Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information for

"Region-dependent Volumetric Oscillation of Self-oscillating Gels with Transducer Gradients"

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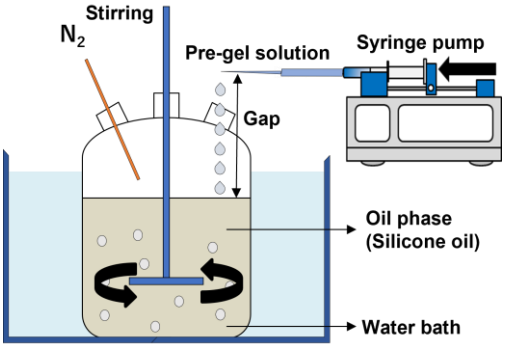
Preparation of spherical base poly(NIPAAm-*co*-NAPMAm) gels



Scheme S1. Schematic illustration of fabricating spherical poly(NIPAAm-*co*-NAPMAm) gels.

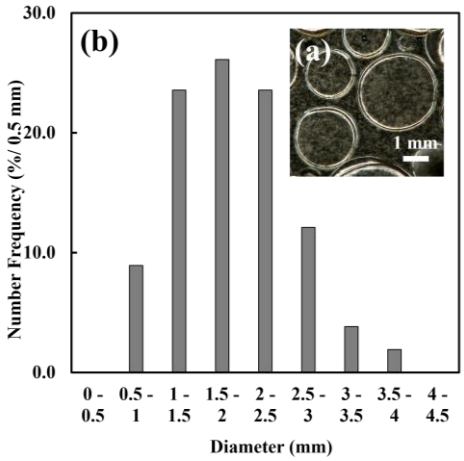


Fig. S1 (a) Image and (b) size distribution of fabricated spherical poly(NIPAAm-*co*-NAPMAm) gels. The images of gels were taken by an optical microscope (Keyence, VHX 900).

Analysis of gray value distribution of the self-oscillating poly(NIPAAm-*co*-NAPMAm) gels

The spatial distribution of conjugated $Ru(bpy)_3$ in the self-oscillating gels was evaluated by the gray value distribution as follows: the gels images were taken by an optical microscope (Keyence, VHX 900), followed by image analysis using Image J software (NIH).

Figs. S2-4 visualize the optical images and gray value distribution of all prepared samples in the reduced state. We drew a line (yellow line in the gel optical images) from Region 2 (with a red arrow) to 1 (with a black arrow) and analyzed the spatial distribution of $Ru(bpy)_3$ by Image J software.

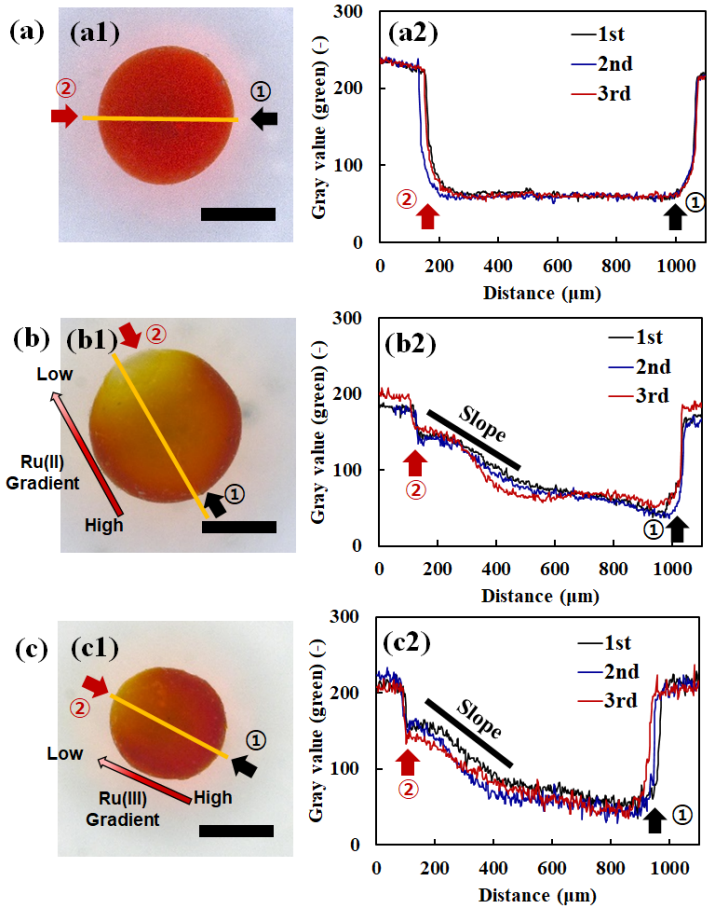


Fig. S2 (a1) NA2_Ru70: an optical image at 20 °C in the reduced state. (a2) the gray value distribution of the yellow line in Fig. S2(a1). (b1) NA2_Gr_Ru70: an optical image at 20 °C in the reduced state. (b2) the gray value distribution of the yellow line in Fig. S2(b1). (c1) NA2_Gr_Ru175: an optical image at 20 °C in the reduced state. (c2) the gray value distribution of the yellow line in Fig. S2(c1). The scale bars are 500 μm. Reduced states ($Ru(bpy)_3^{2+}$) were achieved by adding 894 mM HNO_3 and 84 mM NaCl, and 64 mM MA, respectively.

