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Self-Oscillating Gel Actuator Driven by Ferroin

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In the wake of the Belousov-Zhabotinski reaction catalyzed by ferroin, the swelling-deswelling oscillating soft actuator exhibits 7 min period of self-oscillation for the first time.

Self-oscillating systems are widespread in nature and are a key feature of space-time self-assembly of nonequiliburium systems. As a pioneer attempt to develop self-oscillating gel systems, Yoshida et al. in 1996 reported rhythmically pulsatile mechanical motion (swelling and deswelling) of a hydrogel by utilizing the Belousov–Zhabotinski (BZ) reaction as a driving force.[1] Not surprisingly, therefore, considerable effort has been devoted to constructing autonomous artificial gel systems without external stimuli by Yoshida[2] and others.[3] To this day, a large number of applications have been explored for industrial use by utilizing functional gels, such as a soft actuator (artificial muscle),[4] an enzymatic function,[5] purification of chemicals,[6] and a drug-delivery system.[7] Development of self-oscillating gel possessing living creature's motion would make it possible novel biomimetic actuators such as a self-beating micro-pump and a self-walking robot. The BZ reaction is known as an oscillating reaction with a rhythmic oscillation of the redox potential of metal catalysts such as rhutenium tris(2,2'-bipyridine) ($Ru(bpy)_3$) and iron tris-phenanthroline complexes, namely

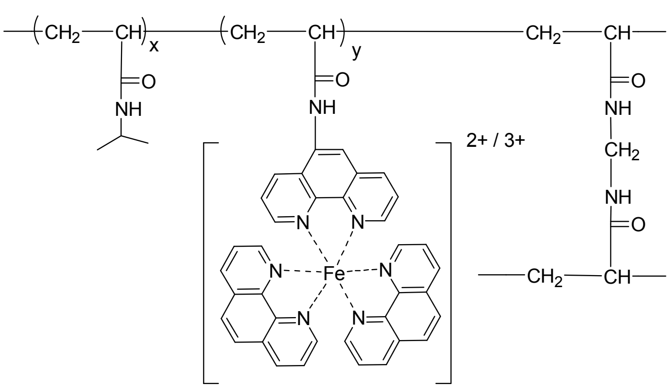

Figure 1 Chemical structure of ferroin cross-linked gel.

ferroin.[8] Although it is necessary to harness a less expensive metal as a catalyst of the BZ reaction for industrial applications, to date, all self-oscillating cross-linked gel systems undergoing swelling-deswelling oscillation are catalyzed only by using the expensive $Ru(bpy)_3$ complex. Herein, we have developed a self-oscillating cross-linked gel, which, for the first time, swells/deswells periodically with the redox oscillation of ferroin. This novel self-oscillating gel exhibits 7% change in the gel length corresponding to the swelling-deswelling oscillation.

Ferroin bearing one acrylamino group, Iron (5-acrylamido-1,10-phenanthroline) bis (1,10-phenanthroline) (ferroin monomer) was prepared using 5-amino-1,10-phenanthroline

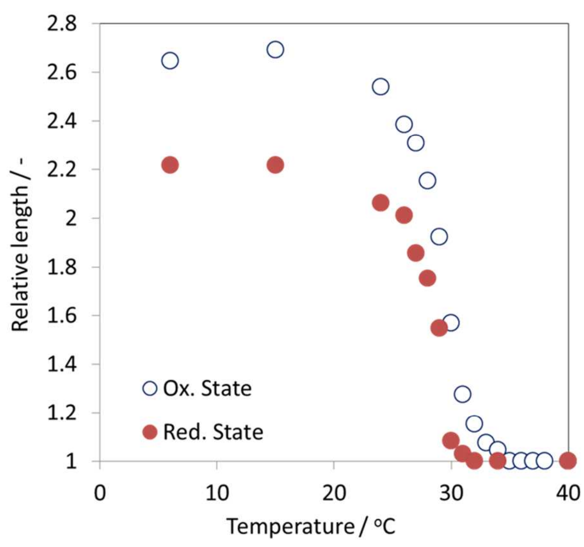

Figure 2 Equilibrium swelling ratio of the ferroin cross-linked gel in cerium sulfate solutions as a function of temperature. (Open circle) $Ce(SO_4)_2$ 1.0 mM and HNO_3 0.30 M; (Close circle) $Ce_2(SO_4)_3$ 1.0 mM and HNO_3 0.30 M. The relative

length is defined as the ratio of characteristic diameter to that at the shrunken state over the phase transition temperature.
according to a reported method.[9] The ferroin-copolymerized N-Isopropylacrylamide (NIPAAm) cross-linked gel was prepared by the radical polymerization of NIPAAm, N,N'-methylenebisacrylamide (BIS) cross-linker, and a ferroin monomer, using 2,2'-azobisisobutylronitrile (AIBN) as an initiator in a mixture of water and EtOH. The chemical structure of the ferroin cross-linked gel is shown in Figure 1.

Prior to examining the swelling-deswelling self-oscillation of the ferroin cross-linked gel, its behavior at the lower critical solution temperature (LCST) was analyzed. NIPAAm hydrogels show stunning swelling and deswelling behavior with change in the temperature, inducing the volume phase transition at 32 °C,[10] which is the LCST of NIPAAm. Figure 2 shows the temperature dependence of the swelling ratio when the ferroin ion is oxidized and reduced in the presence of $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$, respectively, under the same acidity. The oxidation of the ferroin site, wherein the gel shows a blue tinge, induces not only an increase in the degree of swelling but also a rise in the transition temperature to 35 °C. The ferroin site is reduced and the gel quickly turns from blue to red, with a phase-transition temperature of 32 °C, which is lower than that of the oxidized ferroin gel. This indicates that the hydrophilicity of the reduced ferroin gel decreases because of the decrease in the charge of the redox moiety.[11] Despite almost the same ratio of metal catalyst, the swelling ratio of the ferroin gel is a little larger than that of the $Ru(bpy)_3$ gel.[1,12] This finding leads us to propose that the ferroin cross-linked gel will carry out a remarkable swelling-deswelling oscillation when the ferroin moiety is periodically oxidized and reduced.

