Supporting Information

A "Writing" Strategy for Shape Transition with Infinitely Adjustable Shaping Sequences and in situ Tunable 3D Structures

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1. Experimental Section

Materials: Nafion N117 films (DuPont, t = 180 μm, sulfonic acid form) were supplied by Alfa Aesar. All as-received Nafion films were pre-cleaned sequentially in 3% H_2O_2 at 80 °C for 1 h, 1 M H_2SO_4 at 80 °C for 1 h and then washed with deionized (DI) water for several times. Dopamine hydrochloride was purchased from Sigma-Aldrich and used without further purification. Other reagents such as tris(hydroxymethyl) aminomethane, silver nitrate and sulfuric acid were procured from Sinopharm Chemical Reagent Co., Ltd and used as received.

Modification of Nafion 117 films: Pre-cleaned Nafion N117 films were immersed in dopamine hydrochloride aqueous solution (40 mL, 12.5 mg mL^{-1}) for 12 h. Then Tris buffer solution (10 mL, pH 8.5, 250 mM) was added and the concentration of dopamine hydrochloride and Tris buffer solution were eventually 10 mg mL^{-1} and 50 mM, respectively. The solution with the Nafion films was shaken for 12 h at room temperature. Subsequently, the obtained films were treated with 0.5 M H_2SO_4 for 2 h for protonation, washed 3 times with deionized water to remove residual H_2SO_4 and dried in vacuum at 40 °C overnight. All the Nafion films with or without polydopamine (used as control) were annealed at 175 °C for 30 min to reach their equilibrium states.

Characterizations and Measurements: All the thermomechanical analysis (TMA) experiments were conducted in a tensile mode using a DMA Q800 (TA Instruments, USA). Tan δ and storage modulus were determined at a frequency of 1 Hz and a heating rate of 5 °C min^{-1} for each sample. In a stress controlled thermomechanical experiment to evaluate the shape memory effect of PDA modified Nafion films, the sample was stretched from its initial length (L_o) to a suitable elongation at a temperature above its α transition temperature (T_{high} =

175 °C), and cooled down to T_{low} (T_{low} = 20 °C), which was below its transition temperature range, under constant stress with a cooling rate of 6 °C min^{-1} to generate a final length (L). Afterwards, the sample was unloaded, and equilibrated for 5 min, followed by a temperature ramping from T_{low} to T_{high} with a rate of 6 °C min^{-1} in the unloaded mode. Then the sample would be kept at T_{high} for another 40 min.

Energy dispersive X-ray spectroscopy (EDX) mapping of fracture surfaces were running at the field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan) equipped with an energy dispersive X-ray spectroscope. The sample for EDX was pretreated with 5 mM $AgNO_3$ aqueous solution for 24 h and washed several times before drying in vacuum oven at 40 °C. The color of fracture surfaces were observed under an inverted optical microscope (Eclipse TE2000, Nikon, Tokyo, Japan) equipped with a highly sensitive CCD camera (ORCA-ER, Hamamatsu Photonics, Shizuoka, Japan). Attenuated total reflectance Fourier transform infrared (FT-IR/ATR) spectra were collected on an infrared spectrophotometer (Nicolet 6700, USA) equipped with an ATR accessory (ZnSe crystal, 45 ^{o}). UV-vis spectrophotometer (Shimadzu UV-2550 UV-vis spectrometer, Japan) was employed to determine the light transmittance of the stretched Nafion films (Stretching ratio: 150 %) at 808 nm. Temperature differences between the two sides of the film for different irradiation intensities after 10 s irradiation by 808 nm continuous wave (CW) laser (LSR808H-7W, Lasever Inc., China) were determined with an infrared thermal imaging camera (FLIR E60, Flir System, Inc., USA).

Light Writing: The PDA modified films were stretched uniaxially to an appropriate elongation at 175 °C and the obtained temporary shape was fixed at 20 °C. The 808 nm laser was used as a pen to initiate complicated 3D shape transition. The writing process was well-designed to verify "easy-to-implement", stepwise and "personalized tailoring" shape transition in our system. The parameters and process were shown in the main article. All the images in this part were recorded with a digital camera.

