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USING THEORY AND SIMULATION TO DESIGN ACTIVE MATERIALS WITH SENSORY

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14. ABSTRACT

Our aim was to design soft, active materials that: 1) function in an autonomous, self-sustained way, 2) perform multiple, complex functions, and 3) alter their functionality in a "programmable" manner in response to external stimuli. We took advantage of the unique properties offered by polymer gels undergoing the Belousov-Zhabotinsky (BZ) reaction. The BZ gels can transduce chemical energy into mechanical oscillations in the absence of external stimuli. Consequently, these polymer networks can perform autonomous mechanical work. The ruthenium catalyst, which drives the BZ reaction, is typically uniformly distributed within the gel so the material is chemically and physically homogeneous. A level of structural heterogeneity and hierarchy is, however, generally necessary for materials to display higher order or complex functionality. For this reason, we focused on designing heterogeneous or chemically patterned BZ gels, where the catalyst is confined to distinct patches ("BZ patches") within the polymer network. Such heterogeneous gels provide a route for controlling the dynamic behavior and thus, the properties of the system. Furthermore, a number of functions can be integrated within one sample.

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USING THEORY AND SIMULATION TO DESIGN ACTIVE MATERIALS WITH SENSORY AND ADAPTIVE CAPABILITIES

In the proposed research, we will model hybrid materials that encompass both soft and hard components in order to design composites that can adapt to changes in the environment in controllable, "programmable" ways. In our prior studies [1-13], we focused primarily on soft materials—gels—that are highly mutable. The findings from these studies (see below) provide a strong foundation for the new effort in creating mutable hybrid materials.

The specific aim of our previous studies was to design soft, active materials that: 1) function in an autonomous, self-sustained way, 2) perform multiple, complex functions, and 3) alter their functionality in a "programmable" manner in response to external stimuli. In devising these systems, we took advantage of the unique properties offered by polymer gels undergoing the Belousov-Zhabotinsky (BZ) reaction [1-10]. The BZ gels are unique because they can transduce chemical energy into mechanical oscillations in the absence of external stimuli. Consequently, these polymer networks can perform *autonomous* mechanical work. The ruthenium catalyst, which drives the BZ reaction, is typically uniformly distributed within the gel so the material is chemically and physically homogeneous. A level of structural heterogeneity and hierarchy is, however, generally necessary for materials to display higher order or complex functionality. For this reason, we focused on designing *heterogeneous* or chemically patterned BZ gels, where the catalyst is confined to distinct patches ("BZ patches") within the polymer network (see **Fig. I**).

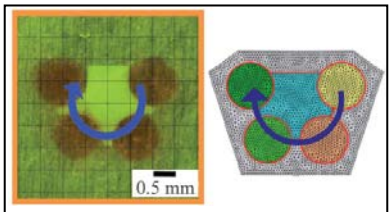

Fig. I. Propagation of traveling waves within heterogeneous self-oscillating gels can be controlled by tailoring the size and catalyst content in the patches [9].

Such heterogeneous gels provide a route for controlling the dynamical behavior and thus, the properties of the system. Furthermore, a number of functions—sensing, communication, shape changing, and actuation—can be integrated within one sample and, thus, the material can be harnessed to perform complex tasks. In order to exploit the unique properties of these active materials, we established a fundamental understanding of the dynamics of heterogeneous BZ gels and determined the optimum heterogeneous structures that will yield the desired functionality [9].

We also considered another form of heterogeneity within this system—instead of a single gel sample, we investigated the behavior of multiple gel pieces that were separated by fluid [1,5,8]. Hence, we took into account not only the chemical reactions in the gel matrix, but also within the surrounding solution. Through these studies, we isolated scenarios where the gel pieces could effectively communicate with each other by emitting, sensing, and responding to the chemicals in the fluid. Namely, through the course of the reaction, the BZ gels generated the activator for the reaction, referred to as u, which then diffused into the surrounding fluid. Neighboring gel pieces could sense the presence of u and respond by undergoing autonomous motion toward the highest concentration of u. In effect, the system exhibited autochemotaxis—moving in response to self-generated chemical gradients (see **Fig. II**).

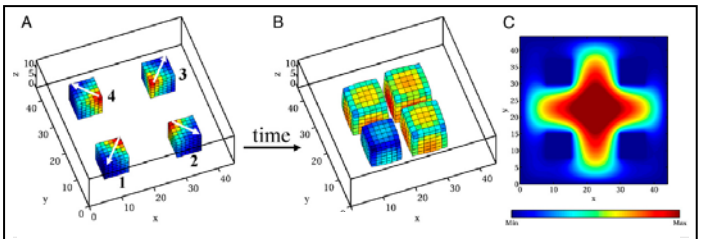

Fig. II. Auto-chemotaxis of four cubic BZ gels, which autonomously self-aggregate in response to self-generated distribution of u in solution. (A) Initial placement of gels. (B) Late-time behavior of system. (C) Distribution of u in solution. Red corresponds to concentration of u [8].

