

# Chemical and optical control of peristaltic actuator based on self-oscillating porous gel

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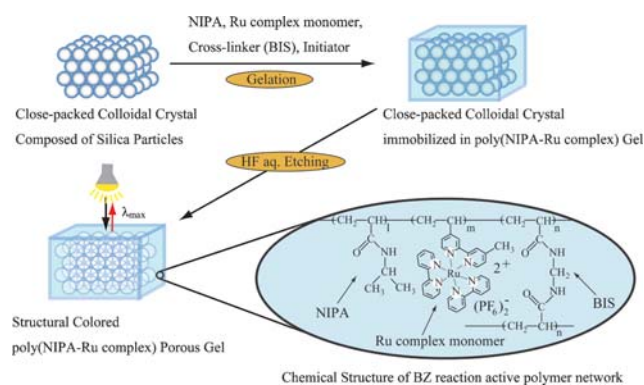
**We demonstrate the chemical and optical control of the self-sustaining peristaltic motion of a structural colored porous hydrogel.**

Stimuli-sensitive soft materials are finding applications in areas ranging from microfluidic device technology to artificial muscles. In particular, polymer hydrogels have been anticipated to be promising candidates for use in these applications. The conversion of external signals into volume changes of the hydrogels, and hence into mechanical force, is known as actuation and is of considerable importance in the development of biomimetic sensors and biotic machines. In macroscopic approaches, however, the low mechanical strength and low power of hydrogel actuators can be drawbacks for actuator applications. The application of stimuli-sensitive hydrogels with the most potential is probably as micro-actuators in the small world and surface field. Recently, autonomous systems using stimuli-sensitive hydrogels have been attracting a great deal of attention in the research areas of lab-on-a-chip<sup>1</sup> and miniature robots.<sup>2</sup> Here we demonstrate the chemical and optical control of self-sustaining peristaltic motion of a hydrogel synchronized with a non-linear oscillatory Belousov–Zhabotinsky (BZ) reaction. The hydrogel used in this paper possesses a periodically ordered interconnecting porous structure that demonstrates chromic phenomena based on the Bragg diffraction of visible light from the ordered voids as well as a rapid response.<sup>3</sup> Thus, this gel exhibits self-sustaining peristaltic motion that is completely synchronized with the BZ reaction, and thereby undergoes periodical color changes reflecting alterations in the thickness of the hydrogel. The amplitude and the period of the peristaltic motion can be controlled by both the amount of the substrate in the BZ reaction solution and the intensity of the irradiated light.

To prepare the porous gel, a thick and fine close-packed colloidal silica crystal as a template was prepared by a solvent evaporation method using a silica colloidal particle suspension. The preparation method and the evaluation of this thick colloidal crystal have previously been reported.<sup>4</sup> We synthesized a porous gel made of a water soluble monomer, *N*-isopropylacrylamide

(NIPA), and a Ru complex derivative monomer, ruthenium (4-vinyl-4'-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis(hexafluorophosphate) (Ru(vmbpy)(bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>), by free-radical polymerization as follows. *N,N'*-Methylenebisacrylamide (BIS) and *N,N'*-azobis(isobutyronitrile) were used as a cross-linker and an initiator, respectively. The appropriate amounts of the above chemicals were dissolved in degassed and nitrogen-saturated methanol, and used as a pre-gel solution. The pre-gel solution was infiltrated into the interstitial regions of the colloidal crystal in a Petri dish, and the polymerization was conducted at 60 °C for 18 h (Scheme 1). Afterwards, the resulting gel was immersed in a 5 wt% HF aqueous solution for 1 week to remove the silica component. The porous gel obtained was washed carefully with a large amount of distilled water to remove HF and other impurities. We confirmed that the polymer network was chemically stable during the etching procedure by <sup>1</sup>H-NMR and by checking the degree of swelling of the gel. The reflection spectra of the porous gel were obtained using an Ocean Optics USB2000 fiber optic spectrometer with a low-power light source. All spectra were monitored at normal incidence to the plane of the samples. The photoirradiation was performed with a Xe–Hg lamp (SAN-EI Electric, SuperCure-203S) through colored glass filters, a bandpass filter, and an IR cutoff filter. The temperature in all of the measurements was controlled by using a circulating water temperature control system.

The porous gel obtained exhibited a bright color under white light. The color was caused by the Bragg diffraction of visible light from the ordered voids regarded as crystallites.



**Scheme 1** Fabrication of a BZ reaction active hydrogel possessing a periodically ordered interconnecting porous structure.