2. Supplementary Figures

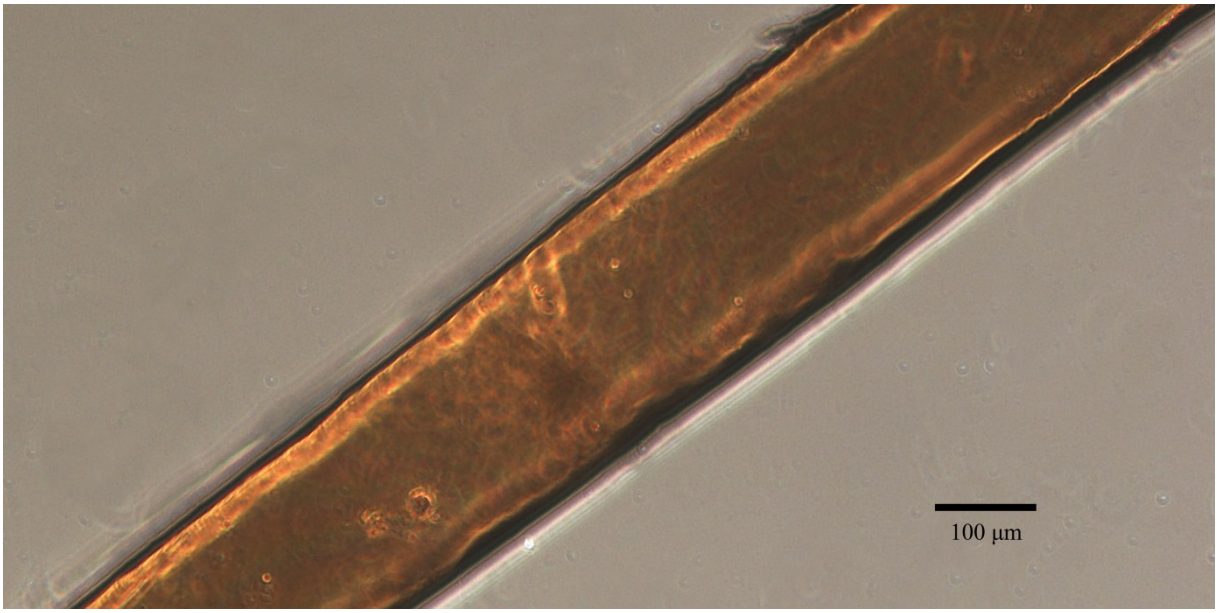

Figure S1. Optical microscopy image of the cross-section of PDA modified Nafion film which shows that both the surface and the bulk turn brown in color.

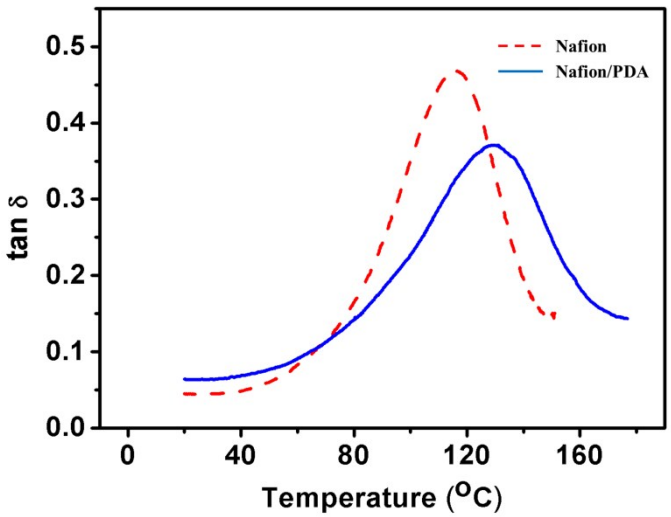

Figure S2. DMA curves of tan δ of nascent Nafion films and Nafion/PDA composite films.

The α transition temperature of Nafion films after modification was studied using dynamic analysis (DMA). Our results show that α transition occurs in a slightly broader temperature range from 55 °C to 175 °C after modification. According to previous works, the thermal relaxations of Nafion at this temperature range are corresponded to the activated ion-hopping process, which leads to significant destabilization of the electrostatic network. Therefore the broader α transition temperature range is reasonable since polydopamine is dispersed in the ionic phase. However, the physical cross-linkers in Nafion are hardly influenced by polydopamine because they cannot be swollen in water. As a result, this kind of modification has no unfavorable influences in shape memory effect of the film (Figure 1e).

