Electronic Supplementary Information

Tunable swelling and deswelling of temperature- and light-responsive graphene oxide-poly(N-isopropylacrylamide) composite hydrogels

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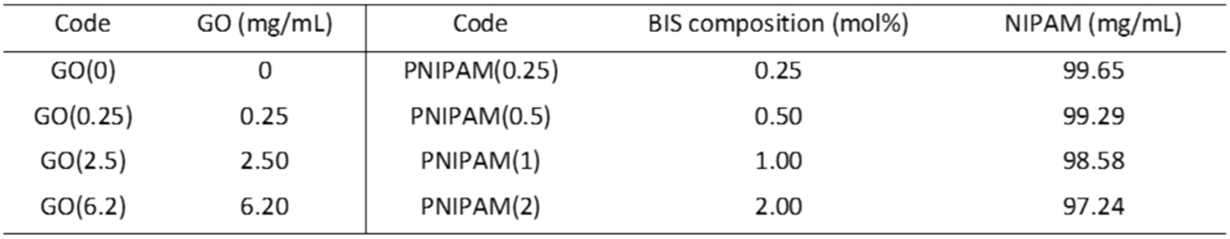
Experimental section

Materials. N-isopropylacrylamide (NIPAM, stabilized with 4-methoxyphenol) was purchased from Tokyo Chemical Industry (TCI) America. N,N'-methylenebisacrylamide (BIS), N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium persulfate (APS) were all obtained from Sigma-Aldrich (St Louis, MO, USA). Aqueous graphene oxide (GO, 6.2 mg mL^{-1}, flake size: 0.5-5 μm) was obtained from Graphene Supermarket (Calverton, NY, USA). All chemicals were used as received without further purification.

Preparation of GO-PNIPAM composite hydrogels. Batch solution (850 μL) was prepared by adding NIPAM, BIS, aqueous GO and deionized (DI) water, mixed by vortex mixer (Dlab Mx-S) until all solid dissolves at 23 °C. To remove oxygen in the batch solution, continuous nitrogen flow was pumped into the batch solution for 4 minutes. Then the batch solution with its container was transferred into a larger container and nitrogen gas was pumped in for 30 seconds to remove oxygen. Both containers were sealed and stood for 30 minutes. 1.5 μL TEMED and 5 μL aqueous APS (10 wt%) were injected into the batch solution to initiate free radical polymerization. The resulting solution was loaded into a capillary channel formed with two clean glass substrates separated by Kapton film spacers for 1 mm. Polymerization was carried in a sealed chamber at 23 °C fulfilled with nitrogen gas for 3.5 hours. After this polymerization, glass substrates and spacers were removed, and the GO-PNIPAM sample was immersed in DI water for 72 hours. DI water was changed every hour for the first three-hour immersion to remove unreacted chemicals. In this experiment, the GO concentration in a batch solution was 0.25, 2.5 and 6.2 mg mL^{-1}, respectively. The feed composition ratios and sample codes are summarized in Table S1. The GO-PNIPAM compositions were designated as "GO(x)-PNIPAM(y)", which "x" represents the concentration of

GO (mg mL^{-1}), and "*y*" indicates the percentage molar ratio of BIS to NIPAM (mol%) in a batch solution. For example, composition GO(2.5)-PNIPAM(1) represents that the GO-PNIPAM composite hydrogel was prepared with a batch solution including the GO with the concentration of 2.5 mg mL^{-1} and the molar ratio of BIS to NIPAM being 1 mol%. GO-PNIPAM composite hydrogels with different GO and BIS concentrations were prepared to investigate their internal microstructures depending on the degree of physical and chemical crosslinking density, respectively.

Table S1. Feed composition for fabricating GO-PNIPAM composite hydrogels with different GO loading and BIS concentration



Code	GO (mg/mL)	Code	BIS composition (mol%)	NIPAM (mg/mL)
GO(0)	0	PNIPAM(0.25)	0.25	99.65
GO(0.25)	0.25	PNIPAM(0.5)	0.50	99.29
GO(2.5)	2.50	PNIPAM(1)	1.00	98.58
GO(6.2)	6.20	PNIPAM(2)	2.00	97.24

Temperature dependent deswelling behaviors of composite hydrogels. GO-PNIPAM composite hydrogels were swollen in DI water for over 72 hours at 23 °C to reach equilibrium swelled state. Then five samples for each composition were biopsy-punched into thin disks with 5 mm diameter and 1 mm thickness. The temperature dependent deswelling behavior of GO-PNIPAM was recorded by a digital microscope (Keyence VHX) in the range from 23 to 61 °C (Fig. S1). The samples were in DI water at each temperature for 1 hour to reach the equilibrium deswelled state. The temperature dependent linear swelling/deswelling ratio λ defined as D_T/D_0, where D_T is the equilibrium diameter at T °C and D_0 is the as-prepared diameter. The result indicates that the difference in λ between 49 and 61 °C is less than 1%. Therefore, the GO-PNIPAM samples were heated up to 49 °C for deswelling tests.

