Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for

"Fabrication of submillimeter-sized spherical self-oscillating gels and control of their isotropic volumetric oscillatory behaviors"

Won Seok Lee[1], Takafumi Enomoto[1], Aya Mizutani Akimoto[1], and Ryo Yoshida[1]*

[1]Department of Materials Engineering, School of Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[1]Tel: +81-3-5841-7112, Fax: +81-3-5841-7112

E-mail: ryo@cross.t.u-tokyo.ac.jp

*To whom correspondence should be addressed.

1. Size distribution of the spherical base poly(NIPAAm-*co*-NAPMAm) gels using different syringe needles

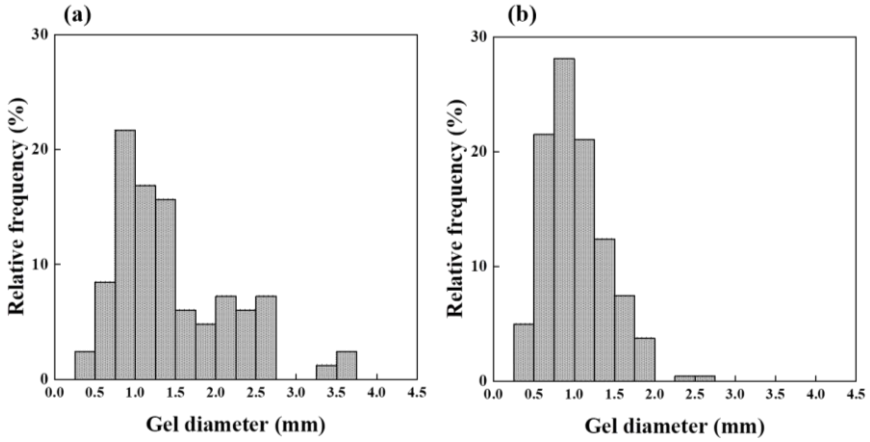

Fig. S1. Size distribution of the spherical base poly(NIPAAm-*co*-NAPMAm) gels. The histogram when the pre-gel solution (NAPMAm 5 mol% in the base gels) droplet was added using an 18 G syringe needle (inner diameter of 0.838 mm and an outer diameter of 1.270 mm**)** to the silicon oil stirred by (a) 150 rpm (n = 83) and (b) 200 rpm (n = 242).

Table S1. The analyzed elements from the size distribution histograms in Fig. S1. Note that the NAPMAm molar composition in the base gels was 5 mol%, and a 18 G syringe needle was used.

Stirring speed	Mean	Median	1st quartile	3rd quartile
150 rpm (Fig. S1(a))	1.460	1.257	0.886	1.937
200 rpm (Fig. S1(b))	1.017	0.955	0.738	1.232

2. Mathematical fitting of the equilibrium swelling ratio

We measured the equilibrium swelling ratio changes in Fig. 3-4 at various temperature points in both redox states. We fitted the data with the Boltzmann sigmoidal equation (Eqn. (S1)). The Boltzmann sigmoidal equation is a practical tool to fit the phase transition of the thermoresponsive gels.

$$y = \frac{A_1 - A_2}{1 + e^{x - x_0/dx}} + A_2 \qquad \text{Eqn. (S1)}$$

The parameters (A_1, A_2, x_0, dx, R^2, and adjusted R^2) analyzed during the fitting process are sorted in Table S2 (from Fig. 3) and Table S3 (from Fig. 4), respectively. We concluded that the fitting process was successful since all R^2 and adjusted R^2 values were greater than 0.993 and 0.986, respectively.

Table S2. Parameters obtained from mathematical fitting of the equilibrium swelling ratio shown in Fig. 3. (OXI) denotes the oxidized state ($Ru(bpy)_3^{3+}$), and (RED) signifies the reduced state ($Ru(bpy)_3^{2+}$).

