Supplementary Information

for

Programmed planar-to-helical shape transformations of composite hydrogels with bioinspired layered fibrous structures

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Experimental Section

Fabrication of composite hydrogels: Patterned PAA SN gel was synthesized by photolithographic patterning an aqueous solution of acrylic acid (AA), *N*,*N*′-methylenebis(acrylamide) (MBAA; as the chemical crosslinker), and 2-2′-azo-bis-(2-methylpropionamidine) (V-50; as the photoinitiator). The precursor solution was injected into the reaction cell consisting of two substrates (upper: glass; bottom: poly(methyl methacrylate)) and a 1 mm-thick silicone rubber spacer. A photo mask prepared by ink-jet printing of parallel black stripes was placed atop the glass substrate. After the reaction cell was exposed to UV light irradiation (UVHAND 100, Hönle; 365 nm, 5 mW/cm²) for 90 s, PAA SN gel stripes were formed in the light-exposed regions. The reaction cell was opened to remove the residual solution; the patterned gel was selectively left on the upper glass substrate. Following the same process, another patterned SN gel with the same composition was prepared. The substrates adhered with patterned gel stripes were assembled face to face with 2 mm spacing. Then, another precursor solution containing NIPAm, MBAA, and V-50 was injected into the interspace of patterned gels. The sample was kept in 4 ^{o}C refrigerator for 6 h to let the reactants diffuse into preformed gel stripes. Finally, the cell was exposed for 90 s to UV light irradiation without photo mask, producing a composite gel with patterned PAA/PNIPAm IPN gel stripes and PNIPAm SN gel stripes. To avoid thermally induced

phase transition of PNIPAm, the reaction cell was placed on a bed of ice during the polymerization. The composite gel sheet was cut into rectangular shape and immersed into solutions with different pH, which triggered the shape transformation of gels.

Different precursor solutions can be used to pattern the SN gel stripes in different layers of composite gel. AA was used as the monomer to prepare one patterned PAA gel; 1-vinylimidazole (VI) and acrylamide (AAm) were used as the monomer to prepared another patterned P(VI-*co*-AAm) gel. After the two patterned SN gels were assembled face to face, the third precursor solution of NIPAm was injected into the interspace, followed immediately by the photopolymerization, resulting a composite gel with patterned SN gel stripes.[13] The compositions of precursor solutions were list in Table S1.

Characterizations: The swelling ratio in length, S, of non-patterned gels was measured at room temperature according to $S = D/D_0$, in which D and D_0 are the diameter of disc-shaped gels in the equilibrium and as-prepared states, respectively. The Young's modulus of gels, E, was measured by using a universal testing machine (RGWT-4000-20, REGER, China). Compression test was performed at room temperature with a velocity of 10% strain per minute. E was calculated from the slopes of the stress-strain curves with strain below 10%.

Table S1. Recipes of precursor solutions for the synthesis of gels.

Components	PAA gel	PNIPAm gel	P(VI-*co*-AAm) gel
AA	1 mol/L	--	--
NIPAm	--	1 mol/L	--
VI	--	--	0.15 mol/L
AAm	--	--	1 mol/L
MBAA[a]	2 mol%	2 mol%	2 mol%
V-50[b]	2 mol%	2 mol%	2 mol%

[a] The concentration of MBAA is relative to the total amount of monomer.
[b] The concentration of V-50 is relative to the total amount of monomer.