In total, this research yielded 13 journal publications [1-13] and 36 invited talks. Below, we highlight some of the findings that emerged from the previous funding period that illustrate the remarkable properties of these BZ gel systems. Notably, we enjoyed successful collaborations with three

experimental groups: *Prof. Ryo Yoshida* at the University of Tokyo, *Dr. Rich Vaia* at Wright-Patterson Air Force Base, and *Prof. Ralph Nuzzo* at the University of Illinois. Through interactions with these experimentalists, we could validate the predictions that emerged from our modeling studies and help experimental studies move in new, fruitful directions.

A. Controlling the Dynamic Behavior of Heterogeneous Self-oscillating Gels

We examined films of heterogeneous BZ gels where the catalyst is localized in distinct sub-millimeter sized patches, and these BZ patches are surrounded by a non-reactive polymer network [9]. To complement our computational studies, we collaborated with *Ryo Yoshida*, who fabricated the first heterogeneous BZ gels (see **Fig. I**), attaining control over the size of the disk-shaped patches, the ruthenium concentration in each of the disks, and arrangement of the disks in the non-reactive matrix. We first considered two distinct disks of the BZ gel that differed in size or the concentration of the ruthenium catalyst, [Ru]. By varying the separation between the disks, we isolated conditions necessary for the synchronization between the chemo-mechanical oscillations within these BZ patches. We then considered an arrangement of four disks and demonstrated that the two-dimensional propagation of the traveling wave within the film could be controlled by tailoring the size and [Ru] in the patches. We demonstrated that the simulations capture the experimentally observed effects of the catalyst concentration, patch size, and inter-patch distance on the synchronization of oscillations in the neighboring BZ gels. Taken together, the experimental and computational studies reveal how the synchronization effects can be utilized to control the dynamical behavior of the entire system.

We also collaborated with the *Vaia* group to validate our prediction that by varying the placement of these BZ patches within the matrix, we could modify the functionality of the material or introduce multi-functional behavior within a single sample [14]. In our computational studies, we considered a horizontal BZ strip within a non-reactive gel matrix (see blue and yellow images in **Fig. III**); in case 1, the strip is placed in the center of the sample and in case 2, this strip is placed at the edge.

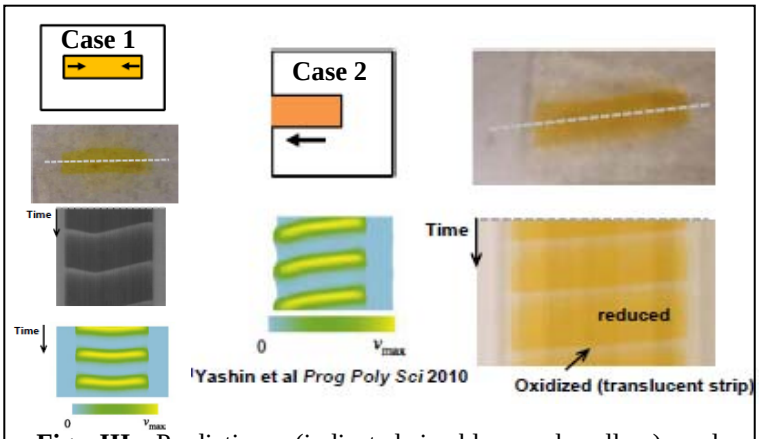

Fig. III. Predictions (indicated in blue and yellow) and experimental studies showing that the placement of rectangular BZ patches within the non-reactive gel matrix affect the mode of wave propagation and, hence, the functionality of the gel.

As predicted in our prior studies [14], the experiments show that the dynamic patterns in the two samples are quite different (see images in **Fig. III**) [15]. Specifically, in case 2, a traveling chemical wave is seen to propagate from the right to the left edge. The differences in the observed behavior can be attributed to the fact that the ends of strips experience different environments in the two scenarios. These examples clearly reveal that the placement of a BZ patch within the sample plays an important role and can be used as a design tool. In particular, case 2 can be harnessed to create a pump that transports fluid and reagents to the edge of the gel. The findings validate our predictions on a new "modular" design approach [14], where different functionality can be achieved by simply varying the spatial arrangement of identical pieces of BZ gels within a polymer matrix.

