

Supporting Information

for

Thermo- and photo-responsive composite hydrogels with programmed deformations

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Experimental Section

Materials. Acrylamide (AAm), potassium persulfate (KPS; thermal initiator), *N,N,N',N'*-tetramethylethylenediamine (TEMED), and ascorbic acid were used as received from Aladdin Chemistry Co., Ltd. *N*-isopropylacrylamide (NIPAm), *N,N'*-methylenebis(acrylamide) (MBAA; chemical crosslinker), and 2-2'-azo-bis-(2-methylpropionamide) (V-50; photoinitiator) were purchased from Sigma-Aldrich. Graphene oxide (GO) was received from Tangushangxi Material Sci. &Tech. Co., Ltd (China). Millipore deionized water was used in all the experiments.

Fabrication of composite hydrogels. The composite hydrogels with heterogeneous structures consisting of non-responsive PAAm gel and responsive PNIPAm-RGO gel were fabricated by combining photolithographic polymerization and thermal-polymerization. The precursor solution containing prescribed amounts of AAm, MBAA, and V-50 was injected into a reaction cell consisting of two glass substrates separated with 1 mm-thick silicone spacer. Patterned PAAm hydrogel was prepared by

photolithographically patterning the precursor solution under UV irradiation (UVHAND 100, Hönle; 365 nm, 5 mW/cm²) for 90 s. PAAm gel was formed in the light-exposed regions. After opening the reaction cell and removing the unreacted solution, the patterned PAAm gel was left atop one glass substrate. Two substrates with patterned PAAm gel (with the same or different features) were assembled face-to-face separated with 2 mm-thick silicone spacer, followed by injecting another precursor solution containing NIPAm, MBAA, GO, KPS, and TEMED into the interspace of preformed PAAm gels. The sample was kept at room temperature for 6 h to complete the thermal-polymerization. The as-prepared composite hydrogel was incubated in a large amount of aqueous solution ascorbic acid (100g/L) for 1 week to reduce GO nanosheets within the gel matrix. The resultant composite hydrogel comprised of PAAm gel and PNIPAm-RGO gel was swelled in water to achieve the equilibrium state. The composite hydrogel with a bilayer structure was prepared in a similar way. The recipe of precursor solutions for gel synthesis was listed in Table S1.

Characterizations. The swelling/shrinkage ratio in length, S , of PAAm gel and PNIPAm-RGO gel was measured at 25 °C and 50 °C according to $S = d/d_0$, in which d and d_0 are the diameter of disc shaped gel in the equilibrated and as-prepared state, respectively. The Young's modulus of PAAm and PNIPAm-RGO gels, E , was measured by tensile test at a certain temperature using a universal testing machine (Instron 3343). The gauge length of the dumbbell-shaped sample is 12 mm, and the tensile rate is 100 mm/min. The value of E was calculated from the slope of the stress-strain curve with a strain below 10%. All the gel samples were kept in water at 25 or 50 °C for 2 h before the test. The localized temperature of different hydrogels under the irradiation of NIR light (700-2900 nm, 5 mW/cm²) was measured using an infrared thermal detector.

Table S1. Recipes of precursor solutions for the synthesis of PAAm and PNIPAm-RGO hydrogels.

Component	PAAm gel	PNIPAm-RGO gel
AAm	1.236 g	--
NIPAm	--	0.993 g
MBAA	0.027 g	0.002 g
KPS	--	0.011 g
TEMED	--	0.001 g
V-50	0.047 g	--
GO	--	0.220 g
H ₂ O	8.690 g	8.774 g

