Photothermally Sensitive Poly(*N*-isopropylacrylamide)/Graphene Oxide Nanocomposite Hydrogels as Remote Light-Controlled Liquid Microvalves

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A photothermally sensitive poly(*N*-isopropylacrylamide)/graphene oxide (PNIPAM/GO) nanocomposite hydrogel can be synthesized by in situ γ-irradiation-assisted polymerization of an aqueous solution of *N*-isopropylacrylamide monomer in the presence of graphene oxide (GO). The colors and phase-transition temperatures of the PNIPAM/GO hydrogels change with different GO doping levels. Due to the high optical absorbance of the GO, the nanocomposite hydrogel shows excellent photothermal properties, where its phase transitions can be controlled remotely by near-infrared (NIR) laser irradiation, and it is completely reversible via laser exposure or non-exposure. With a higher GO loading, the NIR-induced temperature of the nanocomposite hydrogel increases more quickly than with a lower doping level and the temperature can be tuned effectively by the irradiation time. The nanocomposite hydrogel with its excellent photothermal properties will have great applications in the biomedical field, especially as microfluidic devices; this has been demonstrated in our experiments by way of remote microvalves to control fluidic flow. Such an "easy" and "clean" synthetic procedure initiated by γ-irradiation can be extended for the efficient synthesis of other nanocomposite materials.

1. Introduction

Considerable attention has been focused on polymer hydrogels that exhibit reversible structural changes based on variations in the local temperature or pH, and so on.[1,2] Due to their excellent and attractive stimuli-responsive properties, smart hydrogels are highly valued in a range of applications from controlled drug delivery to tissue engineering and microdevices.[3–5] In the past few years, nanocomposite hydrogels have been widely studied due to the fact that nanoparticles incorporated in hydrogels can absorb specific stimuli (e.g., alternating magnetic fields, light) and generate heat for local heating; this remote heating and the ensuing structural changes can be applied by remote control.[6,7]

Although many variables have been explored, light is a particularly attractive stimulus used for controlling biomaterial behavior because its intensity and wavelength can be easily controlled;[8] in particular, light from a near-infrared (NIR) laser penetrates human tissues well without harm.[9] In order to impart remote-laser-controlled capabilities, different types of nanomaterials, such as gold nanorods and carbon nanotubes, have been developed.[9–11] Smart hydrogels containing gold nanorods have been investigated, showing remarkable phase transitions upon NIR laser irradiation.[12] an NIR-light-driven volume transition of single-walled nanotubes/PNIPAM microgels has also been reported.[13] In other words, the nanomaterials turn the temperature-responsive hydrogel into a light-activated one.

Recently, graphene oxide (GO), an abundant and low-cost material, which is synthesized from graphite, has demonstrated in vivo photothermal heating effectively due to its high optical absorbance in the NIR region.[14,15] As compared with other nanomaterials (e.g., gold nanorods, carbon nanotubes) with high NIR light absorption, the abundance and low cost of GO make it attractive in large-scale applications. Although a considerable number of work has been done on graphene oxide/polymer composites,[16] only a few investigations have been made on graphene oxide composite hydrogels. It is interesting to modulate the properties of stimuli-responsive hydrogels through the incorporation of graphene oxide by way of an external signal, such as a laser.

Although many types of stimuli-responsive (e.g., temperature, pH) hydrogels have been explored, those which exhibit a reversible phase transition upon a change in temperature have been the subject of major investigation over the past two decades. These temperature-responsive systems have typically concentrated on biomaterials such as poly(*N*-isopropylacrylamide) (PNIPAM),[17] which is a negative temperature-responsive hydrogel with a lower critical solution temperature