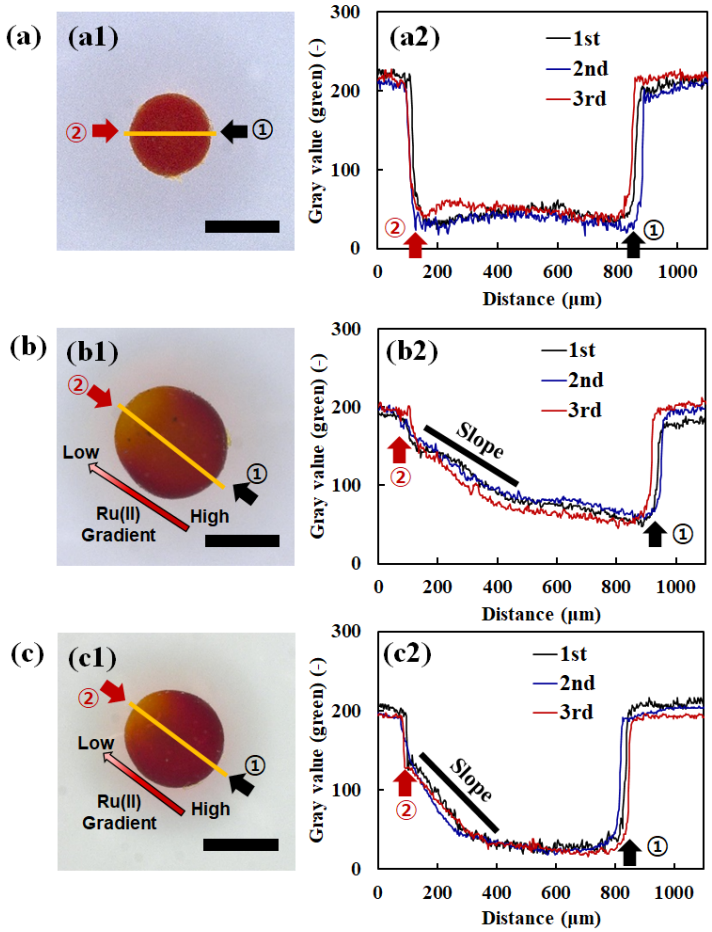


Fig. S3 (a1) NA5_Ru70: an optical image at 20 °C in the reduced state. (a2) the gray value distribution of the yellow line in Fig. S3(a1). (b1) NA5_Gr_Ru70: an optical image at 20 °C in the reduced state. (b2) the gray value distribution of the yellow line in Fig. S3(b1). (c1) NA5_Gr_Ru175: an optical image at 20 °C in the reduced state. (c2) the gray value distribution of the yellow line in Fig. S3(c1). The scale bars are 500 μm. Reduced states ($Ru(bpy)_3^{2+}$) were achieved by adding 894 mM HNO_3 and 84 mM NaCl, and 64 mM MA, respectively.