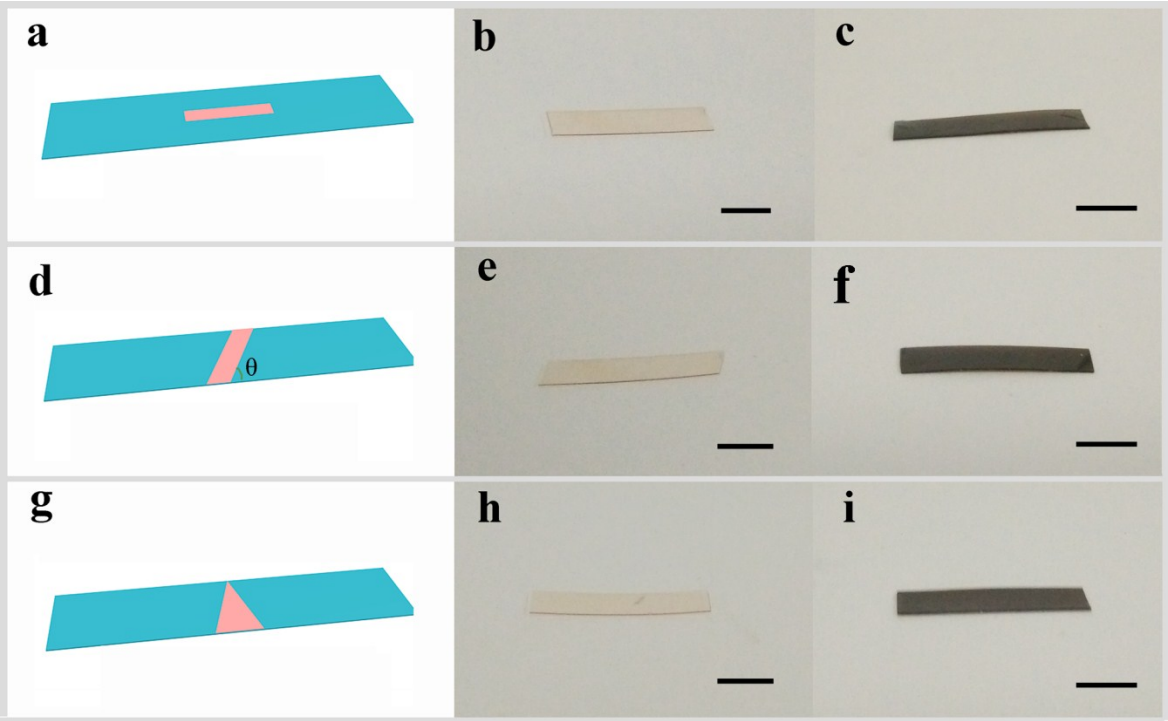

Figure S3. Photographs of the unmodified Nafion films with stretching ratio of 150% and unstretched PDA /Nafion films exposed to the same NIR laser as that in Figure 2. a, d, g) Schematic representation of the planer films treated with NIR laser with the shape of facular regions to be a) rectangular d) parallelogram with an angle of θ to the long side, and g) isosceles triangle whose central axis is perpendicular to the long side. b, e, h) Obtained shapes of stretched unmodified Nafion films after NIR light irradiation. c, f, i) Obtained shapes of unstretched PDA/Nafion films after NIR light irradiation. Laser intensity: 57.4 mW mm^{-2}, Scale bars: 0.5 cm.