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(LCST) of around 32 °C. Below the LCST, PNIPAM hydrogel is hydrophilic, absorbs a high amount of water and exists in a transparent swollen state. When above the LCST, it becomes hydrophobic and exists in a collapsed state. Because of this unique property, numerous studies have been devoted to investigating its application in drug-delivery systems and biomaterials. Thus, the combination of graphene oxide with PNIPAM is promising to lead to NIR-responsive materials with unique properties for various applications. Water-soluble PNIPAM–graphene sheets have been synthesized for drug delivery.[18] Sun and Wu found a facile one-step strategy for GO-interpenetrating PNIPAM hydrogel networks by covalently bonding GO sheets and poly(NIPAM-*co*-AA) microgels directly in water, which exhibited a dual thermal and pH response with good reversibility.[19] However, to the best of our knowledge, very few investigations have been devoted to controlling the shape transition of PNIPAM/GO hydrogels using NIR irradiation. As we know, bulk PNIPAM hydrogel can be easily obtained from a monomer solution by irradiation polymerization.[20] In combination with graphite oxide, which can be easily exfoliated into single-layer graphene oxide in water by ultrasonication,[21,22] in situ polymerization in water by irradiation is an attractive method for the preparation of GO/hydrogel composites. In comparison with similar nanocomposite hydrogels produced by multisteps (i.e., esterification of glycidyl methacrylate with GO; then, mixing the preformed glycidyl methacrylate-functionalized graphene oxide with a hydrogel precursor, followed by photopolymerization in dimethyl sulfoxide solution[23]), the present procedure here is easier, more straightforward and without the use of any organic solvent. Primary species, such as e_{aq}^-, H•, OH•, generated by the γ-irradiation interaction with the solvent water have a certain influence on the reduction of GO.[24,25]

In this paper, we report a simple and environmentally friendly route for the preparation of PNIPAM/GO nanocomposite hydrogels by incorporating GO into a monomer solution followed by γ-irradiation-assisted polymerization. The composite hydrogel can be self-heating on exposure to an NIR laser and, consequently, can display shape transitions. Similar to the shape transition of the pure PNIPAM hydrogel, the swelling and deswelling transitions of PNIPAM/GO hydrogels are also completely reversible. Moreover, the NIR-induced temperature can be adjusted by varying the GO loading and the irradiation time. As an example of applications, a liquid microvalve made by this kind of nanocomposite hydrogel is demonstrated to control fluidic flow remotely by the use of an NIR laser.

2. Results and Discussion

2.1. Characterization of PNIPAM/GO Hydrogels

Since graphite oxide can be easily exfoliated into single-layer graphene oxide in water by ultrasonication, the PNIPAM/GO nanocomposite hydrogel with a homogenous dispersion was successfully obtained via irradiation polymerization. **Figure 1**a shows the XRD patterns of GO and the PNIPAM/GO nanocomposite hydrogel prepared with 1.0 mg mL^{-1} GO, and that of pure PNIPAM. The typical diffraction peak of GO was observed at about $2\theta = 11.05°$, while the two broad peaks that appeared centered at $2\theta = 7.5$ and 21.0° were ascribed to the diffraction peaks of pure PNIPAM. However, after GO was dispersed into the PNIPAM matrix through polymerization, the XRD pattern of the freeze-dried PNIPAM/GO nanocomposite only showed the diffraction peaks of the PNIPAM: the diffraction peak of the GO disappeared. The XRD results obviously demonstrate that the graphene oxide sheets were dispersed well in the polymer matrix and were exfoliated.[26,27] In addition, from the viewpoint of stability, nanocomposite hydrogels stored for more than eight months in water remained unchanged under ambient conditions. The SEM images in **Figure 2** indicate that the nanocomposite hydrogels had more macropores than the pure PNIPAM hydrogel.

Figure 1b shows the dramatic color change in hydrogels with and without GO. The pure PNIPAM hydrogel was transparent (left part of Figure 1b), whereas the PNIPAM/GO nanocomposite hydrogel was black (right part of Figure 1b). In addition, it is worth noting that the PNIPAM/GO nanocomposite hydrogels showed a black (brown) color rather than the yellow color of GO in water. In comparison with methods that resulted in a similar phenomenon, reported recently, which was observed for polystyrene (PS)-grafted graphene sheets and PNIPAM-grafted graphene,[18,28] the reason that makes this irradiation-induced polymerization route unique is the γ-irradiated reduction of the exfoliated GO sheets. It is well known that primary reactive species, including hydrated electrons, OH·, H·, etc., are generated by γ-irradiation interaction with solvent water,[24] and have a significant effect on the synthesis of a polymer and the reduction of GO in the presence of appropriate additives.