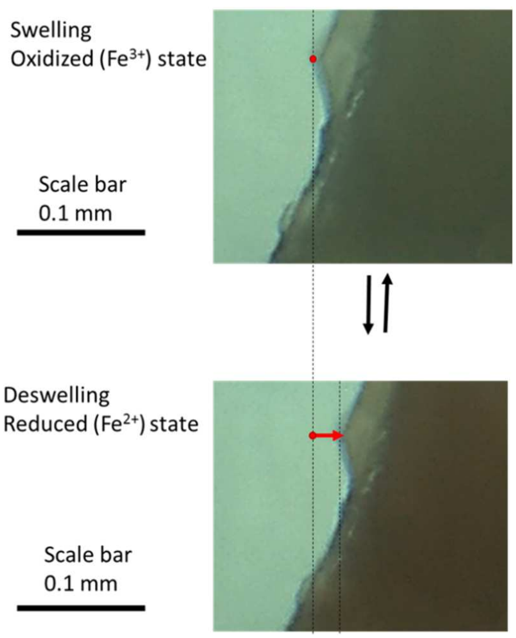

Figure 3 Images of the ferroin cross-linked gel undergoing the redox change.

We first attempted to cut the ferroin cross-linked gel into a cube (approximately 1mm × 1 mm × 1 mm) in pure water, and then immersed it in 24 mL of an aqueous solution containing malonic acid (63 mM) and nitric acid (0.30 M) at 20 °C. Because the BZ oscillation reaction depends on the initial concentration of each reactant,[13] the ratio of the substrates was kept the same as that for the first reported condition[1] in the $Ru(bpy)_3$ cross-linked gel. To commence the BZ reaction within the gel, sodium bromate was added to adjust the concentration to 84 mM in the reaction mixture. The ferroin moiety could periodically change between the Fe^{3+} and Fe^{2+} states. The redox change of the ferroin catalyst caused the swelling degree of the gel (Figure 3), and the chemical self-oscillation took place accompanied with color change along its length. Interestingly, the BZ reaction in the ferroin gel still worked even in the half concentration of nitric acid, although the $Ru(bpy)_3$ gel did not below 0.3 M of nitric acid.[14] The chemical waves and the resulting swelling-deswelling oscillation of the ferroin gel were recorded through a microscope using a charge-coupled device (CCD). The self-oscillation period in the ferroin gel was approximately 7 min and it continued for approximately 6 h. Figure 4 indicates the time course of the swelling-deswelling oscillation of the gel length (also see Movie in ESI). It can be seen that the change in the outer axial diameter with the amplitude of swelling-deswellling was approximately 7% of the gel length corresponding to the swelling-deswellling oscillation. This swelling-deswelling change is relatively smaller than the values of the earlier reported $Ru(bpy)_3$-based gels.[2h, 3d] Further, the BZ oscillation reaction in the ferroin cross-linked gel did not work below 15 °C, since temperature plays an important role in the dynamics of BZ reaction.[15] The BZ reaction in the ferroin gel worked over a temperature range of 18 to 25 °C.

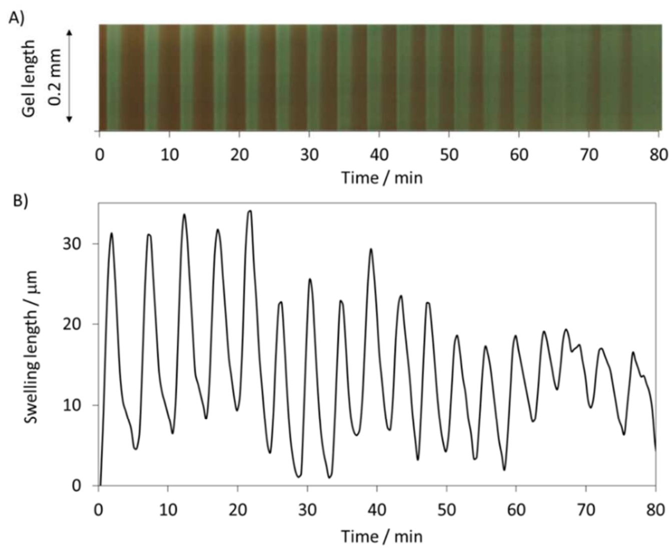

Figure 4 (A) One line images of the ferroin cross-linked gel captured at periodic time intervals (15s) and line up horizontally. (B) The swelling-deswelling oscillation of the ferroin cross-linked gel. Outer solution: [Malonic acid] = 63 mM, [$NaBrO_3$] = 84 mM, [HNO_3] = 0.30 M, 20 °C. Swelling in oxidized state (blue) and deswelling in reduced state (dark red) is apparent. Color enhanced for clarity.

In conclusion, the BZ reaction in the gel generates periodic redox changes of ferroin instead of $Ru(bpy)_3$ and the chemical oscillation induced, for the first time, the swelling-deswelling oscillation of the gel, although more detailed characterization is required to reveal the behavior of the self-oscillating gel. Experiments designed toward elucidating this autonomously oscillating gel system more clearly are in progress.

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Notes and references

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† Electronic Supplementary information (ESI) available: Synthetic experimental procedures of monomer and gel, equilibrium swelling ratio measurement, self-oscillation measurement and experimental details. See DOI

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