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### COMMUNICATION

# Self-deformable gel system with asymmetric shape change based on gradient structure

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A self-deformable gel system is constructed by coupling gradient structured gel with chemical oscillating reaction. The system exhibits periodic and asymmetric shape change. The asymmetric shape change of the gel is based on the gradient structure.

Shape-changing polymer materials (SPMs), an important smart polymer material, has been extensively investigated during last two decades due to their stimuli responsiveness and reversibility.<sup>1</sup> A shape-changing process occurs when SPMs are exposed to certain external stimuli (light, heat, pH, electric field, magnetic field, *etc.*), and the shape change can recover after the elimination of external stimuli. Based on the corresponding relationship between external stimuli and the geometrical shape change of material, SPMs have been utilized to develop intelligent polymer devices, such as micro-sensor, micro-actuator, mass transportation, drug delivery device, *etc..*<sup>2</sup>

In spite that SPMs have been widely studied, the realization of stimuli responsive shape change essentially depends on the ON-OFF switching of external stimuli in most cases. Developing highly intelligent SPMs without external stimuli switching remains a great challenge. There are many natural rhythmic deformations that do not rely on external stimuli, such as *pbummion* flower and heartbeat. The SPMs mimicking natural rhythmic deformation shows a lot of advantages, including autonomous and reversible shape change as well as self-sustained feature. By coupling Ru-contained polymer gel and self-oscillating reaction, Yoshida and co-workers developed a smart gel system which presented autonomous and reversible volume change without ON-OFF switching of external stimuli.<sup>3</sup> Furthermore, by altering shape and size of the gel, a series interesting biomimetic function have accomplished, including

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ciliary motion, cellular beating, *etc.*.<sup>4</sup> However, limited by the isotropic gel structure, the shape change of these gels is symmetric. Thus, realizing the diversified deformation pattern of the SPMs remains a great challenge.



Scheme 1 Concept of the self-deformable gel system based on chemical oscillating reaction.

To our knowledge, most attempts to realize advanced shape change of SPMs point to building an asymmetric structure. For example, Xiong *et al.* fabricated an ion-responsive hydrogel microcantilever with gradient distributed cross-linking density using multiphoton polymerization, which presented controllable bending behavior.<sup>5</sup> By utilizing patterning method, Smith *et al.* developed heterogeneous Ru(II)(bpy)<sub>3</sub>-gelatin composites showed anisotropic deformation.<sup>6</sup> Hu *et al.* prepared a *nepenthes* mimetic gel device by constructing

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multi-layer thermo-responsive gel.<sup>7</sup> In these cases, the deformation of the material is provided by the asymmetric structure of SPMs, such as gradually varied cross-linking density or multi-layer structure.



Figure 1 Preparation method of the gradient  $Poly(Ru(bpy)_3-co-NIPAAm)$  gel. (a) Synthesis of the  $Poly(Ru(bpy)_3-co-NIPAAm)$  gel. (b) Illustration of the preparation process of gradient double network.

Inspired by these works, we attempt to develop a selfdeformable gel system (SGS) based on gradient structured polymer gel and chemical oscillating reaction (COR). In this system, the gradient structured polymer network is designed to be responsive to the chemical environment variation (*e.g.* pH or redox state) that induced by COR, and to be flexible enough to undertake reciprocating shape change. COR is the *in situ* driving source that gives the gel autonomous, reversible and periodic deforming character. As shown in Scheme 1, when COR occurs, a periodic chemical variation spontaneously evolves and propagates in the gel, resulting in responsive and reversible swelling degree change of the gel. On account of gradient distribution of the swelling degree regulating group  $(Ru(II)(bpy)_3)$ , the swelling degree of the gel is uneven, resulting in asymmetric deformation of the gel. In this way, the self-deformation of the gel is periodic, asymmetric and completely regulated by the system itself without ON-OFF switching of external stimuli.