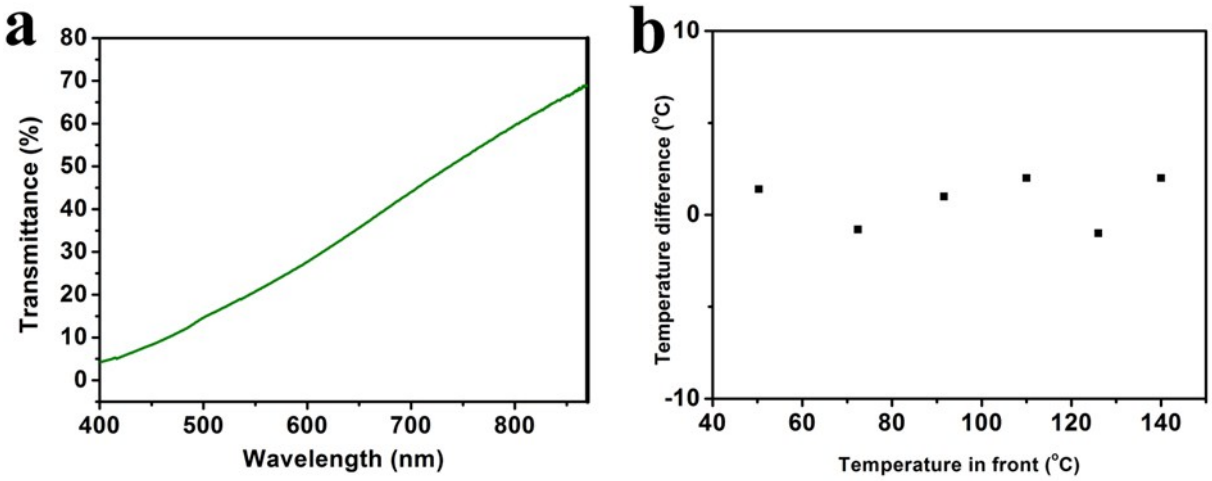

Figure S4. a) Light transmittance of PDA modified Nafion film with uniaxially stretching ratio of 150% at different wavelength ranging from 400 nm to 900 nm. b) Temperature difference between the two sides of the film for different irradiation intensities. For more intuitive expression, the temperature in the front side was set as X axis.

UV–vis spectrum of the stretched film shows that more than 60% of the light in 808 nm transmits through the film (Figure S4a), illustrating that the back side of the film is also exposed to NIR light, although the NIR light intensity is a little weaker. In this respect, at the very beginning of the irradiation, small temperature gradient will be generated but our stretched film is so thin that temperature equilibrium is time costless thus resulting in the indetectable temperature gradient along the thickness. We measured the temperature of the two sides of a stretched Nafion/PDA film with a stretching ratio of 150 % under different irradiation intensity for 10 s, as 10 s was chosen as the irradiation time in a typical light writing process. The results indicate that there is no detectable temperature gradient along the thickness direction of the film (Figure S4b ESI†). As Figure 3a, b shows the inner stress of the film after irradiation for 10 s, temperature equilibrium has already been achieved and there is no stress gradient along the thickness direction. However, the initial temperature gradient is important in determining the direction of shape transition. Take the condition in Figure 2d as an example, the film will transfer to helix structures upon NIR irradiation. In respect of energy, the right- or left-handedness of the helix is equally possible as it is symmetric along

the thickness direction for the final status. But the initial temperature gradient will give a slight perturbation. Such a small perturbation at the beginning of the shape transition is enough to determine the transition direction. Thus the shape transition direction is always predictable in our experiments.

3. Theoretical modelling

a) Sheet parameters

We modeled this system as a sheet on which there is a heated strip with surrounding unheated part. The widths of the heated and unheated parts are w_h and w_{un} respectively. t refers to the thickness of the sheet; t(T) and $w_h(T)$ represent the thickness and width of the heated part at temperature T; l is the length of the faculae. Note that it is not equal to the initial length of the heated part but is actually the obtained length of that after irradiation. The initial length of the heated part is written as L which is also the perimeter of the arc. E(T) and E refer to the modulus at temperature T and the modulus at 20 °C, respectively. The contraction ratio of the film under free condition is f(T). It can be calculated as $f(T) = \frac{\varepsilon - \varepsilon(T)}{1 + \varepsilon}$. ε and ε(T) refer to the initial stretching ratio and stretching ratio at temperature T.