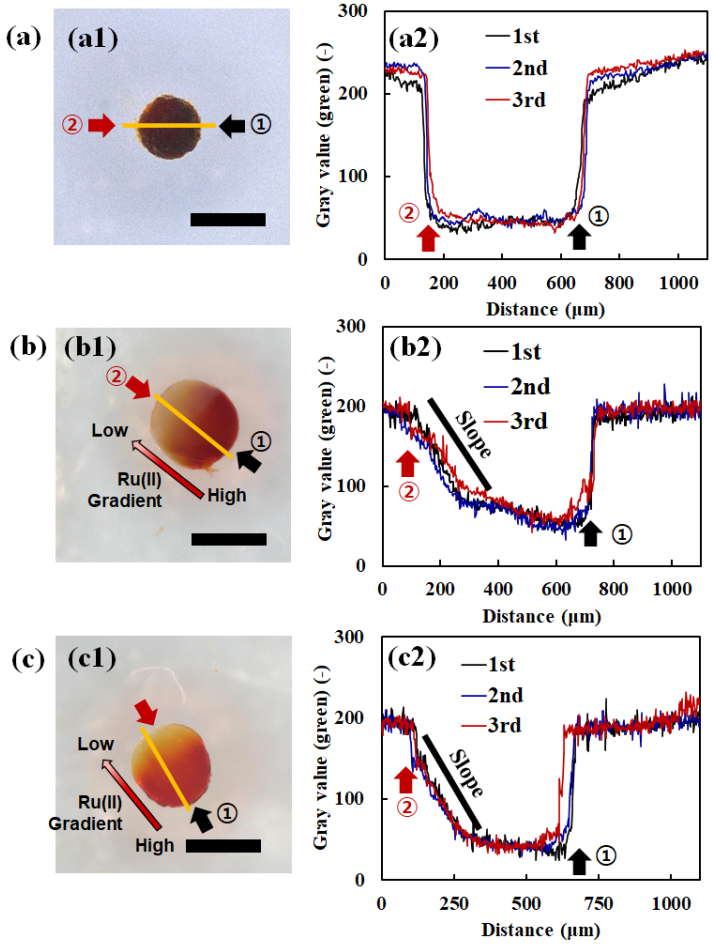


Fig. S4 (a1) NA10_Ru70: an optical image at 20 °C in the reduced state. (a2) the gray value distribution of the yellow line in Fig. S4(a1). (b1) NA10_Gr_Ru70: an optical image at 20 °C in the reduced state. (b2) the gray value distribution of the yellow line in Fig. S4(b1). (c1) NA10_Gr_Ru175: an optical image at 20 °C in the reduced state. (c2) the gray value distribution of the yellow line in Fig. S4(c1). The scale bars are 500 μm. Reduced states ($Ru(bpy)_3^{2+}$) were achieved by adding 894 mM HNO_3 and 84 mM NaCl, and 64 mM MA, respectively.

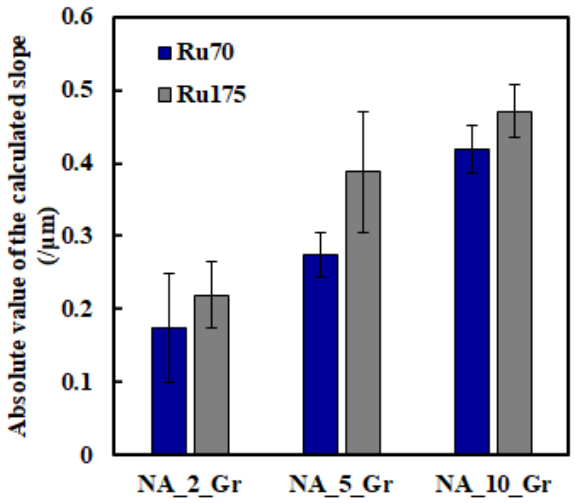


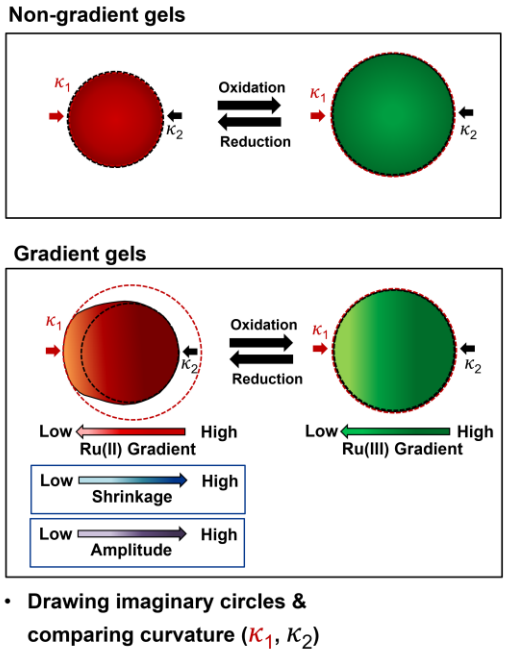
Fig. S5 Absolute values of the calculated slope from the region exhibiting gray-value-gradient section from Figs. S2-4 (*n=3*). Note that only the gradient gels were analyzed. The digit (#) in the legend (expressed as Ru'#') indicates the concentration of Ru(bpy)$_3$-NHS solution in the fabrication process, while the digit (#) in the x-axis (marked as NA_'#'_Gr) signifies the molar composition of NAPMAm in the gradient gels.

