Photothermally Triggered Fast Responding Hydrogels Incorporating a Hydrophobic Moiety for Light-Controlled Microvalves

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S *Supporting Information*

ABSTRACT: Iron oxide nanoparticles dispersed within a thermally responsive poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel matrix effectively convert the photo energy of visible light of modest intensity into thermal energy, providing the efficient means to trigger changes in volumetric swelling of hydrogels. However, long irradiation time (on the order of minutes) and modest volume change limit their applications that need fast response and/or large volume change. In this work, we found that the degree of volume change triggered by light could be maximized by adjusting the lower critical solution temperature (LCST) of the hydrogels. On the basis of the evidence in this investigation, we can develop highly responsive hydrogels that show rapid and significant light-induced volume change, which could be achieved by incorporating a hydrophobic *N,N*-diethylacrylamide moiety in the PNIPAm network. This enhanced responsiveness led to the successful application of this material in a remote-controllable microvalve for microfluidic devices operated by light illumination within a few seconds.

KEYWORDS: *light-responsive hydrogels, iron oxide nanoparticles, photothermal conversion, lower critical solution temperature, microvalves*
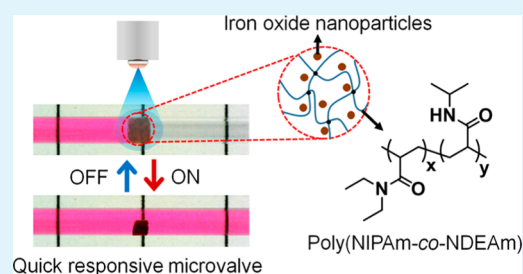
1. INTRODUCTION

Hydrogels are cross-linked elastic networks consisting of hydrophilic polymers that swell without dissolving when brought into contact with water. Stimuli-responsive behavior is one of the most attractive features of hydrogels, and they have displayed the ability to change their volume abruptly in response to external stimuli such as solvent composition,[1,2] temperature,[3,4] pH,[5,6] the presence of an electrical[7] or magnetic field,[8] and exposure to light.[9−23] Their ability to swell and deswell according to physical or chemical conditions makes them potential candidates for a number of diverse applications, such as sensors,[6] drug delivery systems,[24] and tissue engineering.[25] Of the external stimuli for triggering volume change in hydrogels, light is particularly attractive because it enables on-demand rapid switching with high spatial resolution and has easily controllable intensity. Furthermore, it does not require physical contact with the material. This leads to potential applications in remotely controlled systems such as actuators,[11] microvalves,[12,15,16] and drug delivery devices.[23]

Photothermal conversion materials dispersed in thermally responsive hydrogel matrices have been shown to be efficient for controlling the volume phase transition of hydrogels in response to visible or near-infrared (NIR) light.[13−23] In this case, photothermal materials in the hydrogel matrix absorb light and generate heat, thus triggering a volume shrinking of the thermally responsive hydrogel matrix.

Photothermal materials for light-responsive hydrogel systems have been studied extensively by many research groups.[13−23]

Most research on these systems has dealt with carbon-based materials such as single-wall carbon nanotubes[13,14] or graphene oxide (GO)[15−19] or metallic nanoparticles such as iron oxide[20,21] or gold[22,23] as the photothermal material. Recently, by combining iron oxide nanoparticles (NPs) or GO with the thermally responsive poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel, we demonstrated the reversible and repeatable volume change of the hydrogel triggered by visible light irradiation of several tens of mW/cm^2.[19,20]

Even though photothermally mediated light-responsive hydrogels show controllable and reproducible volume change, the long irradiation time necessary (in the order of minutes) and modest volume change limit their application as actuators or microvalves. In our previous study, 3 min of irradiation with visible light induced a change of just ∼10% in the linear swelling ratio, which corresponds to a 27% volume shrinkage.[19,20] Other research groups have reported a light-induced shrinkage in length of less than 25% in hydrogels containing photothermal materials exposed to NIR light irradiation for several minutes.[15,16] The ability to maximize this volume change within short irradiation times is vital for the real-world application of these materials.

In this work, to maximize volume change and/or minimize irradiation time, we investigated the relationship between the

light-induced volume change of hydrogels loaded with photothermal materials and the thermal behavior of the hydrogel matrix. We prepared thermally responsive PNIPAm hydrogels loaded with photothermal NPs and measured the light-induced volume change for various temperatures of the swelling medium. In addition, we adjusted the lower critical solution temperature (LCST) of the PNIPAm matrix by copolymerization with hydrophobic *N*,*N*-diethylacrylamide (NDEAm) and found that the thermal behavior of the hydrogel matrix plays a crucial role in controlling the light-induced volume shrinking. In light of the improved response property of the hydrogel system developed, we fabricated a prototype for a remotely controllable liquid microvalve for use in a microfluidic channel in order to exemplify its potential application.

