Light-driven autonomous swing of a multi-layered hydrogel

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1. EXPERIMENTA SECTION

Materials. N-isopropylacrylamide (NIPAm), N,N′-methylene bis-acrylamide (BIS), Ammonium Persulfate (APS), and N, N, N', N'-Tetramethylethylendiamine (TEMED) were purchased from Wako Pure Chemical Industries, Ltd. Acrylamide (AAm) were purchased from Tokyo Chemical Industry Co., Ltd. Indian ink purchased from Kuretake Co., Ltd. The white pigment supplied kindly by Matsui Shikiso Chemical Co. Ltd. All chemical reagents were used without further purification.

Preparation of single layer gels. The hydrogels used were prepared by free-radical polymerization in an aqueous solution[1]. The reaction solution (pre-gel solution) for preparing the PNIPAm gel consisted of a monomer of NIPAm, a chemical cross-linker of BIS, an initiator of APS, and an accelerator of TEMED. Deionized water purged with nitrogen was used for all preparations. The pre-gel solution for PNIPAm gel was prepared by dissolving 1.00 g of NIPAm, 0.03 g of BIS, and 0.05 g of APS into 2 ml of deionized water. TMEDA of 0.5 ml was added into the pre-gel solution and polymerized. PAAm gel was prepared using the same ingredients in the same amounts in the pre-gel solution except that the AAm was used as the monomer instead of NIPAm. The PNIPAm-co-AAm gel was obtained by adding 0.05 g of AAm to the pre-gel solution of PNIPAm gel. Detailed protocols for the preparation and determination of the swelling ratio of PNIPAm and PNIPAm-co-AAm gel films as a function of temperature can be found elsewhere.[2]

Preparation of multilayer gel bar. The multilayer gel bars were prepared as follows (see Figure S2 (a)). (1) The pre-gel solution of PNIPAm was filled into a glass plate partitioned by 50 mm × 50 mm with curing tape, covered with a Teflon plate, and polymerized for 1 day to form the 1st gel layer. (2) The Teflon plate was removed, and the tape was re-masked over the 1st layer of tape to form the 2nd template. On the top of the polymerized 1st layer, the PAAm pre-gel solution was overlaid and polymerized the same way as the 1st layer. (3) The third layer was obtained using the PNIPAm-co-AAm pre-gel solution the same way as the first and

second layers. (3) The prepared multilayer hydrogels were washed three times with distilled water and then immersed in distilled water for 24 h at room temperature. (5) The obtained multilayer gel pieces were trimmed to 300 mm x 5 mm x 3 mm using a razor blade to form a bar and cut off half of the first layer to create an asymmetrical bar like a toothbrush. The gel bars were frozen and thawed three times for observation to respond to temperature changes quickly.

Measurement of the motion of the gel bar. The experimental apparatus used for the swing observation is illustrated in Fig.2 (a). The gel tail was clamped and hung vertically to a support bar. With the support bar put on the rim of a glass cuvette cell filled with distilled water, the gel bar has immersed the water from the gel head. After leaving the gel bar at room temperature for 1 hour, the swelling of the gel reached equilibrium. The incident laser beam was irradiated to the gel head from the 1st layer of the gel (PNIPAm) side, with an incident angle of 45 degrees. The beam was generated using a green semiconductor laser generator (DPGL-2W, Japan Laser, 10 W, 532 nm) and irradiated with 0.7 mA from the outside of the cuvette cell. The neutral position was set as $X(0)$, and the gel head position at t, $X(t)$, was obtained from the interval photograph using an image analysis software (Image-Pro 6.0, Media Cybernetics, Silver Spring, MD, USA). The images were captured every 10 seconds using a CCD camera (CoolSNAP HQ, Photometrics, CA, USA). The cell temperatures were kept at 10, 20, and 30 °C using a water bath base circulator Haake DC30 (Haake GmbH, Karlsruhe, Germany) and controlled in ±0.1 °C.

2. MOVIE LEGENDS

Legend of Video S1. The steady laser beam irradiation movie of a gel bar suspended in a cell filled with temperature-controlled distilled water (at 20 ˚C). The frame rate is 600 times faster than real-time. The width of the optical cell in the movie is 1cm. The asymmetrically shaped gel bar sides are composed of a transparent PNIPAM layer (left side) and a white PNIPAM-co-AAm layer (right side).