Sample	A_1	A_2	x_0	dx	R^2	Adj. R^2
NA2_Ru70 (OXI)	1.06141	0.69679	21.84303	2.48036	0.9989	0.9978
NA2_Ru70 (RED)	1.07678	0.67645	21.04248	3.45231	0.99752	0.99504
NA5_Ru70 (OXI)	0.69633	0.46315	23.27002	4.14675	0.99814	0.99628
NA5_Ru70 (RED)	0.73473	0.40216	20.69725	9.35085	0.99301	0.98601
NA10_Ru70 (OXI)	0.60779	0.34578	22.00174	6.45552	0.99708	0.99415
NA10_Ru70 (RED)	0.50542	0.37674	16.96688	5.20346	0.99975	0.9995

Table S3. Parameters obtained from mathematical fitting of the equilibrium swelling ratio shown in Fig. 4. (OXI) denotes the oxidized state ($Ru(bpy)_3^{3+}$), and (RED) signifies the reduced state ($Ru(bpy)_3^{2+}$).

Sample	A_1	A_2	x_0	dx	R^2	Adj. R^2
NA5_Ru15 (OXI)	0.97911	0.59682	21.66822	3.28488	0.99639	0.99279
NA5_Ru15 (RED)	0.98177	0.59381	21.03585	3.55871	0.99799	0.99599
NA5_Ru35 (OXI)	0.71769	0.48205	21.99053	2.86824	0.99966	0.99932
NA5_Ru35 (RED)	0.782173	0.49517	18.38589	3.87403	0.99902	0.99803
NA5_Ru70 (OXI)	0.69633	0.46315	23.27002	4.14675	0.99814	0.99628
NA5_Ru70 (RED)	0.73473	0.40216	20.69725	9.35085	0.99301	0.98601

3. The analysis of volumetric oscillation behaviors during the BZ reaction.

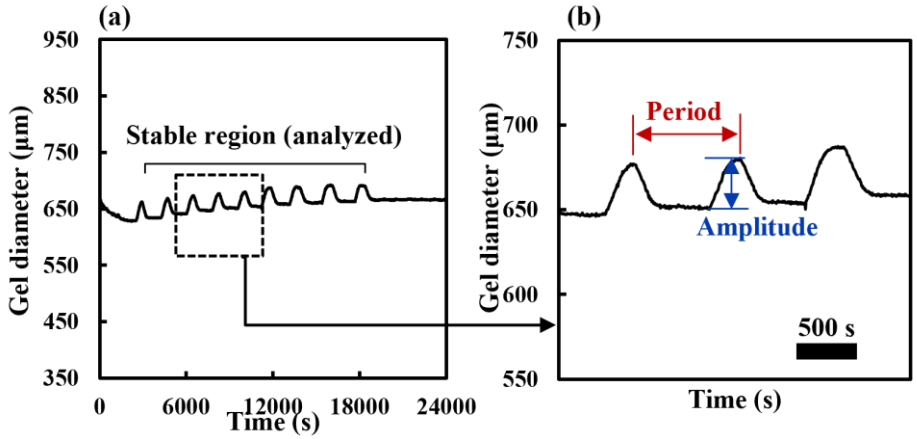

Fig. S2. (a) A representative profile of the gel diameter during the BZ reaction at 20 ℃ until the volume oscillation ends (approximately 20,000s), and (b) enlarged gel diameter profiles describing period and volumetric amplitude. The concentrations of substrates were 894 mM HNO_3, 84 mM $NaBrO_3$, and 64 mM MA.

We analyzed the volumetric oscillation behaviors (i.e., the period and amplitude) during the BZ reaction at 20 ℃ in the stable region. Fig.S2 exhibits a representative gel diameter profile during the BZ reaction. After some time from the start of the BZ reaction, the gel diameter profile displays a repetitive and stable oscillation pattern (Fig. S2(a)). Note that the volumetric oscillations of all gels in this study lasted more than 20,000 seconds. Fig. S2(b) illustrates representative gel diameter profiles in the stable region. We calculate the period and the amplitude in the stable region. The period was defined as the interval between one diameter peak and the next peak. The volumetric amplitude was calculated as the difference between the diameter in the peak and the baseline.