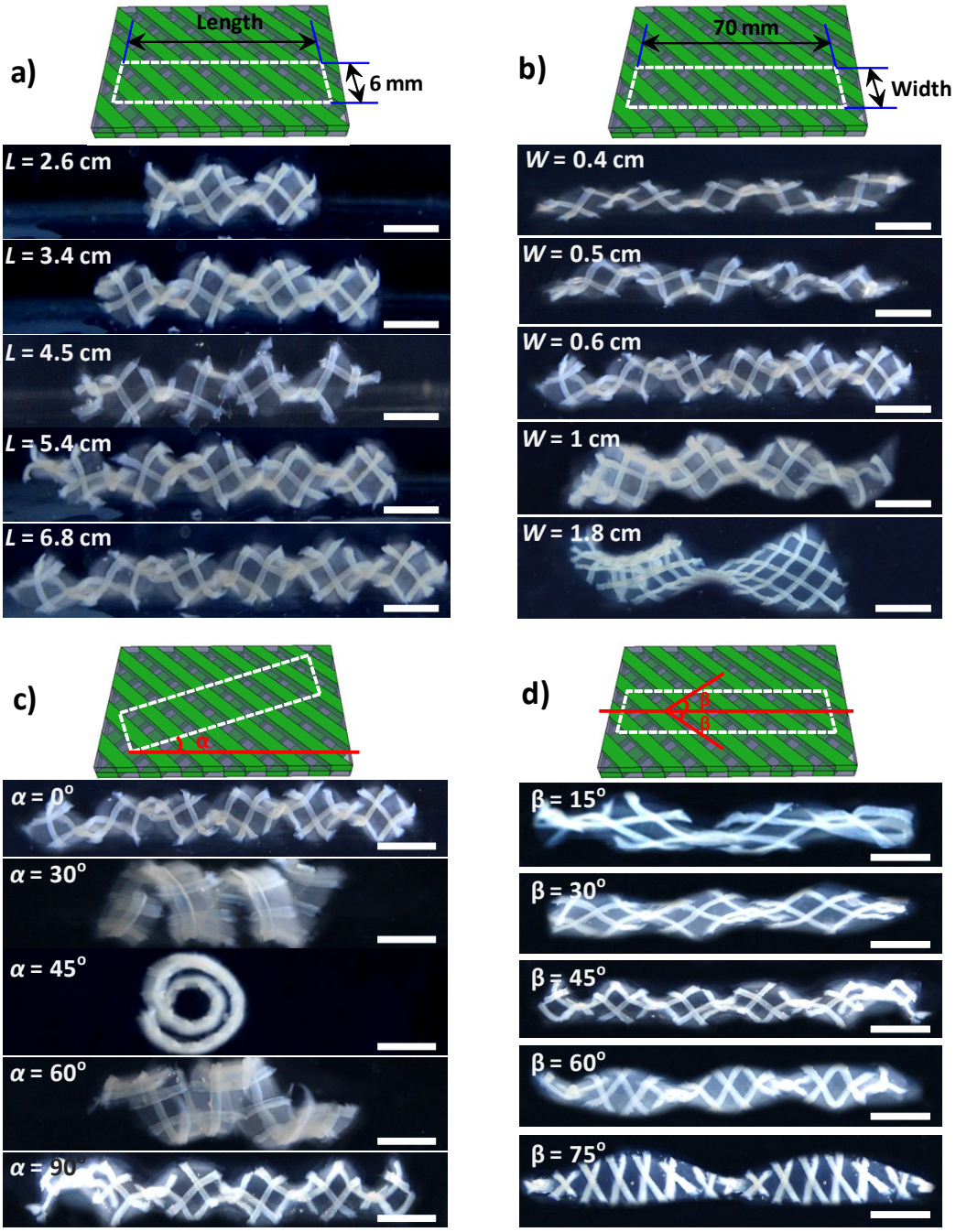

Figure S1. Representative images of the composite gels with different dimensions and structures. (a) different length; (b) different width; (c) different cutting angle, α; (d) different cross angle, β, between the stripes in different layers. Scale bar: 1 cm.

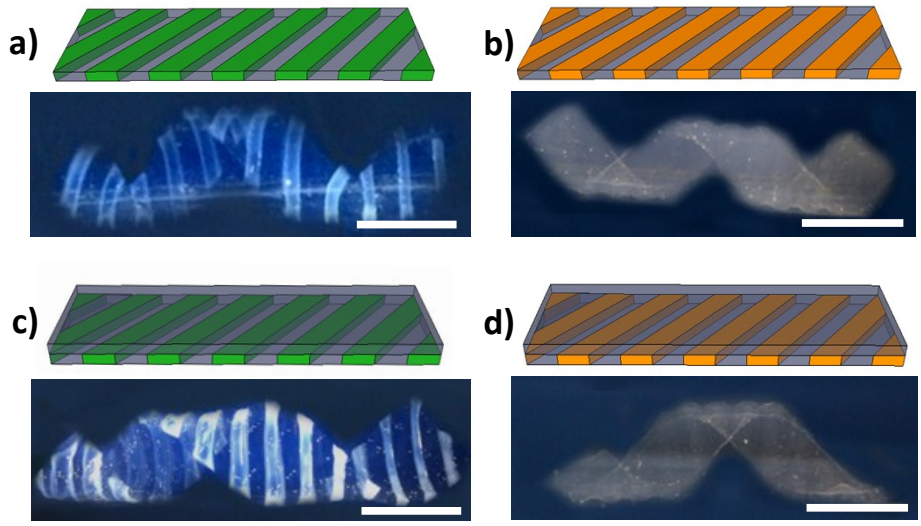

Figure S2. (a,b) Single layer patterned gels with alternating PAA and PNIPAm stripes (a) or P(VI-*co*-AAm) and PNIPAm stripes (b) and their deformations into cylinder helices. (c,d) Bilayer patterned gels with patterned gel at the bottom layer and their deformations into right-handed cylinder helices; the bottom patterned gels consist of PAA and PNIPAm stripes (c) or P(VI-*co*-AAm) and PNIPAm stripes (d), whereas the upper layer is PNIPAm gel. (a,c) pH = 9; (b,d) pH = 1. The dimensions of gel strip and patterned stripes are the same as that in Figure 2a. Scale bar: 1 cm.

Supplemental Movies: Time lapse movies were acquired from a series of images taken by a digital camera during the shape transformation process at particular time intervals. Images were arranged into movies using video editing software (Camtasia Studio). The speed of movies is ~200 times real time.

Movie S1. Planar-to-helical shape transformation of the composite gel in the incubation solution after switching the pH from 1 to 9. The composition and structure of composite gel is shown in Figure 2.

Movie S2. Helical-to-planar shape transformation of the composite gel in the incubation solution after switching the pH from 9 to 1. The composition and structure of composite gel is shown in Figure 2.

Movie S3. Shape transformation of composite gel from right- to left-handed cylinder helix after switching the pH from 9 to 1. The composition and structure of composite gel is shown in Figure 4a.

Movie S4. Shape transformation of composite gel from right-handed cylinder helix to rolls after switching the pH from 9 to 1. The composition and structure of composite gel is shown in Figure 4b.

Movie S5. Shape transformation of composite gel between two right-handed cylinder helices after switching the pH from 9 to 1. The composition and structure of composite gel is shown in Figure 4c.