Legend of Video S2. The movie of the multi-layered gel bar under continuous laser beam irradiation when the gel bar is suspended in an optical cell filled with temperature-controlled distilled water at 10 ˚C. Conditions other than temperature are the same as in Video S2.

Legend of Video S3. The movie of the multi-layered gel bar under continuous laser beam irradiation when the gel bar is suspended in an optical cell filled with temperature-controlled distilled water at 20 ˚C. Conditions other than temperature are the same as in Video S2.

Legend of Video S4. The movie of the multi-layered gel bar under steady laser beam irradiation when the bar suspended in a suspended in an optical cell filled with temperature-controlled distilled water at 30 ˚C. Conditions other than temperature are the same as in Video S2.

Legend of Video S5. The movie of the multi-layered gel bar under continuous laser beam irradiation when the gel bar is suspended in an optical cell filled with temperature-controlled distilled water. Both sides of the asymmetrically shaped gel bar are composed of PNIPAM-co-AAm layers. The conditions are the same as in Movie S1 except for the composition of the multilayer gel bar.
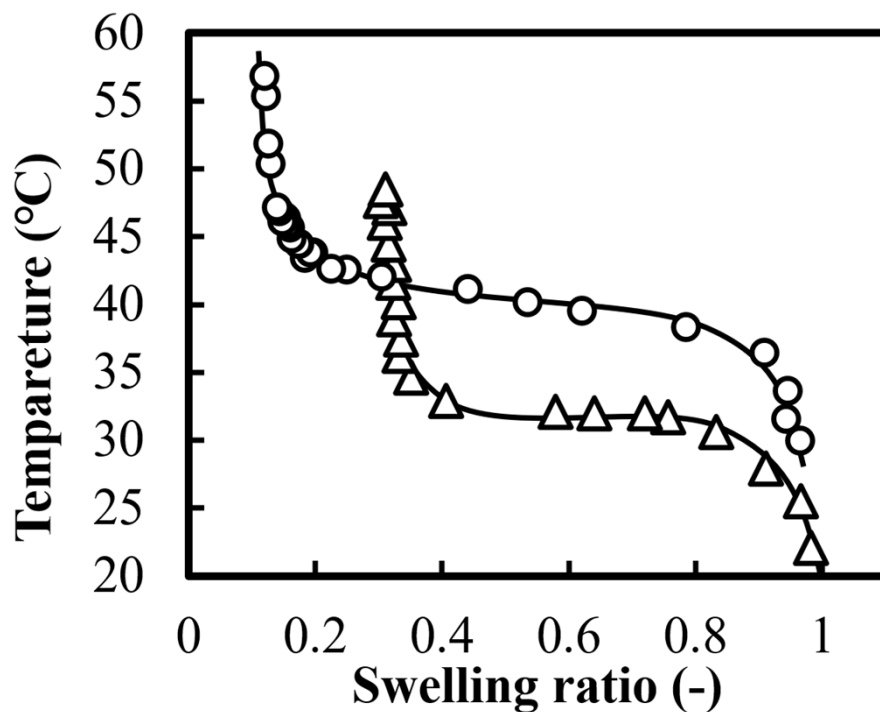
3. SUPPLEMENTAL FIGURES

Figure S1. Figure S1. Temperature dependence of swelling ratio for PNIPAm gel(Δ) and PNIPAm-co-AAm gel(○). The solid curves are drawn as a guide for the eye.
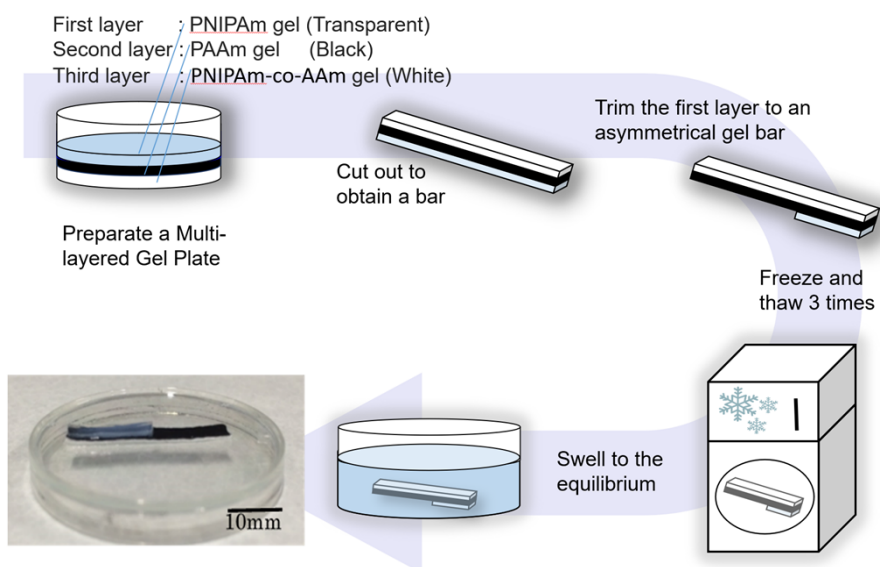