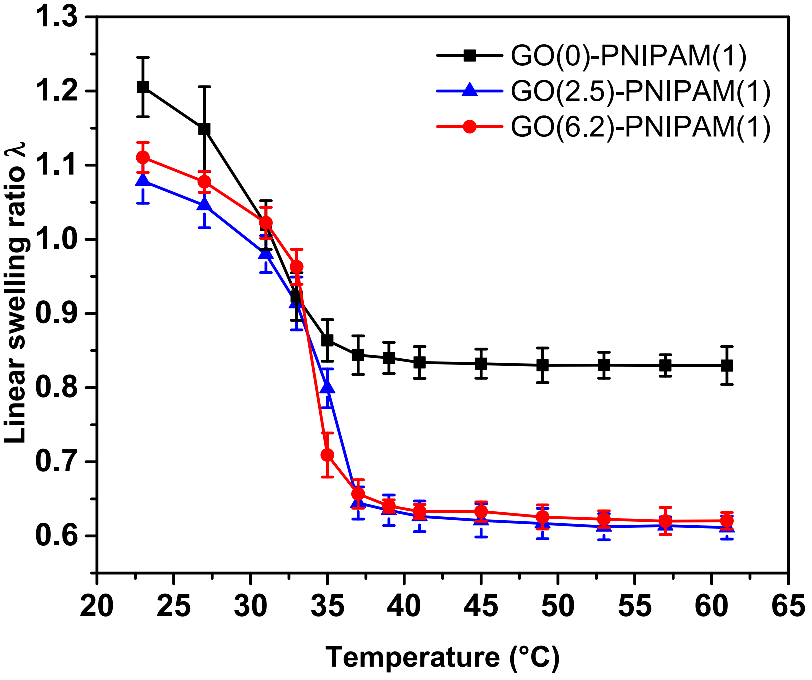


Figure S1. Temperature dependent linear swelling ratio λ of GO-PNIPAM composite hydrogels

Table S2. Linear swelling and deswelling ratio of GO-PNIPAM composite hydrogels by gradual and abrupt external temperature change.

Code	Swelling ratio (gradual cooling)				Code	Swelling ratio (abrupt cooling)			
	PNIPAM(0.25)	PNIPAM(0.5)	PNIPAM(1)	PNIPAM(2)		PNIPAM(0.25)	PNIPAM(0.5)	PNIPAM(1)	PNIPAM(2)
GO(0)	1.49 ± 0.02	1.31 ± 0.04	1.21 ± 0.04	1.10 ± 0.02	GO(0)	1.47 ± 0.01	1.30 ± 0.05	1.23 ± 0.02	1.08 ± 0.03
GO(0.25)	1.41 ± 0.03	1.30 ± 0.01	1.16 ± 0.01	1.11 ± 0.02	GO(0.25)	1.41 ± 0.04	1.26 ± 0.10	1.13 ± 0.07	1.09 ± 0.02
GO(2.5)	1.20 ± 0.02	1.12 ± 0.04	1.08 ± 0.03	1.02 ± 0.02	GO(2.5)	1.20 ± 0.02	1.17 ± 0.03	1.07 ± 0.04	1.04 ± 0.03
GO(6.2)	1.22 ± 0.01	1.15 ± 0.04	1.11 ± 0.02	1.05 ± 0.02	GO(6.2)	1.22 ± 0.01	1.16 ± 0.01	1.12 ± 0.01	1.06 ± 0.01
Code	Deswelling ratio (abrupt heating)				Code	Dewelling ratio (gradual heating)			
	PNIPAM(0.25)	PNIPAM(0.5)	PNIPAM(1)	PNIPAM(2)		PNIPAM(0.25)	PNIPAM(0.5)	PNIPAM(1)	PNIPAM(2)
GO(0)	0.51 ± 0.02	0.71 ± 0.07	1.14 ± 0.02	1.03 ± 0.02	GO(0)	0.55 ± 0.06	0.67 ± 0.07	0.63 ± 0.01	0.68 ± 0.05
GO(0.25)	0.53 ± 0.01	1.08 ± 0.03	1.13 ± 0.01	1.03 ± 0.03	GO(0.25)	0.57 ± 0.01	0.75 ± 0.11	0.91 ± 0.01	0.84 ± 0.01
GO(2.5)	0.51 ± 0.04	0.57 ± 0.04	0.65 ± 0.02	0.62 ± 0.01	GO(2.5)	0.50 ± 0.02	0.65 ± 0.01	0.62 ± 0.02	0.58 ± 0.01
GO(6.2)	0.66 ± 0.02	0.67 ± 0.04	0.62 ± 0.02	0.61 ± 0.01	GO(6.2)	0.70 ± 0.04	0.68 ± 0.04	0.56 ± 0.01	0.62 ± 0.01