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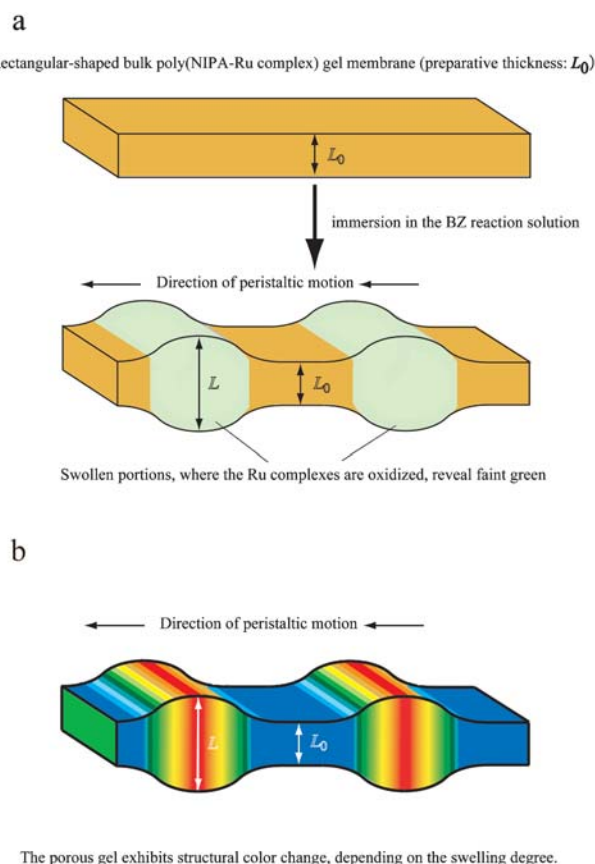
The basic photonic properties can be quantitatively described by Bragg's law combined with Snell's law:<sup>4</sup>

$$\lambda_{\max} = 1.633(d/m)(D/D_0)(n_a^2 - \sin^2\theta)^{1/2} \quad (1)$$

where  $\lambda_{\max}$  is the intensity maximum of the Bragg diffraction;  $d$  is the diameter of the silica particle;  $m$  is the order of the Bragg reflection;  $D$  and  $D_0$  are the characteristic sizes of the hydrogel in the equilibrium state under particular conditions and in the preparative state, respectively;  $n_a$  is the average refractive index of the porous gel; and  $\theta$  is the angle measured from the normal to the plane of the hydrogel membrane. Hence,  $D/D_0$  is defined as the equilibrium swelling degree of the gel. As we observed the Bragg diffraction at normal incidence, the value of  $\theta$  in our results was 0. The value of  $n_a$  is calculated as a weighted sum of the refractive indices of the sphere portion and the gel portion:  $n_a^2 = \sum n_i^2 \phi_i$ , where  $\phi_i$  is the volume fraction of each  $i$  portion. For the closely packed structure, the value of  $\phi$  of the sphere portion was 0.74. The change in the equilibrium swelling degree of the gel can be up to a factor of 10, while the change in  $n_a$  for the inverse opal-type periodic porous gel was found to be vanishingly small when the volume underwent drastic changes; we can treat the value of  $n_a$  as a constant under varying degrees of  $D/D_0$ . Therefore, the value of  $D/D_0$  during the BZ reaction can be estimated by using the spectroscopically observed value of  $\lambda_{\max}$ .<sup>5</sup> It follows that we can calculate the variable thickness of the gel membrane,  $L$ , using the spatio-temporally observed value of  $\lambda_{\max}$ , the preparative thickness of the gel membrane,  $L_0$ , the diameter of the silica particles used,  $d$ , and the invariable average refractive index of the porous gel,  $n_a$ , as follows:

$$L = L_0(D/D_0) = L_0 m \lambda_{\max} / 1.633 d n_a \quad (2)$$

The BZ reaction is a non-linear oscillatory reaction that serves as a classical example of non-equilibrium thermodynamics.<sup>6</sup> This reaction is far from equilibrium and remains over a long period of time. In this sense, it provides an interesting chemical model of non-equilibrium biological phenomena. Indeed, the chemical traveling waves observed in the BZ reaction are very similar to the electromagnetic traveling waves in muscle tissue. In addition, in living things, there are analogies to this periodic behavior such as heartbeats and circadian rhythms. The heart rate can be controlled by concentrations of chemicals such as adrenaline and acetylcholine, which are produced in the bloodstream when stimulated by external stimuli. Similarly, in the BZ reaction, the concentrations of chemicals that play key roles in the reaction are controlled by external stimuli. When the porous gel is immersed in a BZ reaction solution including appropriate amounts of malonic acid (MA), sodium bromate ( $\text{NaBrO}_3$ ), and nitric acid ( $\text{HNO}_3$ ), spatio-temporal pattern formation due to the BZ reaction occurs in the gel.<sup>7</sup> It is known that, in the BZ reaction, each substrate acts as follows: MA = reducing agent,  $\text{NaBrO}_3$  = oxidizing agent, and  $\text{HNO}_3$  = strong acid medium.<sup>6b</sup> As the Ru complex, covalently bound to the polymer network, works as the catalyst for the periodic redox reaction between MA and  $\text{NaBrO}_3$ , the Ru complex autonomously exhibits periodic changes between the oxidized