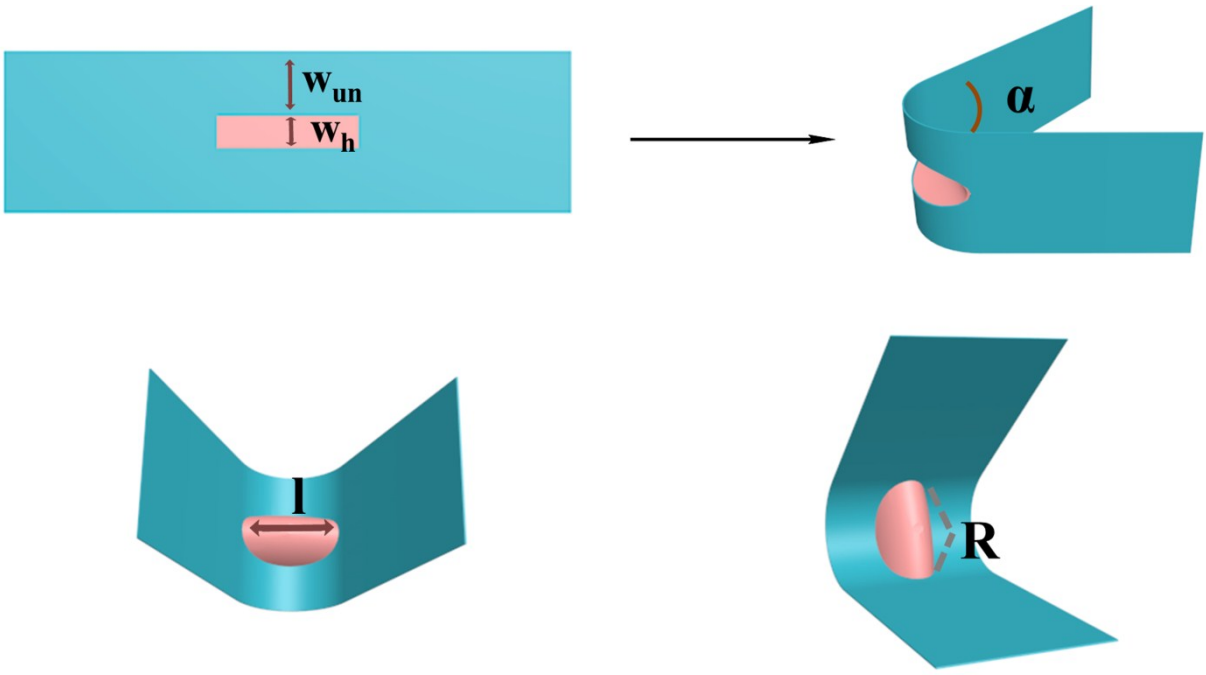

Figure S5. Schematic representation of stretched Nafion/PDA films (stretching ratio: 150%) treated with NIR laser with the facular region in the shape of rectangular parallel to the stretching direction and its shape transformation from planar sheet to saddle-like shape and its visual illusions from different angles.

b) Approximations

We predict the parameters of the obtained shape by minimizing the energy of the Non-Euclidean-Plates generated after irradiation to find the energy-minimizing configuration. Thus we should express elastic energy in an analytical expression at first. For simplification, we made a few reasonable approximations. 1) This material is incompressible which means that the volume of the sheet will remain constant upon shape shifting and the Poisson ratio $\vartheta = \frac{1}{2}$; 2) as $\frac{E}{E(T)} \gg 1$ over most of the parameter range which means that the unheated part is much stiffer than the heated part, the unheated part is considered to be inextensible. Therefore, all the stretching energy is contained within the heated part, while the bending energy is only related to the unheated parts; 3) the thickness of the film is small enough so that the force to maintain bending is quite weak. That means the force to constrain shape recovery of the heated part is weak, and the resulted length of the heated part is beyond but close to its equilibrium length.

3.3 Derivation of elastic energy expression

The bending energy of a film thin enough[1, 2] can be calculated as

$$E_{bending} = \frac{1}{2} D[(k_x + k_y)^2 + 2(1-\vartheta)({k_{xy}}^2 - k_x k_y)WLt \tag{S1}$$

The bending stiffness D is defined by

$$D = \frac{Et^2}{12(1-\vartheta^2)} \tag{S2}$$

k represents curvature of the arc. In this experiment, most of the unheated part only bends in one direction, and the radius of the arc is R. Thus the bending energy equals to

$$E_{bending} = \frac{Et^3 w_{un} L}{9R^2} \tag{S3}$$

The stretching energy in the heated part is resulted from the recovery in restricted conditions.

$$E_{stretching}(T) = \frac{1}{2} E(T) w_h(T) lt(T) [\frac{l - L(1-f(T))}{L(1-f(T))}]^2 \tag{S4}$$

As the material is incompressible, $w_h(T)lt(T) = w_hLt$, leading to

$$E_{stretching}(T) = \frac{1}{2}E(T)w_hLt[\frac{l - L(1-f(T))}{L(1-f(T))}]^2 \quad \text{(S5)}$$