Reversibility test. The reversibility of swelling/deswelling behaviors (*i.e.*, linear swelling or deswelling ratio, λ) of GO-PNIPAM composite hydrogels upon abrupt external temperature change (Fig. S2) was investigated by alternately immersing the GO-PNIPAM samples in DI water at 49 °C for 1 hour, and at 23 °C for 24 hours. For each composition, five samples were pre-cut into small disks (10 mm in diameter and 1 mm thick). Linear swelling (or deswelling) ratio λ is defined as D_T/D_0, where D_T is the equilibrium diameter at 23 °C or 49 °C and D_0 is the as-prepared diameter. The GO(2.5)-PNIPAM(1) and GO(6.2)-PNIPAM(1) composite hydrogels exhibited rapid deswelling behavior in response to immersion in DI water at 49 °C (< 1 hour) and reswelled to the equilibrium state in DI water at 23 °C after ~ 24 hours. For GO(0)-PNIPAM(1) and GO(0.25)-PNIPAM(1), the λ difference between 23 °C and 49 °C was less than 10% for each cycle. This result shows that the thermal response of GO-PNIPAM composite hydrogels is reversible and reproducible over multiple cycles of swelling/deswelling under abrupt external temperature changes.

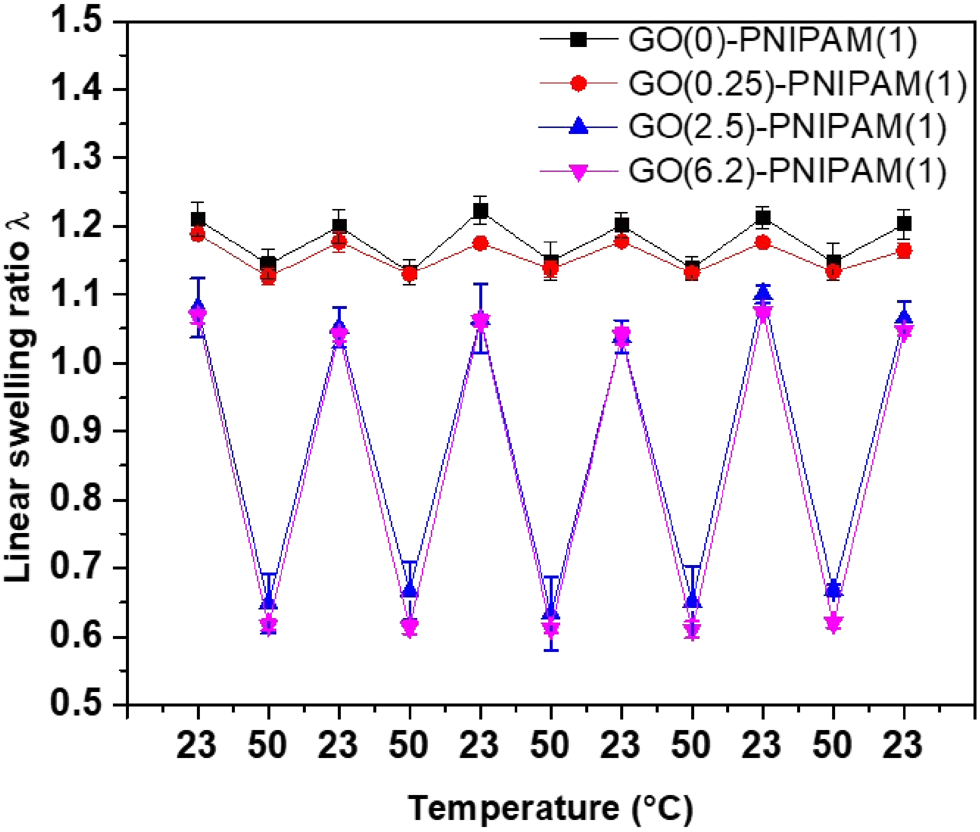


Figure S2. Linear swelling ratio λ of GO-PNIPAM composite hydrogels by alternately immersing samples in DI water at 49 °C for 1 hour and at 23 °C for 24 hours.