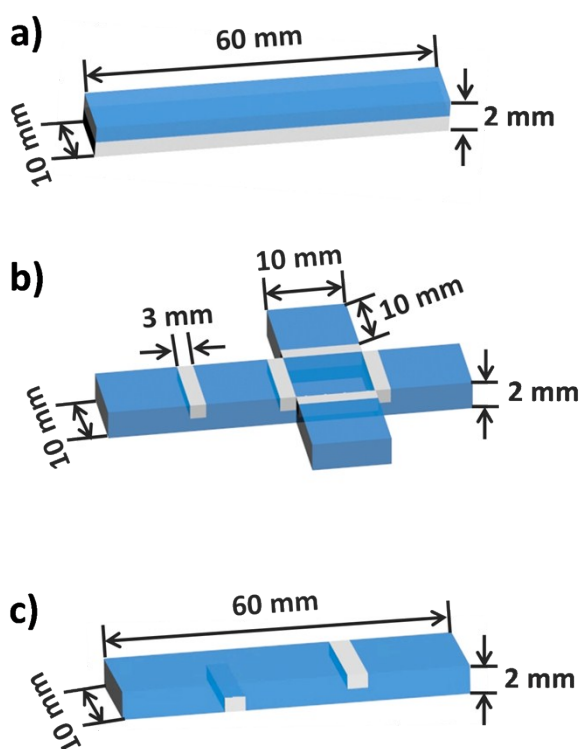


Figure S1. Schematic to show the dimensions of the composite hydrogels used in Figure 2a (a), Figure 3a (b), and Figure 3b (c).

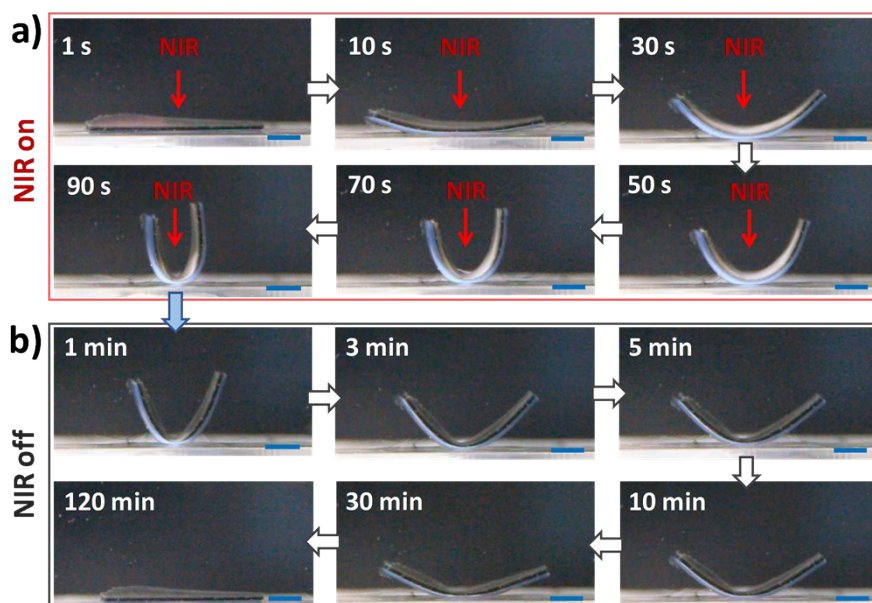


Figure S2. Photos to show the bending and unbending deformations of the PAAm/PNIPAm-RGO hydrogel with a bilayer structure by switching on and off the localized irradiation (indicated by the red arrow) of NIR light, respectively. The deformations of composite hydrogel was investigated at room temperature (25 °C). Scale bar: 1 cm.

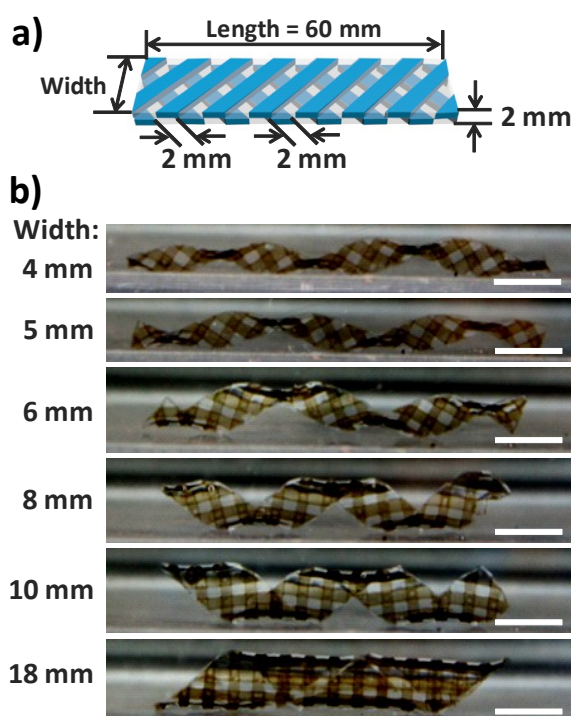


Figure S3. Dimensions of the composite hydrogel (a) and corresponding 3D configurations of the composite hydrogel strips with different widths activated by heating or irradiation under NIR light. Relatively narrow gel strips deformed into twisted helices, whereas wide gel strips deformed into cylinder helices. Scale bar: 1 cm.