Curvature analysis

In this study, the effect of $Ru(bpy)_3$ concentration gradient was quantitatively expressed by curvature (κ) at each opposite region (**Scheme 2**). The gradient of the metal catalyst is continuous. Therefore, the gradient structure brings about not discrete deformation but sequential. To analyze those effects quantitatively, we calculated the curvature at both (1) Region 1 and (2) Region 2. In specific, the concentration of $Ru(bpy)_3$ will be the highest at Region 1 and will decrease continuously toward Region 2. Therefore, the difference of $Ru(bpy)_3$ concentration will be greatest between Regions 1 and 2. In other words, comparing the curvature value of those two regions will offer more noticeable results of gradient structure in a single gel.

$$Curvature\ (\kappa) = \frac{1}{R\ (radius\ of\ imaginary\ circle)} \qquad \textbf{(Equation S1)}$$

The curvature at each side was calculated with **Equation S1** by drawing an imaginary circle based on the curves of both ends (**Scheme 2**). Those circles were drawn by using ImageJ software. More shrinkage causes a smaller imaginary circle. We note that the smaller the radius of the imaginary circle, the greater the value of curvature.



Scheme S2. The effect of $Ru(bpy)_3$ concentration gradient structure in the self-oscillating gels.

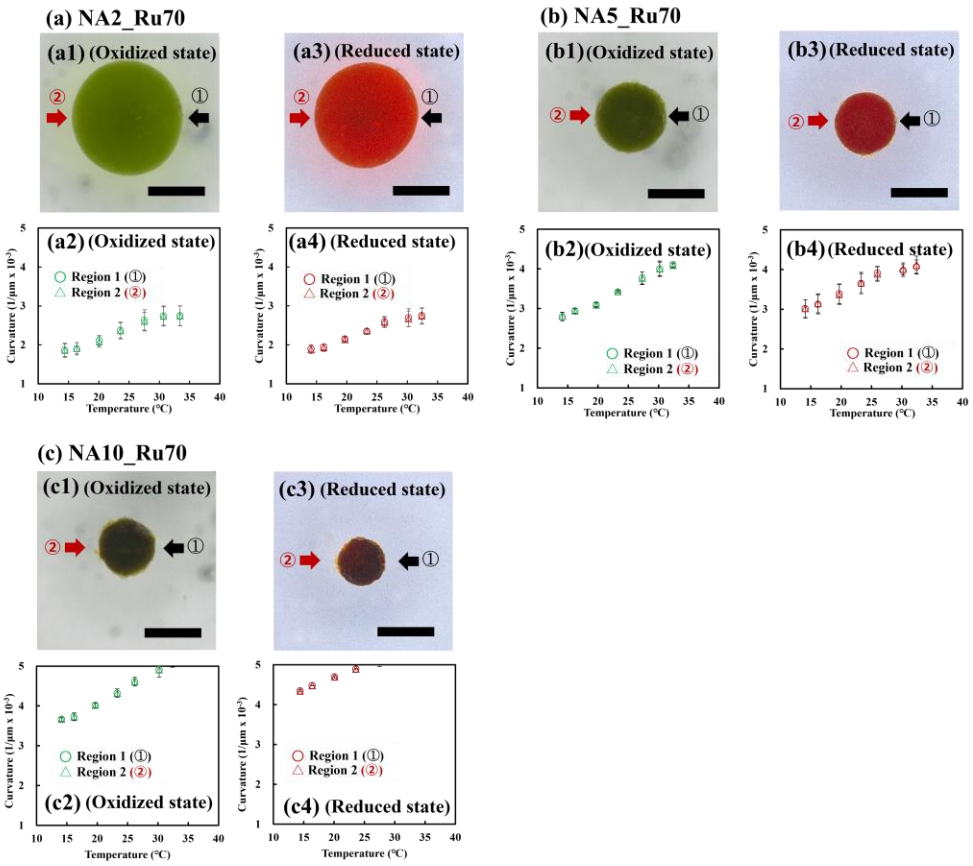


Fig. S6 Isotropic deformation of (a) NA2_Ru70, (b) NA5_Ru70, and (c) NA10_Ru70 in each redox states. Optical images at 20 °C in the ("#"1) oxidized state and ("#"3) reduced state. Temperature dependence of the curvature in ("#"2) the oxidized state and ("#"4) Region 2 in the reduced state. Note that "#" indicates the plot annotation in this figure, such as (a), (b), etc. The scale bars are 500 μm. The oxidized state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3 and 84 mM $NaBrO_3$, whereas the reduced state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3, 84 mM NaCl, and 64 mM MA. 84 mM NaCl was added to maintain ionic strength.