Weight swelling ratio of the composite hydrogel. GO-PNIPAM composite hydrogels were swollen in DI water at 23 °C for over 72 hours to reach the equilibrium swelled state. Then five samples for each composition were carefully biopsy-punched into thin disks with 5 mm diameter and 1 mm thickness. Then GO-PNIPAM thin disks were transferred into a water bath at 49 °C abruptly and deswelled for 1 hour. The weight of the swelled and deswelled samples was measured after carefully absorbing excessive water on the sample surface by filter papers. Dried hydrogels were weighted after air drying of swelled hydrogels in an oven at 70 °C for 12 hours. The weight swelling ratio of composite hydrogels is defined by the weight of water absorbed by $\eta = (W_T - W_{dry})/W_{dry}$, where W_T is the weight of hydrogel equilibrated at T (23 or 49 °C), W_{dry} is the weight of the dried hydrogel. The weight swelling ratio indicates the water absorption ability per unit hydrogel weight.

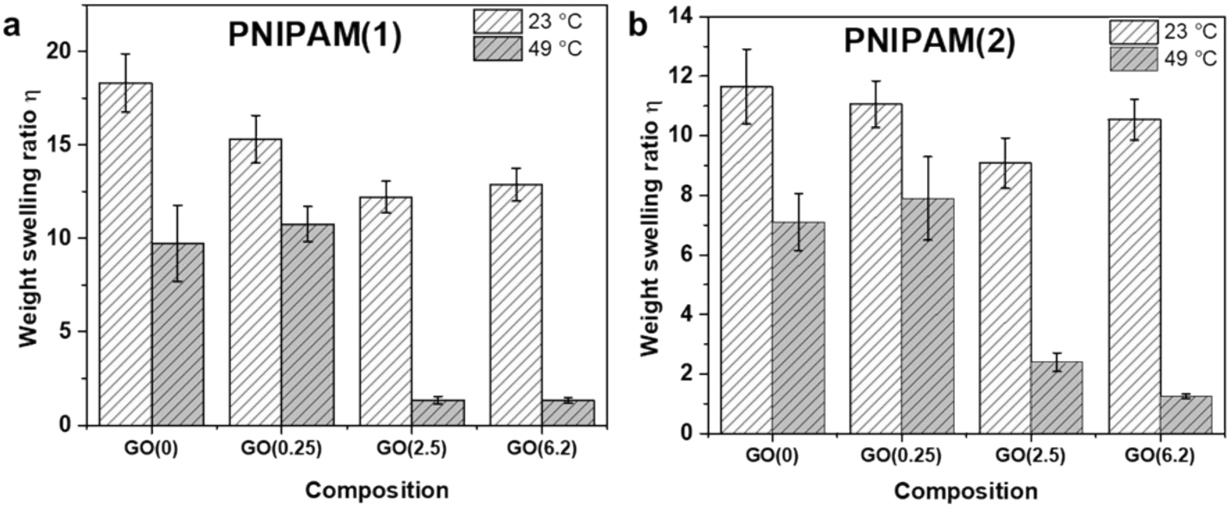


Figure S3. Weight swelling ratio η of composite hydrogels with various GO concentration and (a) PNIPAM(1) matrix and (b) PNIPAM(2) matrix swelling at 23 °C and deswelling when external temperature increases abruptly from 23 to 49 °C.