Thus, it is interesting to verify the changes in the LCST of the PNIPAM/GO hydrogel resulting from the hydrophilic-hydrophobic properties of the reduced GO in the composite hydrogel. Compared with pure PNIPAM hydrogel, increasing the amount of GO in the composite hydrogel decreased the LCST firstly, and, afterwards, increased it when the GO concentration was above 0.5 mg mL^{-1} (Figure 1c). It is well known that PNIPAM hydrogels contain both hydrophilic –CONH– and hydrophobic $-CH(CH_3)_2$ groups, and the temperature sensitivity of PNIPAM hydrogels arises from abrupt alterations in the hydrophilic/hydrophobic properties of these side groups at different temperatures.[29] Therefore, the LCST of PNIPAM-based hydrogels is typically altered upon copolymerization with a second monomer, and is generally decreased by the incorporation of hydrophobic comonomers or increased with hydrophilic comonomers.[2,30–33] The mechanism for the LCST decrease here is similar to that of nanocomposite hydrogels reported previously, and is due to the hydrophobic nature of the incorporated materials (e.g., r-GO).[18,34] This decrease in the LCST verifies the hydrophobic nature of the reduced GO after irradiation. However, with an increasing amount of GO, the reduction species of the system were not sufficient and the hydrophilicity of the reduced GO remained predominant, which led to a higher LCST. It should be noted that the phase-transition temperature ranged from 34.1 °C to 35.5 °C and the variation in quantity compared with pure PNIPAM (34.4 °C) was small. This was probably due to the partial reduction of the GO sheets during the PNIPAM/GO preparation, and their hydrophilicity-hydrophobicity remained.

As shown in Figure 1d, the Raman spectra of the PNIPAM/GO composite hydrogels showed a remarkable peak shift

