-induced second wave. Increasing $[NaBrO_3]_0$ directly accelerates the autocatalysis of $HBrO_2$ (process B). Raising $[MA]_0$ produces more Ru(II) via process C, which indirectly accelerates the autocatalysis of $HBrO_2$ (process B).

CONCLUSION

In summary, additional capillary forces at the two ends of an active gel act in opposite directions, resulting in a decreasing velocity of gel movement along the locomotion direction and an increasing catalyst concentration at the compressed end of the gel to initiate an oppositely directed traveling wave. This reversal of wave propagation engenders a slowing down, and potentially (in a more robust medium) reversal of gel locomotion. In studying one-dimensional active dynamics in narrow tubes or in analogous biological structures, the effects of capillary forces should be borne in mind.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c01087.

Part 1, synthesis and characterization of the $Ru(bpy)_2$(4-acryloylmethy-l-4′-methyl bpy)$(PF_6)_2$ catalyst, and part 2, full description of Movie S1 (PDF)

Movie S1, reaction speeded up by a factor of 207 (MP4)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Merindol, R.; Walther, A. Materials learning from life: concepts for active, adaptive and autonomous molecular systems. *Chem. Soc. Rev.* **2017**, *46*, 5588−5619.

(2) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. Self-Oscillating gel. *J. Am. Chem. Soc.* **1996**, *118*, 5134−5135.

(3) Zaikin, A. N.; Zhabotinsky, A. M. Concentration wave propagation in two-dimensional liquid-phase self-oscillating system. *Nature* **1970**, *225*, 535−537.

(4) Maeda, S.; Hara, Y.; Sakai, T.; Yoshida, R.; Hashimoto, S. Self-Walking gel. *Adv. Mater.* **2007**, *19*, 3480−3484.

(5) Lu, X.; Ren, L.; Gao, Q.; Zhao, Y.; Wang, S.; Yang, J.; Epstein, I. R. Photophobic and phototropic movement of a self-oscillating gel. *Chem. Commun.* **2013**, *49*, 7690−7692.

(6) Kuksenok, O.; Balazs, A. C. Modeling the photoinduced reconfiguration and directed motion of polymer gels. *Adv. Funct. Mater.* **2013**, *23*, 4601−4610.

(7) Nakata, S.; Yoshii, M.; Suzuki, S.; Yoshida, R. Periodic reciprocating motion of a polymer gel on an aqueous phase synchronized with the Belousov−Zhabotinsky Reaction. *Langmuir* **2014**, *30*, 517−521.

(8) Epstein, I. R.; Vanag, V. K.; Balazs, A. C.; Kuksenok, O.; Dayal, P.; Bhattacharya, A. Chemical oscillators in structured media. *Acc. Chem. Res.* **2012**, *45*, 2160−2168.

(9) Hanke, W.; Sieber, M.; Spencer, P.; Schwertner, J.; Fernandes de Lima, V. M. Properties of wave propagation in a gel-type Belousov−Zhabotinsky Reaction under micro-gravity. *Microgravity Sci. Technol.* **2009**, *21*, 239−246.

(10) Lu, X.; Ren, L.; Gao, Q.; Yang, Y.; Zhao, Y.; Huang, J.; Lv, X.; Epstein, I. R. Multiple length scale instabilities of unidirectional pulse propagation in a diffusion-fed gel. *J. Phys. Chem. Lett.* **2013**, *4*, 3891−3896.

(11) Arimura, T.; Mukai, M. A self-oscillating gel actuator driven by ferroin. *Chem. Commun.* **2014**, *50*, 5861−5863.

(12) Buskohl, P. R.; Vaia, R. A. Belousov-Zhabotinsky autonomic hydrogel composites: Regulating waves via asymmetry. *Sci. Adv.* **2016**, *2*, No. e1600813.

(13) Yashin, V. V.; Van Vliet, K. J.; Balazs, A. C. Controlling chemical oscillations in heterogeneous Belousov-Zhabotinsky gels via mechanical strain. *Phys. Rev. E* **2009**, *79*, No. 046214.

(14) Chen, I. C.; Kuksenok, O.; Yashin, V. V.; Balazs, A. C.; Van Vliet, K. J. Mechanical resuscitation of chemical oscillations in Belousov−Zhabotinsky Gels. *Adv. Funct. Mater.* **2012**, *22*, 2535−2541.

(15) Yuan, P.; Kuksenok, O.; Gross, D. E.; Balazs, A. C.; Moore, J. S.; Nuzzo, R. G. UV patternable thin film chemistry for shape and functionally versatile self-oscillating gels. *Soft Matter* **2013**, *9*, 1231−1243.

(16) Murase, Y.; Maeda, S.; Hashimoto, S.; Yoshida, R. Design of a mass transport surface utilizing peristaltic motion of a self-oscillating gel. *Langmuir* **2009**, *25*, 483−489.

(17) Mikhailov, A. S.; Engel, A. Multiple pattern creation and synchronization phenomena. *Phys. Lett. A* **1986**, *117*, 257−260.

(18) Blasius, B.; Tönjes, R. Quasiregular concentric waves in heterogeneous lattices of coupled oscillators. *Phys. Rev. Lett.* **2005**, *95*, No. 084101.

(19) Kheowan, O. U.; Mihaliuk, E.; Blasius, B.; Sendina-Nadal, I.; Showalter, K. Wave mediated synchronization of nonuniform oscillatory media. *Phys. Rev. Lett.* **2007**, *98*, No. 074101.

(20) Dayal, P.; Kuksenok, O.; Balazs, A. C. Using light to guide the self-sustained motion of active gels. *Langmuir* **2009**, *25*, 4298−4301.

(21) Ren, L.; She, W.; Gao, Q.; Pan, C.; Ji, C.; Epstein, I. R. Retrograde and direct wave locomotion in a photosensitive self-oscillating gel. *Angew. Chem., Int. Ed.* **2016**, *55*, 14301−14305.

(22) Field, R. J.; Körös, E.; Noyes, R. M. Oscillations in chemical systems. II. Through analysis of temporal oscillation in the bromate-cerium-malonic acid system. *J. Am. Chem. Soc.* **1972**, *94*, 8649−8664.