Characterization of the internal microstructures of composite hydrogels. The microstructures of GO-PNIPAM composite hydrogels were characterized by scanning electron microscopy (SEM) (FEI Quanta FEG 250). To prepare freeze-dried swelled samples, the GO-PNIPAM samples were first swelled in DI water at 23 °C for at least 72 hours to allow them in the fully swelled state. Next, these fully swelled samples were rapidly frozen in liquid nitrogen for 10 minutes. For preparing freeze-dried deswelled samples, the GO-PNIPAM samples were first immersed in DI water at 23 °C for 72 hours and transferred to DI water at 49 °C to deswell for 1 hour, then the samples were rapidly frozen in liquid nitrogen for 10 minutes. The frozen samples were dried by freeze dryer (Labconco FreeZone) at - 50 °C for 72 hours. Subsequently, the freeze-dried samples were coated with iridium for 8 seconds in order to prevent the charging of specimens during SEM imaging. The internal pore sizes of GO-PNIPAM composite hydrogels were obtained by SEM imaging and calculated by ImageJ. First, the SEM images were thresholding by Threshold function in *ImageJ*. Then the process—setting Auto-threshold mode as Default, Display mode as Over/Under, Minimum threshold value as 0, Maximum threshold value as 75—is to distinct pore region and polymer network region. Next, the pore sizes of SEM images were collected by Analyze Particle functions. The size was defined from 0.1 μm^2 to infinity. The lower bound was set to 0.1 μm^2 to exclude mis-collecting of pores.

Table S3. Pore size of swelled or deswelled GO-PNIPAM composite hydrogels with different compositions of GO and BIS at the center or surface of freeze-dried samples.

Figure	Hydrogel state	Composition	Position	Pore size (μm)
Fig 3a	Swelled	GO(0)-PNIPAM(0.25)	Center	27.9 ± 2.3
Fig 3b		GO(0)-PNIPAM(2)	Center	6.3 ± 3.2
Fig 3c		GO(6.2)-PNIPAM(0.25)	Center	11.5 ± 7.5
Fig 3d		GO(6.2)-PNIPAM(2)	Center	7.3 ± 3.6
Fig S2a		GO(0.25)-PNIPAM(0.25)	Center	23.3 ± 3.9
Fig S2b		GO(0.25)-PNIPAM(2)	Center	6.6 ± 3.2
Fig 3e	Deswelled	GO(0)-PNIPAM(2)	surface	Non-porous
			Center	6.6 ± 3.4
Fig 3f		GO(6.2)-PNIPAM(2)	Surface	2.4 ± 1.3
			Center	2.1 ± 1.3

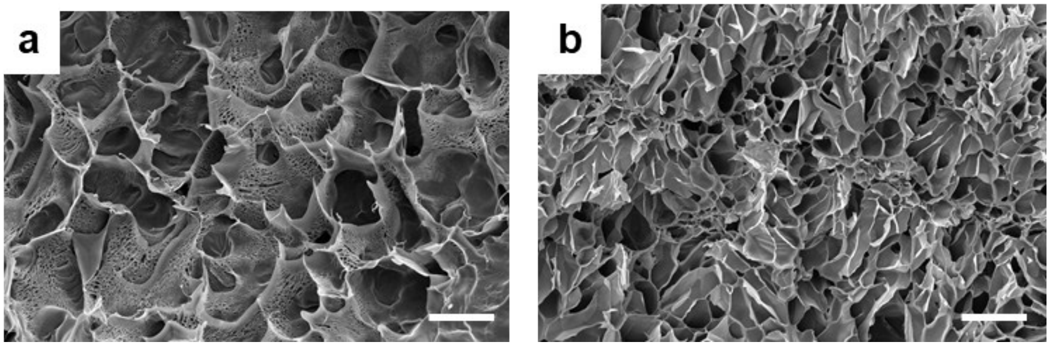


Figure S4. SEM micrographs of swelled (a) GO(0.25)-PNIPAM(0.25) (b) GO(0.25)-PNIPAM(2) samples at 23 °C. Scale bar = 25 μm.

Characterization of the surface topologies of deswelled composite hydrogels. The surface topologies of GO-PNIPAM composite hydrogels were characterized by atomic force microscope (AFM) (Veeco Scanning Probe Microscope) and optical microscope (Keyence VHX1000). To prepare freeze-dried deswelled samples, the GO-PNIPAM composite hydrogels were first swelled in DI water at 23 °C for at least 72 hours to allow them reaching the fully swelled state. Next, samples were biopsy-punched into a disk shape with 10 mm diameter and 1 mm thickness. The samples were transferred to DI water at 49 °C to deswell for 1 hour, then these were rapidly frozen in liquid nitrogen for 10 minutes. The frozen samples were dried by a freeze dryer (Labconco FreeZone) at - 50 °C for 72 hours. The surface topologies of GO-PNIPAM were characterized by AFM with a scanner of 10×10 μm (XY) and 2.5 μm (Z). The AFM height images and height profiles of GO-PNIPAM were obtained by *Nanoscope Analysis.*