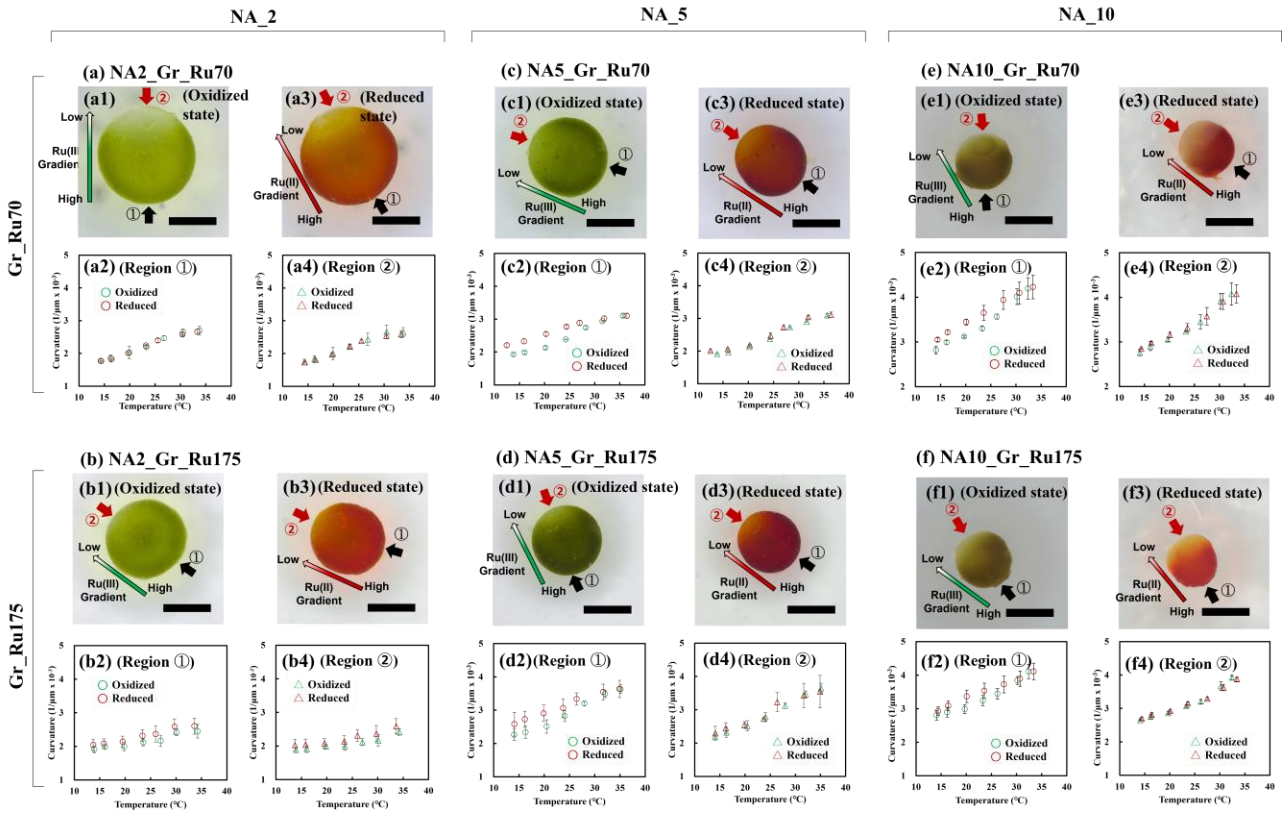


Fig. S7 Region-dependent anisotropic deformation of (a) NA2_Gr_Ru70, (b) NA2_Gr_Ru175, (c) NA5_Gr_Ru70, (d) NA5_Gr_Ru175, (e) NA10_Gr_Ru70, and (f) NA10_Gr_Ru175 in two regions. Optical images at 20 °C in the ("#"1) oxidized state and ("#"3) reduced state. Temperature dependence of the curvature in ("#"2) Region 1 and ("#"4) Region 2 in both redox states. Note that "#" indicates the plot annotation in this figure, such as (a), (b), etc. The scale bars are 500 μm. The oxidized state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3 and 84 mM $NaBrO_3$, whereas the reduced state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3, 84 mM NaCl, and 64 mM MA. 84 mM NaCl was added to maintain ionic strength. Note that Fig. S7 is the result of rearranging the graphs in Fig. 2.