4. Volumetric oscillation behavior of the various-sized gels

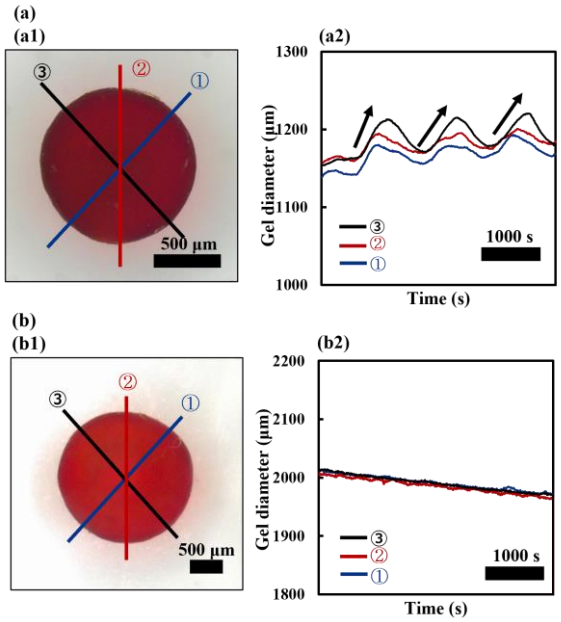

Fig. S3. (a) The volumetric oscillation of the NA5_Ru70 with the base gel size of "2 mm"; (a1) the image of the corresponding gel, and (a2) the gel diameter profiles during the BZ reaction at 20 ℃. (b) the volumetric oscillation of the NA5_Ru70 with the base gel size of "3 mm"; (b1) the image of the corresponding gel, and (b2) the gel diameter profiles during the BZ reaction at 20 ℃. The concentrations of substrates were 894 mM HNO_3, 84 mM $NaBrO_3$, and 64 mM MA.

We analyzed the volumetric oscillations of the self-oscillating gels during the BZ reaction at 20 ℃ with the following fabrication conditions: the diameter of the base gels before $Ru(bpy)_3$ conjugations was varied to 2 mm, (Fig. S3(a) and Movie S6), and 3 mm (Fig. S3(b) and Movie S7). Note that the NAPMAm molar composition in the base gels and the concentration of $Ru(bpy)_3$-NHS were fixed as 5 mol% and 70 mM, respectively. As shown in Fig. S3(a1) and S3(b1), we evaluated the diameter profiles during the BZ reaction in 3 regions: Region 1 (blue line), Region 2 (red line), and Region 3 (black line). As shown in Fig. S3(a2) and Movie S6, the gels with the base gel diameter of 2 mm exhibited not isotropic volume oscillations, but instead propagating BZ chemical wave-dependent swelling/deswelling pattern. Each diameter profile was not synchronized because the swelling can start only in the region where the BZ chemical wave reaches. In contrast, as displayed in Fig. S3(b2) and Movie S7, the gels with a base gel diameter of 3 mm did not volumetrically oscillate. We estimate that the solid and bulk structure of the corresponding gels could inhibit a significant water diffusion subordinated by the redox state changes during the BZ reaction. From this viewpoint, exploiting the base gel of 3 mm diameter cannot be appropriate to realize volumetric oscillations during the BZ reaction in spherical self-oscillating gels.

Supporting movies

Movie S1 Isotropic swelling/deswelling oscillation of the NA2_Ru70 at 20 °C during the BZ reaction. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S2 Isotropic swelling/deswelling oscillation of the NA5_Ru70 at 20 °C during the BZ reaction. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S3 Isotropic swelling/deswelling oscillation of the NA10_Ru70 at 20 °C during the BZ reaction. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S4 Isotropic swelling/deswelling oscillation of the NA5_Ru15 at 20 °C during the BZ reaction. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S5 Isotropic swelling/deswelling oscillation of the NA5_Ru35 at 20 °C during the BZ reaction. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S6 Non-isotropic volumetric oscillation of the NA5_Ru70 (2 mm) at 20 °C during the BZ reaction. Note that the diameter of the base gel before $Ru(bpy)_3$ conjugation was 2 mm. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.

Movie S7 Volumetric oscillation of the NA5_Ru70 (3 mm) at 20 °C during the BZ reaction. Note that the diameter of the base gel before $Ru(bpy)_3$ conjugation was 3 mm. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 300× actual speed. The scale bar is 500 μm.