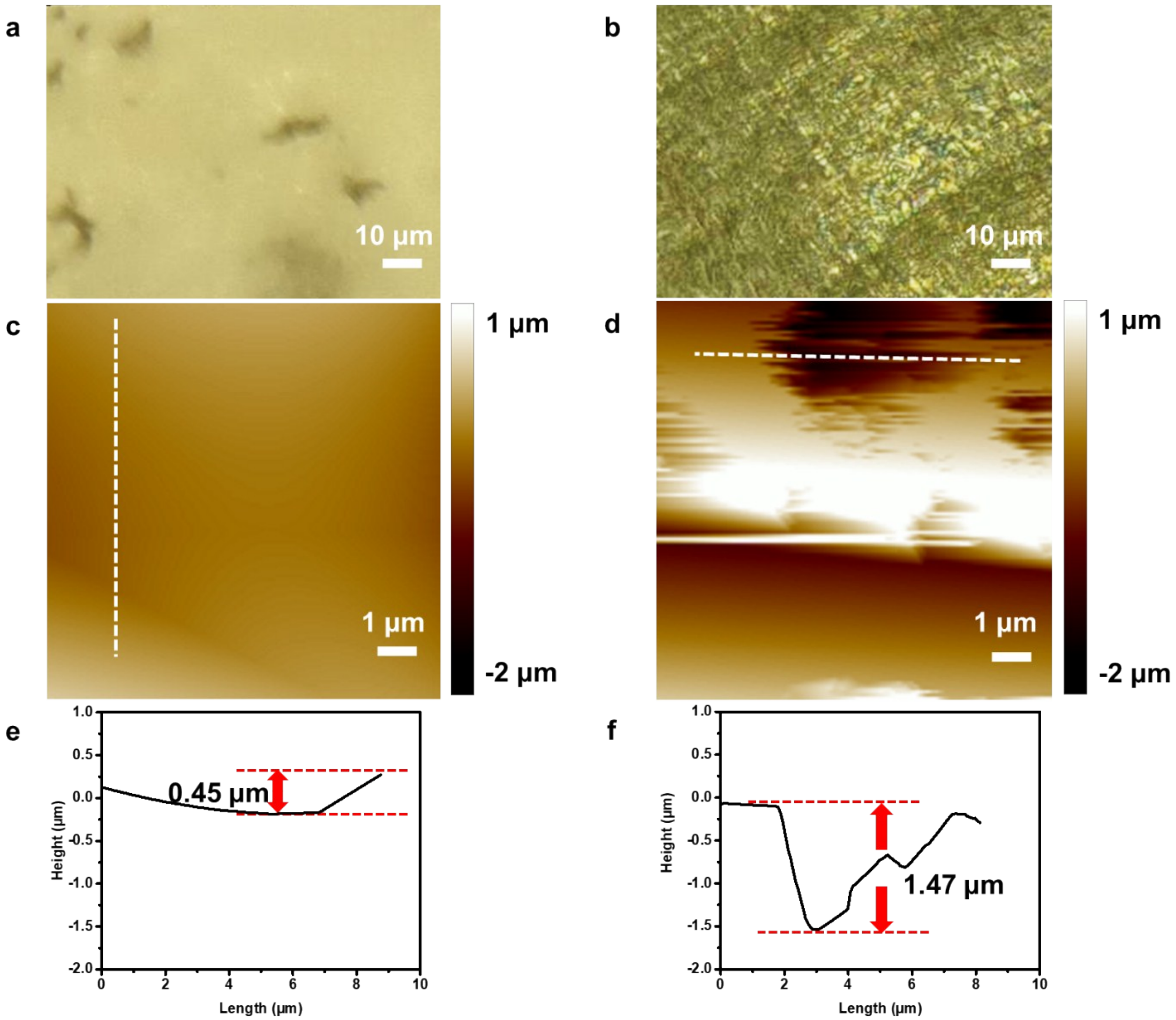


Figure S5. Optical images of surface topologies of deswelled (a) GO(0.25)-PNIPAM(2) (b) GO(6.2)-PNIPAM(2) after deswelling at 49 °C and freeze-dried. AFM height images and height profiles of deswelled (c) and (e) GO(0.25)-PNIPAM(2); and (d) and (f) GO(6.2)-PNIPAM(2). White dash line in (c) and (d) indicates height profile scan in (e) and (f), respectively.