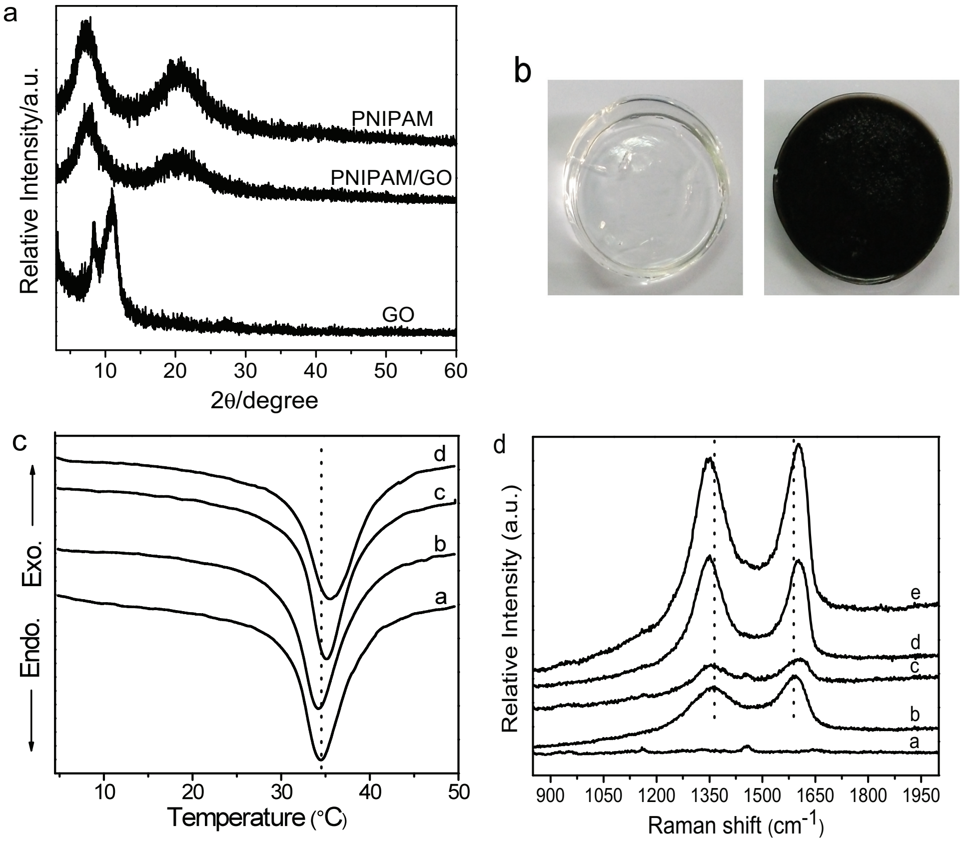

Figure 1. a) XRD patterns of GO, PNIPAM, and PNIPAM/GO prepared with 1.0 mg mL^{-1} GO. b) Photographs of pure PNIPAM (left) and PNIPAM/GO prepared with 1.0 mg mL^{-1} GO (right). c) DSC thermograms of pure PNIPAM hydrogel (a) and PNIPAM/GO prepared with various amounts of GO (b: 0.1 mg mL^{-1}; c: 0.5 mg mL^{-1}; d: 1.0 mg mL^{-1}). d) Raman spectra for PNIPAM (a), GO (b) and PNIPAM/GO prepared with various amounts of GO (c: 0.1 mg mL^{-1}; d: 0.5 mg mL^{-1}; e: 1.0 mg mL^{-1}).

compared with the GO, although the peak positions in the different Raman spectra of the PNIPAM/GO composite hydrogels with different GO loading were the same. That is to say, the G peak at 1591 cm^{-1} was blue-shifted to 1604 cm^{-1} while the D peak at 1361 cm^{-1} was red-shifted to 1348 cm^{-1}, going from GO to the PNIPAM/GO composite hydrogels. The opposite peak-shifting phenomenon of the G and the D peaks indicates that more defects were brought into the GO sheets during the irradiation polymerization.[19,28,35]

2.2. Photothermal Behavior of the PNIPAM/GO Hydrogels

The photothermal phase transition of the nanocomposite hydrogel was investigated by irradiation using a focused NIR laser of wavelength 808 nm at a power of 2 W. **Figure 3**a shows photographs of different PNIPAM/GO hydrogels, in terms of size and color before and after NIR laser irradiation for 2 min and cooling. Significant heating of the hydrogels was observed in PNIPAM/GO within 2 min, leading to an obvious volume

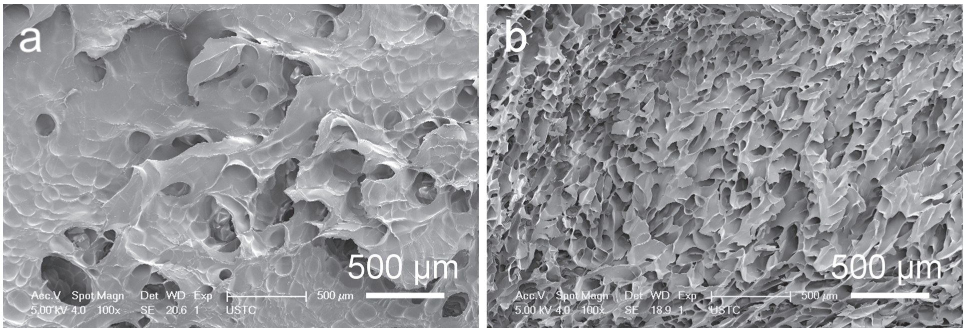

Figure 2. a,b) SEM images of freeze-dried, pure PNIPAM (a) and PNIPAM/GO composite hydrogel (b) prepared with 1.0 mg mL^{-1} GO.