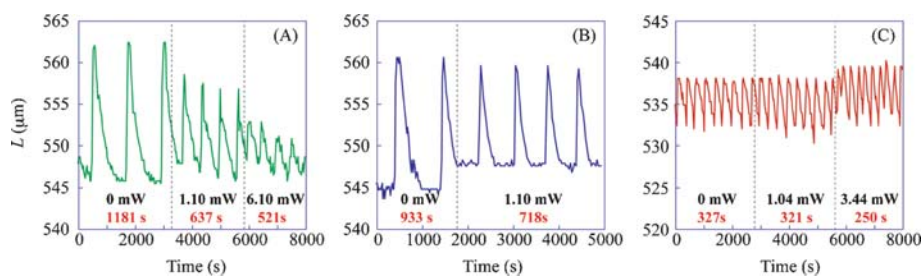
The porous gel exhibits structural color change, depending on the swelling degree.

**Scheme 2** Models for peristaltic motion in the BZ reaction active hydrogel membranes. (a) A spatio-temporal color pattern of oscillating behavior for a rectangular bulk poly(NIPA–Ru complex) gel can be observed because of the difference in color between the reduced state and the oxidized state of the Ru complex. (b) A spatio-temporal structural color change of a rectangular-shaped porous poly(NIPA–Ru complex) gel during the BZ reaction shows that the gel moves like an earthworm.

(Ru(III)) and the reduced (Ru(II)) states. The portion of the gel where the Ru complex enters an oxidized state reveals a higher swelling ratio than that where the Ru complex is in a reduced state. As a result, the porous gel moves in a winding fashion, like a snake or a worm.<sup>5</sup> The dynamic alteration in the volume can be converted to a change in structural color based on Bragg diffraction (Scheme 2). Consequently, the thickness of the porous gel during the BZ reaction can be evaluated by measuring the reflection spectrum of the gel.

The self-sustaining peristaltic motion of the porous gel coupled with the Ru complex-catalyzed BZ reaction can be manipulated by light irradiation, because the illumination of visible light produces bromide ions, which can act as inhibitors of the oscillatory chemical reaction, by the photochemical reaction of the Ru complex.<sup>8</sup> As a result, the periodicity and amplitude of the peristaltic motion decreased with the intensity of the irradiated light (Fig. 1).

The cyclic rhythm can also be tuned by the external concentration of each substrate in the BZ reaction solution. Generally, the oscillation period of the BZ reaction varies depending on the initial concentration of the substrates.<sup>9</sup> However, there are upper and lower limits to the substrates' concentrations, also these limits bring about stable BZ



**Fig. 1** Irradiated light intensity and sodium bromate concentration tuning of self-sustaining peristaltic motion of the porous hydrogel synchronized with a non-linear oscillatory BZ reaction at 13 °C. The initial compositions of the reaction solutions were as follows: [malonic acid] = 0.0625 M, [HNO<sub>3</sub>] = 0.890 M, and [NaBrO<sub>3</sub>] for (A) 42 mM, (B) 60 mM, and (C) 84 mM. The periods of the self-sustaining peristaltic motions for each condition are shown.

oscillation. Therefore, it is expected that the self-sustaining peristaltic motion can also be tuned by the initial concentration of the substrates. Since it is common knowledge that the period is more sensitive to the concentration of NaBrO<sub>3</sub>, [NaBrO<sub>3</sub>], we observed the [NaBrO<sub>3</sub>] dependence on the period and amplitude of the self-sustaining peristaltic motion. Fig. 1 shows the oscillating behavior of the porous gel under different [NaBrO<sub>3</sub>] under the stable oscillation conditions, while the concentrations of other substrates were fixed. As expected, the period of the peristaltic motion decreased with increasing [NaBrO<sub>3</sub>]. Meanwhile, the amplitude was almost independent of [NaBrO<sub>3</sub>] at lower concentrations, whereas it was drastically changed at higher [NaBrO<sub>3</sub>]. We interpret this phenomenon as follows. Judging from the previous result, [NaBrO<sub>3</sub>] has a limited impact on the swelling–deswelling amplitude during the BZ reaction. However, since the swelling–deswelling change cannot follow the BZ reaction with high frequency at higher [NaBrO<sub>3</sub>], the amplitude of the peristaltic motion notably decreased.

In conclusion, the rhythmical self-sustaining peristaltic motion of the porous gel can be controlled by changing the intensity of the irradiated light and the initial concentration of NaBrO<sub>3</sub>. Furthermore, other smaller sized pores, which may be available for the separation or recognition of specific molecules, may be generated in our porous gel.<sup>10</sup> Hence, this newly developed system may be useful in various approaches for the development of opto- and chemo-mechanical transducers, micromachines capable of imitating biological functions, future lab-on-a-chip systems, and functional surfaces that transport fluids. Research into the use of this system with

lab-on-a-chip systems and microactuators is currently under way.

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