Characterization of UV/vis absorption. The UV/vis spectra (Fig. S6) of NIPAM-BIS solution (0.1 g mL^{-1}), aqueous GO solution (2.5 mg mL^{-1}), fully swelled GO(0)-PNIPAM(1) and GO(2.5)-PNIPAM(1) hydrogel sheets (1 mm thickness in as-prepared state) were characterized by UV/vis spectroscopy (Agilent, Cary 8454). A quartz cuvette was used for liquid samples.

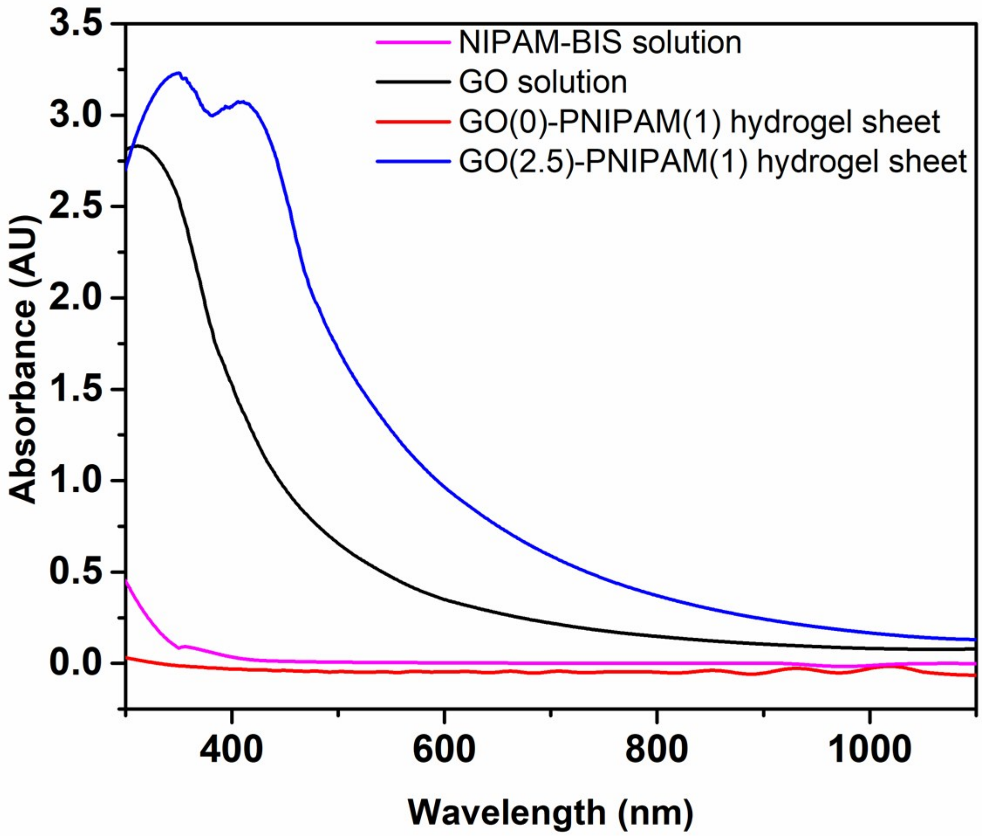


Figure S6. UV/vis spectra of 0.1 g mL^{-1} NIPAM-BIS solution (pink line), 2.5 mg mL^{-1} GO solution (black line), GO(0)-PNIPAM(1) hydrogel sheet (red line), and GO(2.5)-PNIPAM(1) hydrogel sheet (blue line).

Characterization of bending of composite hydrogel thin sheets by UV exposure. Three different composite hydrogels, GO(0.25)-PNIPAM(1), GO(2.5)-PNIPAM(1) and GO(6.2)-PNIPAM(1), were cut into 7.5 cm × 0.5 cm with 1 mm thickness. Each sheet was put in a Petri dish with 150 mL of water. The Petri dish was put close to a UV lamp (Jaxman) having 2.4 cm aperture. The distance between the UV lamp and sheet was less than 1 mm. Each sheet was illuminated by UV (365 nm) with 160 mW cm^{-2} for 30 min. The time for visible bending was recorded when the deflection between the substrate and the bottom surface of the GO-PNIPAM hydrogel sheet exceeded 1 mm. The bending curvature was calculated by *ImageJ*. A circle with radius R is drawn to fit the curve within the exposed region (within the white dash line) and the curvature is calculated by 1/R. To ensure the bending is not actuated from heat generated by the UV lamp. GO(0)-PNIPAM(1) thin sheet was tested under the same condition of UV exposure (Fig. S7a). The fully swelled GO(0)-PNIPAM(1) was immersed in DI water with red food coloring (Spice Supreme) for 1 hour to give contrast within water. There was no obvious bending observed on GO(0)-PNIPAM(1) thin sheet after 30 min UV exposure. Also, the temperature of water on the UV exposing area was measured every 5 min until 45 min when the UV lamp was turned on (Fig. S7b).