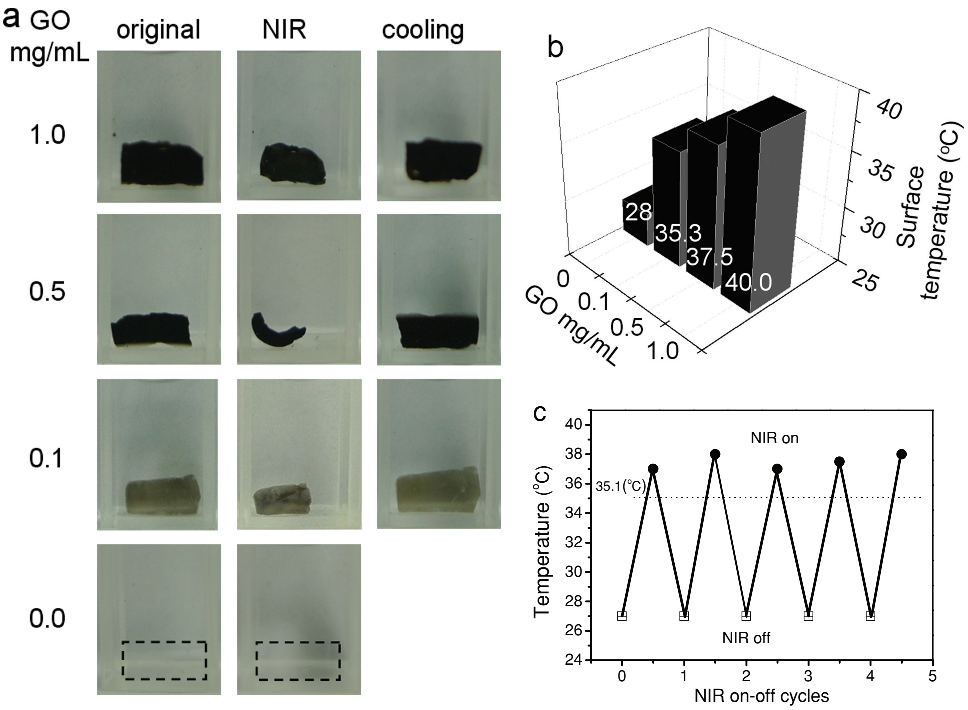

Figure 3. a) Photographs of the PNIPAM/GO hydrogels prepared with various amounts of GO (0.0/0.1/0.5/1.0 mgmL^{-1}): the original hydrogel; the hydrogel after NIR laser irradiation for 2 min; and the hydrogel after cooling. b) Temperatures response of the PNIPAM/GO hydrogels after NIR laser irradiation for 2 min. The temperatures were measured immediately after the removal of the NIR laser irradiation. c) Temperature changes of the PNIPAM/GO hydrogels as a function of heating-cooling cycle. The LCST of the nanocomposite hydrogel prepared with 0.5 mg mL^{-1} GO was 35.1 °C.

change. As reported previously, the photoexcitation of the GO with an NIR laser leads to the generation of excitons, which decay into heat, and result in a strong warming of composite.[36] Along with the increase in temperature, the hydrophobic interactions in the PNIPAM-based hydrogels are strengthened, while the hydrogen bonding (between hydrophilic groups and water) becomes weaker.[1,2] In the end, the hydrophilic hydrogel turned into a hydrophobic one, leading to an obvious volume change. The collapsed hydrogel was observed to recover to a swollen and elastic gel state upon cooling the hydrogel, indicating a thermoreversible behavior. On the contrary, no heating was observed in the hydrogels without GO.

As reported previously, the concentration of Au nanorods in a hydrogel and the time of exposure to an NIR laser can be used to control the increase of the NIR-induced temperature effectively.[10,37] In our Au-free nanocomposite-hydrogel system, the GO was expected to have the same effect, adding additional tunability to the speed of heating, and to the subsequent temperature. The nanocomposite hydrogel changed color from brown-yellow to black on increasing the amount of GO, indicating an increased laser absorption, which was verified by the increased temperature of the hydrogel surface after the same laser exposure. The samples were all set to room temperature in the beginning, and the surface temperature after laser exposure for 2 min is shown in Figure 3b. Significant and rapid heating was observed in the samples containing GO, and the temperature of hydrogel increased sharply as the weight content of the GO increased. For example, the temperature of the hydrogel surface prepared with 0.1 mg mL^{-1} GO rose from room temperature to 35.3 °C when exposed to NIR laser irradiation for 2 min, and, with increasing amounts of GO, the samples were heated to 40 °C under the same irradiation conditions. In contrast, no obvious changes in temperature were observed for water and the sample free of GO, which is consistent with the results mentioned above.