B. Modeling the Behavior of New UV Patternable Self-oscillating Gels

We also collaborated with *Prof. Ralph Nuzzo* to analyze the behavior of a new class of BZ gels, which can be dynamically shaped and patterned with light [7]. In contrast to the PNIPAAm-based systems, these polyacrylamide (PAAm)-based BZ gels contract when the Ru catalyst is in the oxidized state and the gels swell when the Ru is in the reduced state. We developed a model to explain this

distinctive behavior and obtained results that show agreement with experimentally measured quantities [7], as indicated by **Fig. IV**. Notably, these PAAm-based BZ gels exhibit larger degrees of swelling and faster oscillatory rates and hence, provide ideal systems for realizing the full potential of these responsive, autonomously functioning materials.

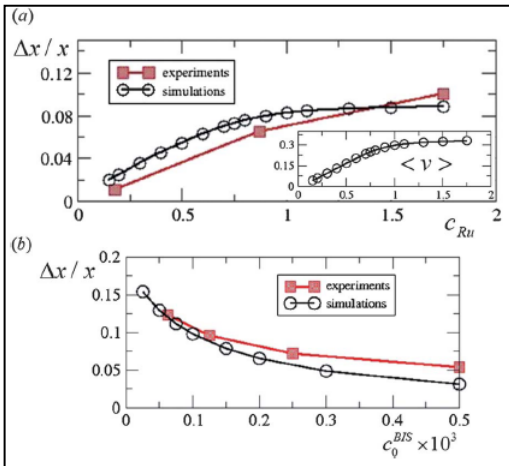

Fig. IV. (a) Amplitude of oscillation of the sample size as a function of the total catalyst concentration, c_{Ru}. The inset shows the average concentration of the oxidized catalyst, <ν>, for the same values of c_{Ru}. (b) Amplitude of oscillations of the sample size as a function of the density of permanent cross-links, c_0^{BIS} [7]. The lines with the empty circles mark the experimental data, while the lines with the red squares indicate the results from our simulations.

C. Controlling the Motion of Multiple BZ Gels in Solution: Forming Self-rotating Pinwheels and Interacting Gears

We showed that millimeter-sized BZ gels can spontaneously self-aggregate to form macroscopic, self-rotating pinwheels [5] (see **Fig. V**). Notably, we found that the system is bistable and the formation of the pinwheels depends on initial random fluctuations. The pinwheel formation can, however, be promoted by tailoring the local concentration of the activator for the BZ reaction. Furthermore, we demonstrated approaches for controlling the chirality of the pinwheels' motion. These materials could form simple self-propelled machines, such as gears, that perform autonomous work.

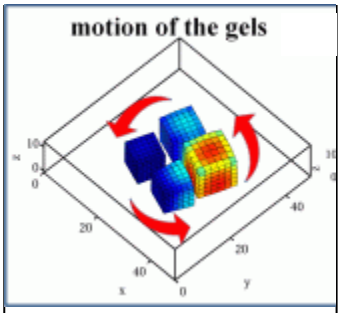

Fig. V. We showed that BZ gels can form self-rotating pinwheels, which could act as self-propelled gears [5].

We also showed that light, which suppresses the oscillations in the illuminated regions, could be used to regulate the interaction between the four-gel clusters and promote the robust formation of two gears [1] (see **Fig. VI**). These studies point to a novel form of photo-chemo-mechanical transduction, where light is harnessed to control the conversion of chemical and mechanical energy in the system. Moreover, the interaction between the gears reveals a new form of entrainment between these moving units. Namely, their coordinated motion is achieved through chemical coupling or communication, rather than a mechanical coupling. These findings can lead to the formation of chemically "communicating" devices that can be programmed to perform autonomous work through the use of light.

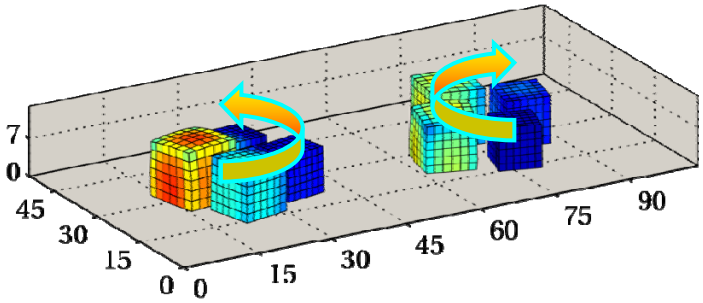

Fig. VI. With the aid of light, the BZ gels can be driven to form two self-rotating pinwheels or gears. The arrows show the direction of rotation of the gears, which interact through a form of chemical "communication", rather than mechanical coupling [1].

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