Table S4. UV exposure time (160 mW cm^{-2} at 365 nm) for initial bending, bending curvature of GO-PNIPAM thin sheets with different GO concentrations and corresponding Young's modulus.

Hydrogel composition	Time for initial bending (s)	Bending curvature (cm^{-1})	Young's modulus (kPa)
GO(0.25)-PNIPAM(1)	90	0.41	10.21 ± 0.99
GO(2.5)-PNIPAM(1)	60	0.45	24.43 ± 4.62
GO(6.2)-PNIPAM(1)	30	0.42	31.48 ± 2.40

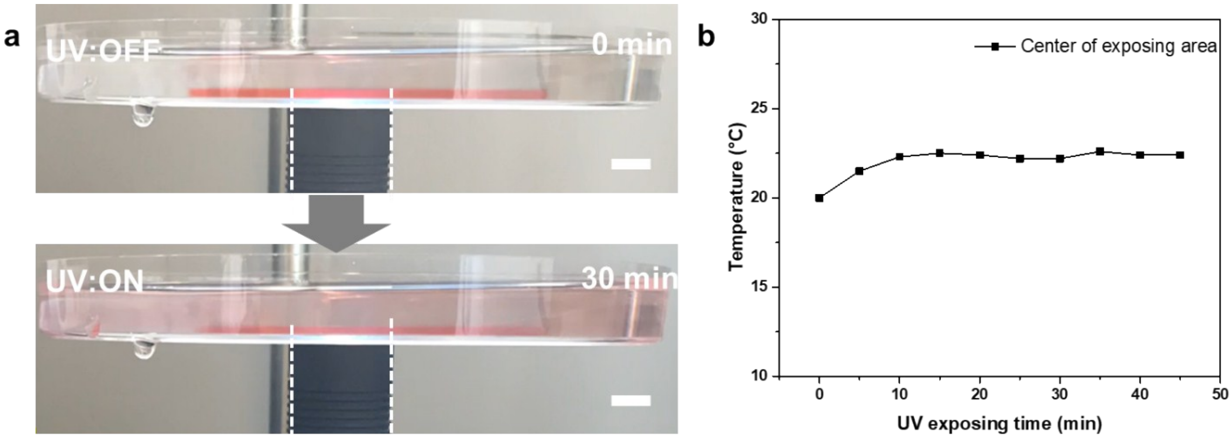


Figure S7. (a) UV exposing to GO(0)-PNIPAM(1) hydrogel thin sheet. (b) Temperature of water on the center of UV exposing area. Scale bar is 1cm.

Mechanical properties of composite hydrogels. Young's moduli of GO-PNIPAM composite hydrogels were characterized by Nanoindenter (OPTICS11, PIUMA). Composite hydrogels were first swelling in DI water at 23 °C for at least 72 hours to reach the equilibrium swelled state. Then samples were biopsy-punched to a disk shape with 5 mm diameter and 1 mm thickness. Five samples for each composition were prepared, and three measurements were recorded for each sample. We note that modulus values were taken when GO-PNIPAM samples were immersed in water and in the fully swelled state.

Table S5. Young's moduli for GO-PNIPAM composite hydrogels with different concentrations of GO and crosslinker BIS in DI water at 23 °C.

Code	Young's modulus (kPa)			
	PNIPAM(0.25)	PNIPAM(0.5)	PNIPAM(1)	PNIPAM(2)
GO(0)	2.39 ± 0.02	2.58 ± 0.40	7.90 ± 0.18	13.49 ± 1.16
GO(0.25)	3.18 ± 0.64	3.89 ± 0.24	10.21 ± 0.99	20.18 ± 0.92
GO(2.5)	3.94 ± 0.44	15.91 ± 1.23	24.43 ± 4.62	27.53 ± 3.31
GO(6.2)	6.21 ± 1.16	22.51 ± 1.81	31.48 ± 2.40	44.32 ± 5.20