Figure S2. Schematic diagram of the fabrication process of a thermosensitive multilayer gel bar and the image of the resulting object (bottom left).
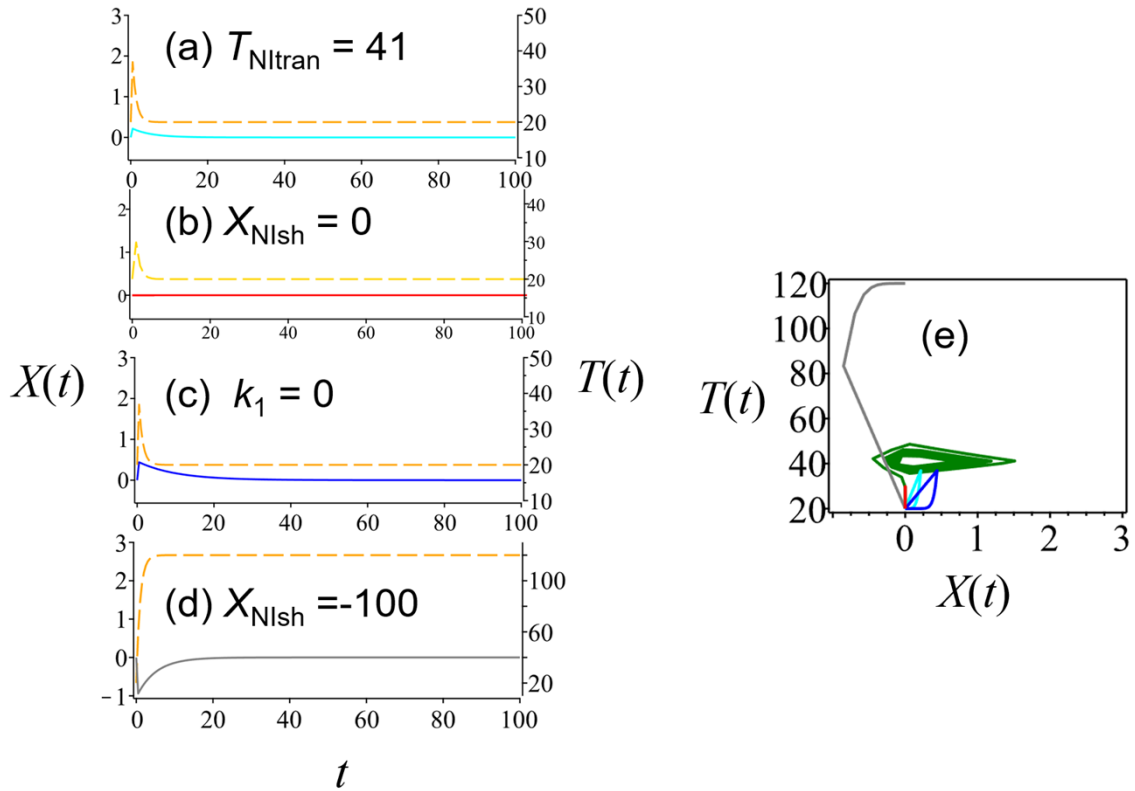
Figure S3. The theoretical results of $X(t)$ and $T(t)$ obtained by numerically solving eq. (1) and eq.(2). The equations were solved using the parameters presented in Fig. 6, except for (a) T_{NItran} (use 41 instead of 33), (b) X_{NIsh} (use 0 instead of -50), (c) k_1 (use 0 instead of 0.1), (d) X_{NIsh} (use -100 instead of -50). (a)~(d): the time courses of $X(t)$(solid curve) and $T(t)$ (dash curve). (e) the phase diagrams of $X(t)$ vs. $T(t)$ calculated using the above parameters. The colors of the circle curves correspond to (a)~(d). The green curve gives the results obtained in Figure 6 (b) calculated at $T_{base} = 20$ as a reference.