According to the third approximation, $L(1-f(T))\sim l$. Thus we can rewrite Equation. S5 as follows:

$$E_{stretching}(T) = \frac{1}{2}E(T)w_hLt\frac{[l - L(1-f(T))]_2}{L(1-f(T))l} = \frac{1}{2}E(T)w_ht\frac{[l - L(1-f(T))]_2}{(1-f(T))l} \quad \text{(S6)}$$

L is the initial length of the heated part and also the length of the arc. It is determined by l and R.

$$L = Rarcsin\left(\frac{L}{2R}\right)\sim l + \frac{l^3}{8R^2} \quad \text{(S7)}$$

Replacing L in Eq. S3 and Eq. S6 according to Eq. S7, we obtain that

$$E_{bending} = \frac{Et^3w_{un}(l + \frac{l^3}{8R^2})}{9R^2} \quad \text{(S8)}$$

$$E_{stretching}(T) = \frac{1}{2}E(T)w_htl\frac{[1 - (1 + \frac{l^2}{8R^2})(1-f(T))]}{1-f(T)}^2 \quad \text{(S9)}$$

The total energy can be obtained by adding the bending energy and stretching energy up.

$$E_{elastic} = \frac{Et^3w_{un}\left(l + \frac{l^3}{8R^2}\right)}{9R^2} + \frac{1}{2}E(T)w_htl\frac{\left[1 - \left(1 + \frac{l^2}{8R^2}\right)(1-f(T))\right]_2}{1-f(T)}$$

(S10)

3.4 Structural characteristics of the saddle-like shape

The estimation of the radius of the arc in saddle-like shape of the sheet is obtained by minimizing the elastic energy $E_{elastic}$ as follows:

$$R^2 = \frac{9(1-f(T))E(T)w_h l^4 + 16Ew_{un}t^2 l^2}{8(9f(T)E(T)w_h l^2 - 8Ew_{un}t^2)}$$

(S11)

The angle of the saddle α (Figure S5) can be calculated via R and l:

$$\alpha = \pi - 2arcsing(\frac{l}{2R}) \quad \text{(S12)}$$

4. Validation of the theoretical model

To verify the predictive capability of the model, we examined experimentally a negatively correlated variation in α versus light intensity (Figure 3d). In the meantime, we measured the recovery ratio Rr(T), contraction ratio f(T), and modulus at different temperature (Figure S6a, b, c). As the NIR irradiation time in this experiment was set as 20 s, the films in temporary shape were kept at each temperature for 20 s to measure the recovery ratio and contraction ratio. The elastic modulus of the film was estimated with the storage modulus at low frequencies (Figure S6c). The modeling results show that α decreases with temperature (Figure 3c) which is approximately in agreement with the variation in α versus light intensity.