In this study, we prepared a COR responsive double network gel with gradient Ru(II)(bpy)<sub>3</sub> distribution. At first, a non-CORresponsive poly(N-isopropylacrylamide) (PNIPAAm) network was synthesized as framework (named 1<sup>st</sup> network) via free radical polymerization, the multi-vinylated PNIPAAm micro-gel was used as crosslinker. Then, the swelling degree regulating group Ru(II)(bpy)<sub>3</sub> (acted as the catalyst of COR) was introduced to construct gradient structured poly(Ru(bpy)3-co-NIPAAm) network (named 2<sup>nd</sup> network) interpenetrating the 1<sup>st</sup> network. Specifically, the 1<sup>st</sup> network gel was partially immersed in the 2<sup>nd</sup> network gelating solution (see ESI). A spontaneous concentration graidient of Ru(II)(bpy)<sub>3</sub> moiety was formed inside the gel. After that, the gel underwent UVirradiation to crosslink the 2<sup>nd</sup> network. Due to the rapidity of photo-polymerization,<sup>8</sup> the Ru(II)(bpy)<sub>3</sub> concentration gradient was fixed during the UV-irradiation. As a result, the  $2^{nd}$ network possessed of gradient distribution of Ru(II)(bpy)<sub>3</sub> moiety (Figure 1b). In this way, an interpenetrating PNIPAAm/Poly(Ru(bpy)3-co-NIPAAm) double network gel with gradient distribution of Ru(II)(bpy)<sub>3</sub> was achieved. To intuitively investigate thermo and redox responsiveness of Poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel, we prepared isotropic poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel in a similar way. Detailed preparation method and characterization can be seen in ESI. By utilizing Belousov-Zhabotinsky (BZ) reaction (a typical COR presents periodic redox variation) as in situ driving source, a self-deformable gel system exhibiting autonomous and periodic bending-stretching motion was established based on asymmetric swelling-deswelling behaviour of gradient Poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel.

There were two aspects of concern when we tried to establish the SGS. First, the polymer network should be flexible enough to accomplish the reversible and periodic shape change. Therefore, the monomer concentration of both  $1^{st}$  and  $2^{nd}$ network was set to be slightly above the critical solid content value to form comparatively sparse double network. It can be seen in Table 1, the solid content of prepared gel was 15.2 %, and the gel was quite tender and easily deformable. Furthermore, the response of  $2^{nd}$  network to COR should be rapid. It could help to reduce the hysteresis and mechanical loss during reciprocating deformation. Thus the micro-gel with multi-vinyl group was selected as the crosslinker for both  $1^{st}$ and  $2^{nd}$  network, since the multi-vinylated micro-gel or nanogel crosslinked networks were proved to be rapid responsive.<sup>9</sup> The swelling degree responsiveness of the Poly(Ru(bpy)<sub>3</sub>-co-

Table 1 Structural profiles of the gradient Poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel

	NIPAAm <sup>a</sup>	Microgel <sup>a</sup>	Ru(II)(bpy)₃ <sup>a</sup>	1 <sup>st</sup> Network <sup>b</sup>	2 <sup>nd</sup> Network <sup>b</sup>	Solid content <sup>c</sup>
	(m %)	(m %)	(m %)	(m %)	(m %)	(m %)
1 <sup>st</sup> Network	79.0	21.0	-	-	-	14.3
2 <sup>nd</sup> Network	44.4	33.3	22.3	-	-	-
Gel	74.0	22.6	3.4	85.6	14.4	15.2

<sup>a</sup> Feed ratio. <sup>b</sup> Determined by weighing the gel in thoroughly dry state before and after the construction of 2<sup>nd</sup> network. <sup>c</sup> Determined by weighing the gel in thoroughly dry state and equilibrium swelling state

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NIPAAm) gel to the redox variation is crucial in SGS. It determines the deformation degree of the gel during repeated shape change. Besides, temperature plays an important role in swelling-deswelling process of the gel due to the thermoresponsive nature of main component PNIPAAm. Therefore, equilibrium swelling ratio of isotropic Poly(Ru(bpy)3-co-NIPAAm) gel as a function of temperature in oxidized/reduced state was investigated firstly.  $Ce(SO_4)_2$  and  $Ce_2(SO_4)_3$  were used as oxidizing/reducing agent to keep the gels in Ru(II) or Ru(III) state. The gels were totally immersed in the redox solution for 20 min to reach equilibrium. The volume of the gel in Ru(III) state at 10 °C was set as 100 %. Equilibrium swelling ratio of the gels continuously decreased with increasing temperature, and tended to be stable at 35 °C in both Ru(II) and Ru(III) states (Figure 2). At constant temperature, the volume of gels in Ru(III) state was larger than that in Ru(II) state because the molecule chain in Ru(III) state was more hydrophilic. It is easy to imagine that if we combine the gradient structured gel with BZ oscillating reaction, a periodic and reversible self-deformable gel system can be established. The Self-deforming behaviour of the gradient gel was investigated at 20 °C since the gel volume deviation between Ru(III) and Ru(II) is largest at 20 °C.



Figure 2 Equilibrium swelling ratio of the Poly(Ru(bpy)<sub>3</sub>-*co*-NIPAAm) gel as a function of temperature. The swelling ratio of oxidized gel at 10 °C was set as 100 %. Green square:  $[Ce_2(SO_4)_3]$ =5 mM and  $[HNO_3]$ =0.89 M; Orange rhombus:  $[Ce(SO_4)_2]$ =5 mM and  $[HNO_3]$ =0.89 M.