Interestingly, this swelling-shrink transition of the light-activated nanocomposite hydrogel was completely reversible, based on laser exposure or non-exposure (Figure 3c). The temperature of the water (0.5 mL, with PNIPAM/GO hydrogels) increased with irradiation time from 26 °C to 56 °C in 6 min, as shown in **Figure 4**, and this could be used as a heating source in future work. Compared with other work on light-induced changes in polymer networks that has focused on photoresponsive molecular switches and interpenetrating molecules,[38] the present method, which is based on incorporating GO, is easier and more straightforward.

Based on the excellent photothermal properties of our nanocomposite hydrogel, a liquid microvalve was fabricated to control fluidic flow, with the use of a quartz tube as a microfluidic channel. As shown in **Figure 5**a, the nanocomposite hydrogel could block the fluidic flow before the laser exposure, the light-yellow $NiSO_4$ and red rhodamine solutions on the two sides of the hydrogel remaining stable. Once the laser was turned on, the nanocomposite hydrogel shrank to allow the flow of liquid from left to right, resulting in the color change shown in Figure 5b. In contrast, the color remained unchanged before and after laser irradiation when a pure PNIPAM hydrogel was used (Figure 5c,d). The results show

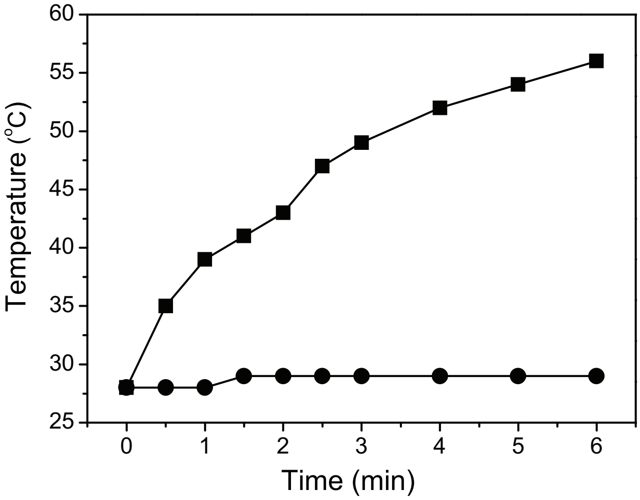

Figure 4. Temperature of 0.5 mL of water in a quartz-type cell with (squares) and without (circles) the PNIPAM/GO hydrogel upon NIR irradiation (808 nm) as a function of irradiation time. The nanocomposite hydrogel was prepared with 1.0 mg mL^{-1} GO.

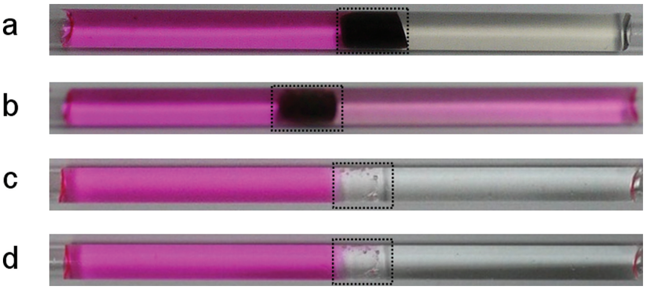

Figure 5. a–d) Liquid microvalves made with the PNIPAM/GO hydrogel (a,b) and a PNIPAM hydrogel (c,d). The photographs show the microvalves before (a,c), after (b,d) NIR (808 nm, 2 W) irradiation for 2 min, where the positions of the hydrogels are marked by the rectangular boxes. The solutions encapsulated in the left and right sides are a red rhodamine solution and light-yellow $NiSO_4$, respectively.

that the microvalve was valuable, and could be controlled remotely by an NIR laser.

3. Conclusions

In summary, we report a facile and straightforward method for the preparation of PNIPAM/GO nanocomposite hydrogels by in situ γ-irradiation-assisted polymerization of an aqueous solution of *N*-isopropylacrylamide and graphene oxide. The combination of GO with PNIPAM hydrogel leads to excellent photothermal properties, where the phase transition of the nanocomposite hydrogel can be remotely controlled by laser exposure or non-exposure. Such a transition is completely reversible. The NIR-induced temperature can be tuned effectively by way of the GO doping level and the irradiation time. The present "clean" and "easy" synthetic approach through in situ γ-irradiation-assisted polymerization can generate other multifunctional nanocomposite materials in the future. Furthermore, we have demonstrated that a liquid microvalve under control of an NIR laser can be fabricated using this PNIPAM/GO nanocomposite hydrogel. These light-activated nanocomposite hydrogels, with their excellent photothermal sensitivity, will have further promising application potential in biomaterials, drug delivery, and microdevices etc.