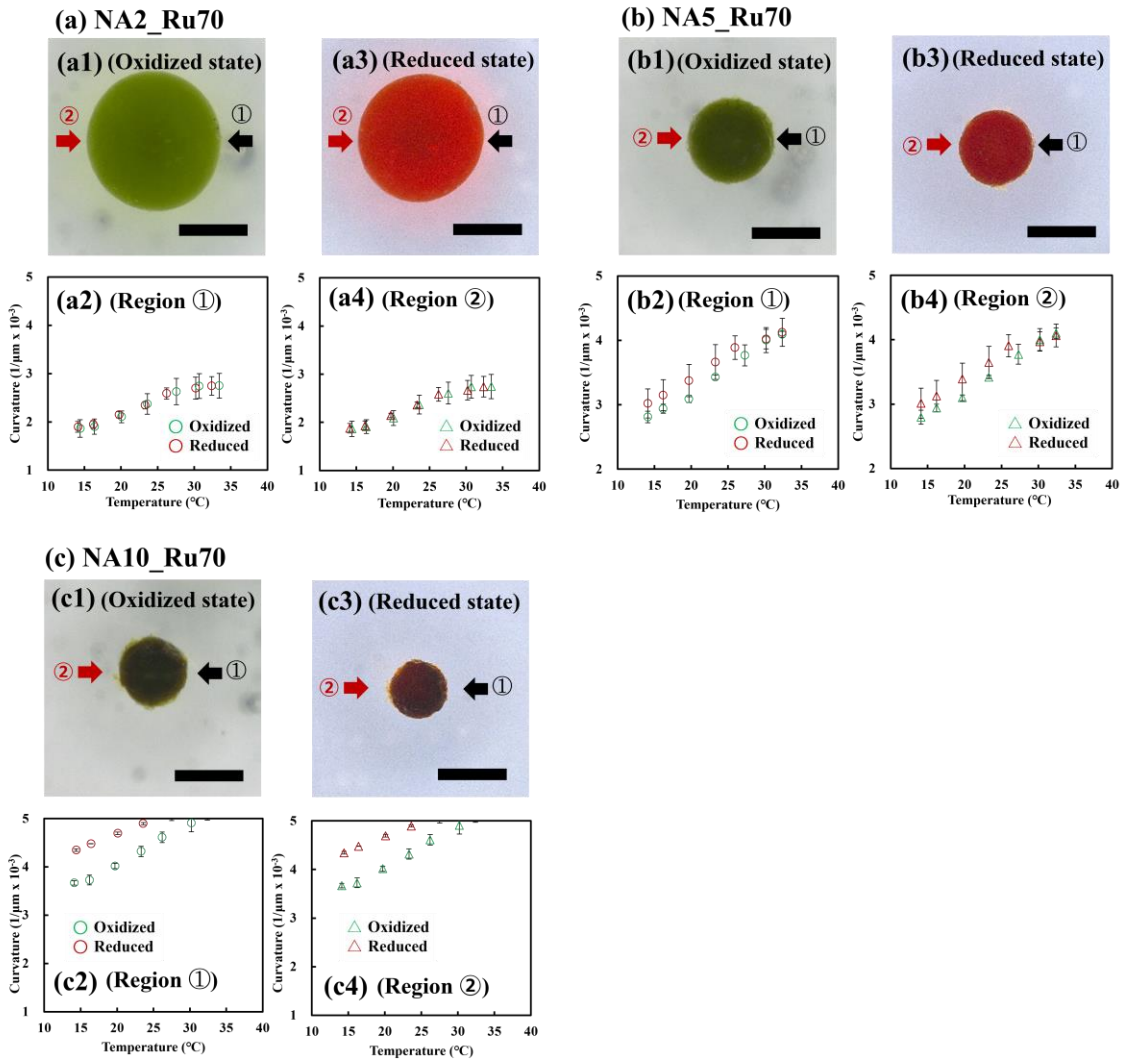


Fig. S8 Isotropic deformation of (a) NA2_Ru70, (b) NA5_Ru70, and (c) NA10_70 in two regions states. Optical images at 20 °C in the ("#"1) oxidized state and ("#"3) reduced state. Temperature dependence of the curvature in ("#"2) Region 1 and ("#"4) Region 2 in both redox states. Note that "#" indicates the plot annotation in this figure, such as (a), (b), etc. The scale bars are 500 μm. The oxidized state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3 and 84 mM $NaBrO_3$, whereas the reduced state ($Ru(bpy)_3^{2+}$) was obtained by combining 894 mM HNO_3, 84 mM NaCl, and 64 mM MA. 84 mM NaCl was added to maintain ionic strength. Note that Fig. S8 is the result of rearranging the graphs in Fig. S6.

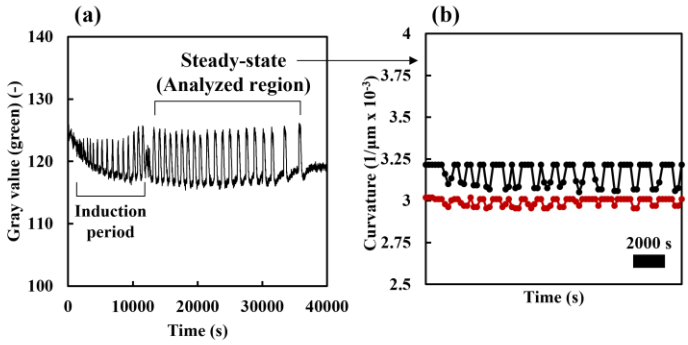


Fig. S9 (a) A representative profile of the BZ chemical signal until the signal generation ends (approximately 40,000 s), and (b) the curvature oscillation profiles in the steady-state of the NA5_Gr_Ru175. The concentrations of substrates were 894 mM HNO_3, 84 mM $NaBrO_3$, and 64 mM MA.