The SGS was successfully constructed by immersing the gradient  $Poly(Ru(bpy)_3-co-NIPAAm)$  gel (5×1×1 mm<sup>3</sup>) in BZ reaction substrate (aqueous solution of 0.89 M HNO<sub>3</sub>, 84 mM NaBrO<sub>3</sub>, 62.5mM malonic acid (MA)). The gel was thoroughly oxidized after approximate 270 s of induction period, and then the BZ reaction occurred inside the gel. Thereafter, the gel showed autonomous and periodic bending-stretching deformation without any external stimuli (ESI video S1). Figure 3 showed the colour and shape change of the gradient Poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel in one redox cycle at 20 °C. The dimension of the gel was larger than the wavelength of BZ reaction, thus the gel cannot be synchronously oxidized or reduced. A chemical wave of redox oscillation was generated and propagated inside the gel periodically. At first, an oxidizing

region (turned to light green) emerged in central part of the gel and expanded along the length to both ends (Figure 3a). Then, almost the entire gel was oxidized as the chemical wave propagated in the gel (Figure 3b). After that, oxidizing region was gradually reduced (restored to orange) (Figure 3c). The chemical wave of reducing state propagated from centre to both ends until the whole gel was back to original reduced state (Figure 3d). The concentration of Ru(II)(bpy)<sub>3</sub> at left side was higher than that of right side of the gel. The swelling degree at left side of the gel was higher when the gel was oxidized, so the gel was forced to bend to the right side. Accordingly, the deswelling degree at left side of the gel was higher when the gel was reduced, which made the gel stretched. It is notable that the 2<sup>nd</sup> network was COR responsive and in minority (Table 1) in the Poly(Ru(bpy)<sub>3</sub>-co-NIPAAm) gel. The deformation of the gel was caused by the  $2^{nd}$ network, and the 1<sup>st</sup> network was forced to deform. Due to the robustness and high deformability that multi-vinylated microgel cross-linker conferred to the 2<sup>nd</sup> network, the deformation of the gel could accomplished.9



Figure 3 Image of the autonomous bending-stretching motion of the gradient Poly(Ru(bpy)<sub>3</sub>-*co*-NIPAAm) gel in one redox cycle. Green (oxidized) and orange (reduced) arrows represent the direction and range of redox chemical wave, black arrows represent the motor direction of the gel. The time interval is 100 s.

In a closed system, BZ reaction can self-sustain for several cycles until all organic acid is consumed, and the redox oscillating amplitude gradually weaken over time.<sup>10</sup> Correspondingly, the self-deforming motion of gradient Poly(Ru(bpy)<sub>3</sub>-*co*-NIPAAm) gel driven by BZ reaction showed similar character. Figure 4 shows the self-deforming process included 5 complete bending-stretching cycles which consumed  $2.5 \times 10^{-4}$  mol MA, and the deforming process continued for 2500 s. The period of one self-deforming cycle was approximate 500 s. The stretching degree of the gradient Poly(Ru(bpy)<sub>3</sub>-*co*-NIPAAm) gel in oxidized state was relatively large at early stage of the self-deforming process because there was sufficient MA in the system. The direct distance

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Figure 4 Autonomous and periodic bending-stretching deformation profiles of the gradient Poly(Ru(bpy)<sub>3</sub>-*co*-NIPAAm) gel in the solution of BZ substrates ([HNO<sub>3</sub>]=0.89 M, [NaBrO<sub>3</sub>]=84 mM, [MA]=62.5 mM, 20 °C). (a) L is the direct distance between two ends of the gel at 2500 s (when MA is completely consumed);  $\Delta$ L is the displacement of two ends distance of the gel during bending-stretching process. (b) (x,y) is the two dimension coordinate of marked position on the gel. The time interval of data collection is 20 s.

In conclusion, a self-deformable gel system exhibiting autonomous, periodic and asymmetric deformation was established by coupling gradient structured gel with chemical oscillating reaction. The asymmetric deformation of the gel relies on the gradient structure of the gel. This work could enlighten the development of diversified and self-sustained SPMs and motivate further work on advanced smart polymer materials. The two-step strategy of gradient structure provides an opportunity to realize those theoretically feasible but unimplemented deformation pattern.<sup>11</sup> More broadly, the SGS could be regarded as a template for constructing other autonomous shape changing systems, by utilizing other asymmetric structured polymer materials and chemical oscillating reaction (*e.g.* pH oscillator).

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#### **Conflicts of interest**

There are no conflicts to declare.

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