4. Experimental Section

Chemicals: *N*-isopropylacrylamide (NIPAM) was obtained from the Shanghai Wujing Chemical Technology Co. Ltd. *N*,*N′*-methylenebisacrylamide (MBA) was received from the Tianjin Guangfu Fine Chemical Institute. Graphite powder, potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2), and sulfuric acid (98%) were purchased from Sinopharm. All of the reagents were used as received.

Synthesis of GO: Graphite oxide was synthesized according to the Hummers method.[39] Briefly, graphite (1.0 g) and $NaNO_3$ (1.2 g, analytical reagent, A. R.) 0 were placed in a flask. Then, H_2SO_4 (46 mL, analytical reagent, A. R.) was added with stirring in a water bath. After 10 min, $KMnO_4$ (6.0 g, analytical reagent, A. R.) was gradually added. The mixture was kept at 35 °C for 6 h under stirring. Subsequently, H_2O (80 mL) was added into the mixture slowly, which made the mixture rise quickly in temperature to ≈80 °C. Stirring was continued for 0.5 h at this temperature. Afterwards water (200 mL) and H_2O_2 (6 mL) solution were added. The resulting suspension was filtered. The solid mixture was repeatedly washed with copious amounts of distilled water until the solution pH reached a constant value at ≈4.0. Then, the resulting GO solution was frozen in liquid nitrogen and subsequently dried in freeze-drying equipment.

Synthesis of the PNIPAM/GO Composite Hydrogels: Various amounts of GO were dispersed in distilled water (10 mL) by ultrasonication for 0.5 h; *N*-isopropylacrylamide (0.3600 g) and *N*,*N′*-methylenebisacrylamide (0.006 g) were added with stirring. The resulting solution was transferred into glass bottles and purged with pure nitrogen for 10 min to remove any dissolved oxygen. The bottle was sealed prior to the γ-irradiation, which was carried out using a ^{60}Co source. Polymerization was carried out at a dose rate of ≈1.83 kGy h^{-1} for 24 h at room temperature. After the polymerization, the resulting hydrogel was removed from the bottle and was washed extensively in distilled water for at least 7 d to remove excess monomer and GO.

Photothermal Irradiation: The samples and water (1 mL) in a quartz-type cell (optical path = 1 cm) were exposed to laser irradiation for 2 min at a distance of 5 cm. The source of irradiation was an 808 nm laser (2 W) with a spot size 1 cm long and 0.5 cm wide. The sample temperature was measured at the front surface with a probe immediately upon removal of the laser source. To investigate the thermal reversibility, the swelling and deswelling transition of the PNIPAM/GO hydrogel was repeated several times. To examine the photothermal heating ability of the composites, the water in the quartz-type cell was reduced to 0.5 mL.

For the microfluidic-device experiment, a quartz tube was filled with diluted, light-yellow $NiSO_4$ solution, red rhodamine B solution, and the nanocomposite hydrogel, where the nanocomposite hydrogel blocked the flow of the two solutions. When the 808 nm laser irradiation (2 W) was on for 2 min, the nanocomposite hydrogel collapsed, the solutions passed through the valve, and the color of the solution changed. In contrast, when pure PNIPAM was used, no flow was observed.

Characterization: The XRD patterns of the samples were obtained using a theta-theta rotating anode X-ray diffractometer (Rigaku TTR-III) with Cu K$_\alpha$ radiation (λ = 0.15418 nm). A Raman spectrophotometer (LABRAM-HR) was used to characterize the GO and the PNIPAM/GO. The laser was excited by an argon-ion laser with a wavelength of 514.5 nm. Differential scanning calorimetry (DSC) was carried out from 0 to 50 °C on a TA DSC-Q2000 instrument under a N_2 atmosphere at a heating rate of 3 °C min^{-1}.

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