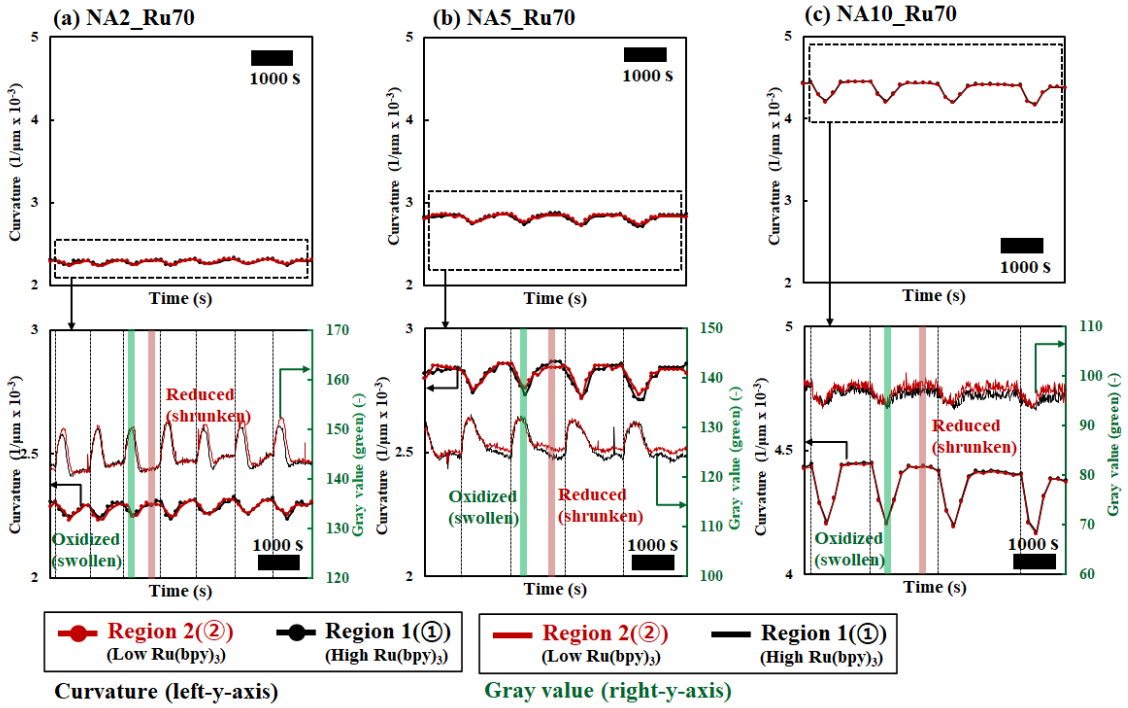


Fig. S10 Curvature oscillation profiles during the BZ reaction at 20 °C of the non-gradient gels: (a) NA2_Ru70, (b) NA5_Ru70, and (c) NA10_Ru70. The enlarged profiles, surrounded by dotted squares, are also displayed below the original profile. Note that the highlighted region shows synchronized profiles of curvature and gray values during the BZ reaction. The concentrations of substrates were 894 mM HNO_3, 84 mM $NaBrO_3$, and 64 mM MA.