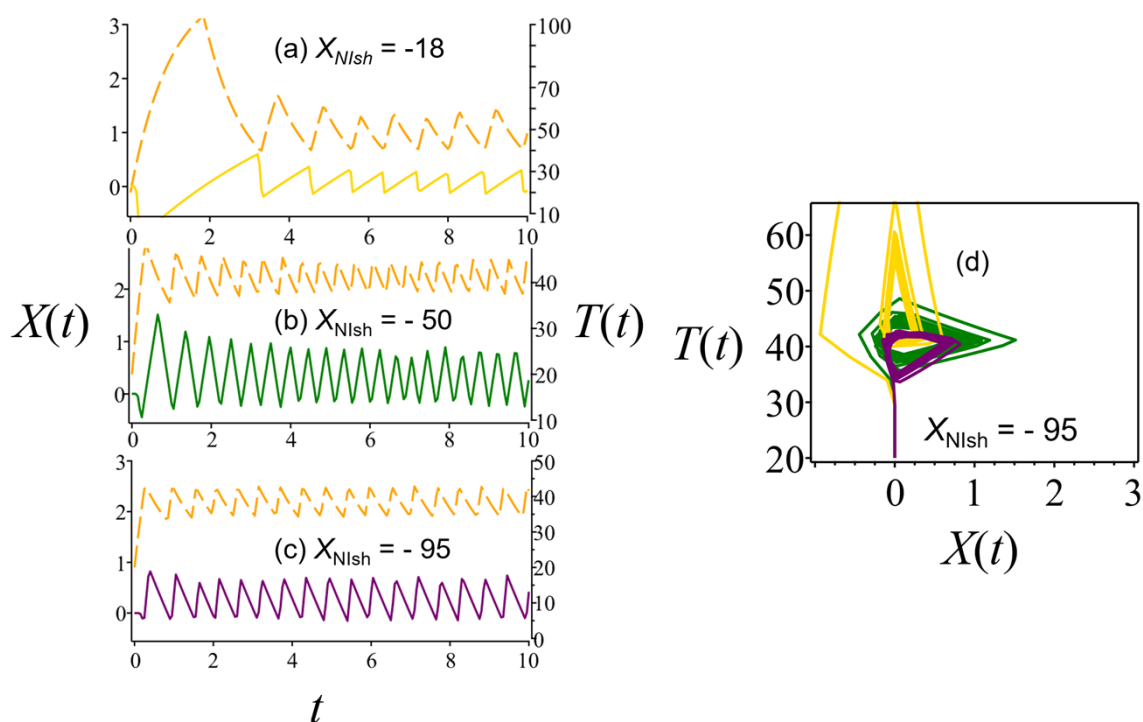
Figure S4. The dependence of X_{Nish} of the theoretical results $X(t)$ (solid) and $T(t)$ (dash) obtained by solving eq. (1) and eq.(2) using the parameters presented in Fig. 6 at $T_{\text{base}} = 20$. *(a)-(c):* the time courses of $X(t)$ and $T(t)$ calculating as $X_{\text{Nish}} =$(a)-18, (b)-50, (c)-95. (d) the phase diagrams of X(t) vs. $T(t)$ calculated in these X_{Nish}. The colors of the circle curves correspond to (a)~(c).

4. SUPPORTING REFERENCES

(1) Klouda, L.; Mikos, A. G. Thermoresponsive hydrogels in biomedical applications. *European journal of pharmaceutics and biopharmaceutics* **2008**, *68* (1), 34-45.

(2) Nakamura, S.; Onimaru, S.; Oishi, Y.; Narita, T. Volume and temperature change behaviors of photothermal convertible hydrogels. *Polymer* **2017**, *116*, 534-539.