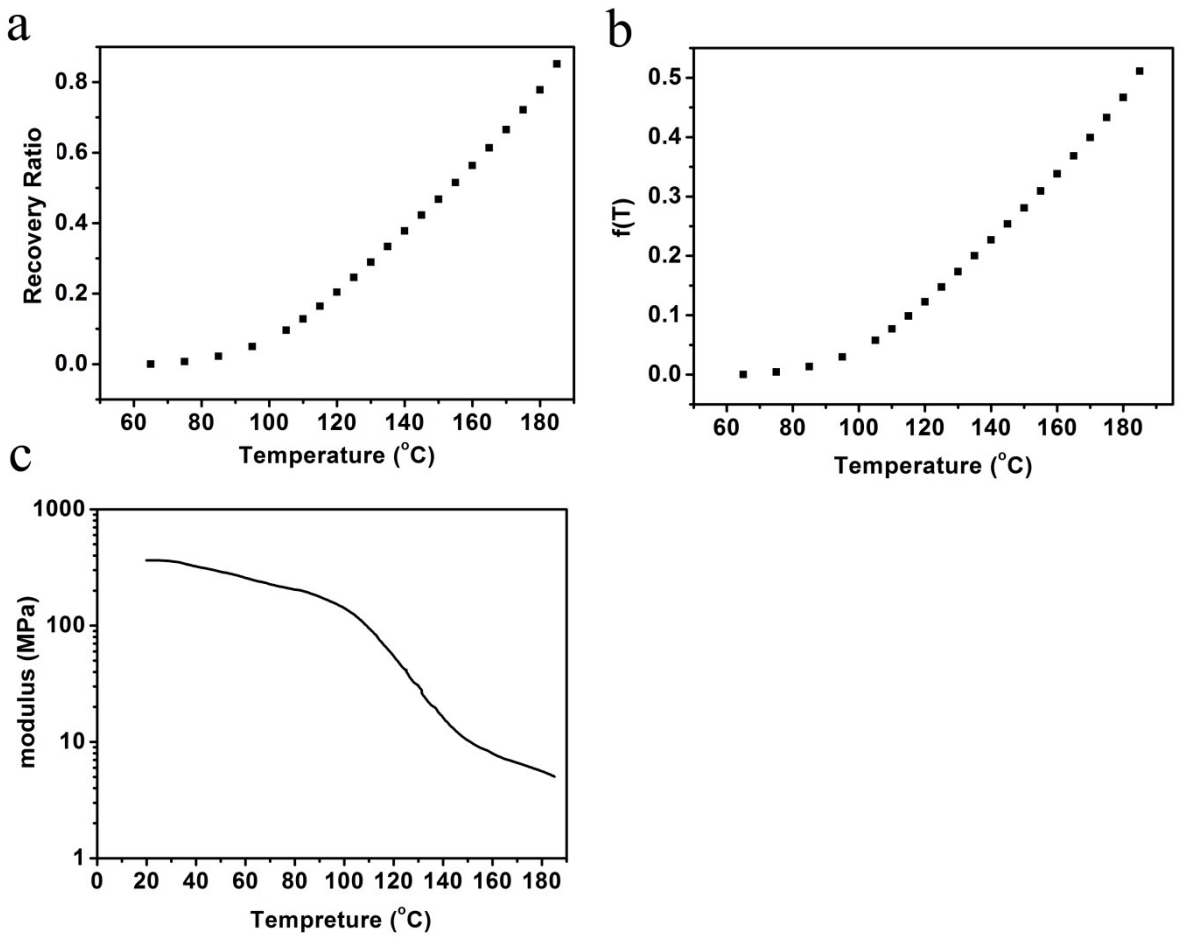

Figure S6. a) Recovery ratio of PDA modified Nafion films at different temperature for 20 s. b) Contraction ratio of PDA modified Nafion films in the stretched temporary shape under free condition at different temperature for 20 s (Stretching Ratio: 150%). c) Storage modulus of PDA modified Nafion films at different temperature.

5. Evaluation of the theoretical modelling

The purpose of the modeling in this manuscript is to qualitatively investigate the bending behavior of the stretched film in response to NIR light intensity. A few possible reasons for the quantitative differences between the modeling and the experiment results may be induced both in the modeling and experiments:

For the modeling:

1) The approximation that the unheated part is much stiffer than the heated part is not suitable at low temperature.
2) Thermal diffusion is inevitable, especially at high temperature induced by NIR light with high intensity.

For the experiments:

1) An ideal uniform material model in the aspect of mechanics was used in the theoretical modelling. However, all the materials in our life, actually, are not ideally uniform. Neither are the planer sheets in this research.
2) The NIR light in the experiments is not perfectly parallel light. That means light intensity varies slightly from the center to the sides.

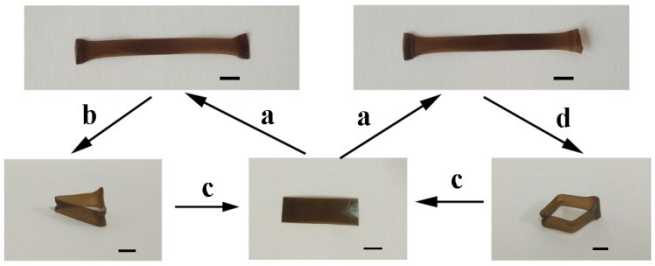

Figure S7. Shape erasing and rewriting. a) Stretching the film to ε = 150% at 175 °C followed by cooling down to room temperature with maintained stretching ratio. b) Locally irradiating the stretched film to obtain a triangle. c) Heating the obtained 3D shape to 175 °C to recover the permanent shape. d) Rewriting the film to obtain a different 3D shape (rhombus). Scale bars: 0.5 cm.

References

[1] E. Efrati, E. Sharon, R. Kupferman, Journal of the Mechanics & Physics of Solids, 2008, 57, 762.

[2] Z. L. Wu, M. Moshe, J. Greener, H. T. Aubin, Z. Nie, E. Sharon, E. Kumacheva, Nat. Commun, 2013, 4, 1586.