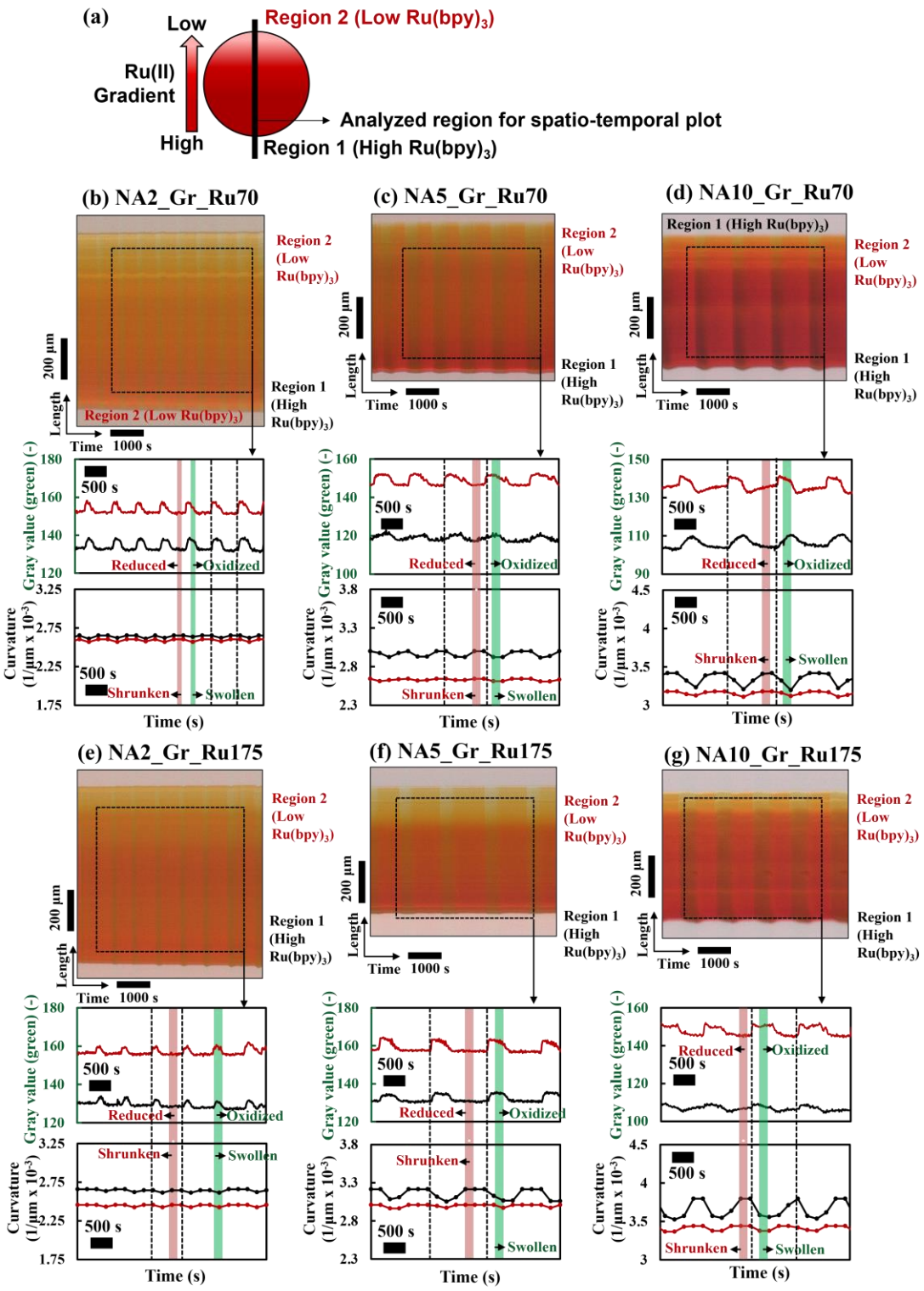


Fig. S11 (a) Schematic illustration of the region for analyzing (1) curvatures and gray values and (2) spatio-temporal plot during the BZ reaction. The spatio-temporal plot, the gray value (green

channel) profiles, and the curvature profiles of each gradient gel during the BZ reaction; (b) NA2_Gr_Ru70, (c) NA5_Gr_Ru70, (d) NA10_Gr_Ru70, (e) NA2_Gr_Ru175, (f) NA5_Gr_Ru175, (g) NA10_Gr_Ru175. The profiles of the gray value and the curvature corresponds to the highlighted box in spatio-temporal plot. Note that each curvature profile is also from Fig. 3. The concentrations of substrates were 894 mM HNO_3, 84 mM $NaBrO_3$, and 64 mM MA.

Supporting movies

Movie S1

Anisotropic swelling/deswelling oscillation of a NA2_Gr_Ru175 (gradient gel) 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

Anisotropic swelling/deswelling oscillation of a NA5_Gr_Ru175 (gradient gel) 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

Anisotropic swelling/deswelling oscillation of a NA10_Gr_Ru175 (gradient gel) 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 a NA2_Ru70 (non-gradient gel) 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 a NA5_Ru70 (non-gradient gel) 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

Isotropic swelling/deswelling oscillation of a NA10_Ru70 (non-gradient gel) 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 S7

Anisotropic swelling/deswelling oscillation of a gradient gel with a larger size (approximately 1.5 mm) at 20 ℃ during the BZ reaction. This sample was fabricated the dipping a part of the base poly(NIPAAm-*co*-NAPMAm) gel (2 mm size) into the 70 mM $Ru(bpy)_3$-NHS solution for 24 h at 45 ℃. Concentrations of the BZ substrates: [HNO_3] = 894 mM, [$NaBrO_3$] = 84 mM, and [MA] = 64 mM. The movie speed is 250× actual speed. The scale bar is 500 μm.