2. EXPERIMENTAL SECTION

2.1. Materials. Iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O), iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O), and sodium hydroxide (NaOH) were purchased from Junsei Chemical Co. Ltd. (Nihonbashi-honcho, Tokyo, Japan). *N*-Isopropylacrylamide (NIPAm) and *N*,*N*-diethylacrylamide (NDEAm) were obtained from TCI (Nihonbashi-honcho, Tokyo, Japan). All other chemicals were purchased from Sigma-Aldrich (St Louis, MO, USA) and used without further purification.

2.2. Synthesis of NPs. Iron oxide nanoparticles were prepared using a modified literature procedure.[26] Iron(II) chloride tetrahydrate (0.99 g, 4.98 mmol) and iron(III) chloride hexahydrate (2.70 g, 10.0 mmol) were dissolved in distilled water (30 mL) with vigorous stirring. The solution was maintained at pH 7 by the careful addition of 1 M ammonium hydroxide under a nitrogen atmosphere. After 30 min of stirring, aqueous sodium oleate (SO) (2 wt %, 20 mL) was added, and the reaction was heated to 80 °C for 30 min before being allowed to cool to room temperature. The pH was then adjusted to 5 by the careful addition of 1 M hydrochloric acid, causing the aggregation of the particles. The black aggregate was isolated by magnetic decantation and washed 3 times with an excess of deionized water to remove unreacted surfactant. Sodium dodecyl benzenesulfonate (SDBS) (2 wt %, 5 mL) was then added to the black solid, and the black solution was stirred at room temperature (RT) for 30 min. As a result, iron oxide nanoparticles dispersed in water were obtained.

2.3. Preparation of Hydrogels Loaded with NPs and Preparation of Microvalves. To prepare hydrogels loaded with NPs, 85 μL of water containing the amounts of monomer and cross-linker shown in Table 1 was mixed with 15 μL of a 15 mg/mL aqueous

Table 1. Composition of the Polymerization Batches for Poly(*N*-isopropylacrylamide) and Poly(*N*-isopropylacrylamide-*co*-N,N-diethylacrylamide) Copolymers

sample name	NIPAm composition (mol %)	NIPAm (mg)	NDEAm (mg)	BisAA (mg)
PNIPAm	100	8.44	0	0.06
p(NIPAm-*co*-NDEAm) (95/5)	95	8.02	0.42	0.06
p(NIPAm-*co*-NDEAm) (90/10)	90	7.59	0.84	0.06
p(NIPAm-*co*-NDEAm) (80/20)	80	6.75	1.68	0.06

dispersion of iron oxide nanoparticles. A dilute aqueous suspension of fluorescent polystyrene beads was then added to the mixed solution. The concentration of the fluorescent beads was determined by yield that averages ~10 to 20 beads per ~1 mm^2. Free radical polymerization was initiated by adding *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.15 μL) and aqueous ammonium persulfate (10 wt %, 0.5 μL) to 100 μL of degassed monomer solution. The resulting solutions were immediately loaded into a capillary channel formed with two

coverslips separated by spacers of 150 μm. Gelation was carried out in a sealed chamber under a positive pressure of nitrogen for 1 h. After polymerization, the coverslip and spacers were removed, and the hydrogel was immersed in water. In order to extract unreacted components, the swelling medium was changed at least three times over a period of 3 h.

To fabricate the hydrogel microvalves in the microfluidic channels, cylindrical fragments of p(NIPAm-*co*-NDEAm) (80/20) hydrogel loaded with NPs were inserted into plain capillary tubes of 1.1 mm inner diameter. Rhodamine B (1.0 MB) was introduced to the capillary channels in order to visualize the fluidic flow. The visible light-induced openings of these microvalves were observed and photographed using an optical microscope (Mighty Scope 5 M USB Digital Microscope, AVEN, USA).

2.4. Measurements. To measure the swelling ratios of the composite hydrogels, the position of at least 10 embedded fluorescent beads within the hydrogel was tracked as a function of irradiation time, as described previously.[27] The change of the linear swelling ratio is identical to the movement of the fluorescent beads. The reported values are the average of the linear expansion determined for each bead, with the uncertainties being the standard deviation. Blue light irradiation was provided by exposing samples to light from a high-pressure mercury short arc lamp (EL-6000, Leica) through a blue excitation filter (450−490 nm, I3, Leica), which yielded an intensity of 43.5 mW/cm^2, as measured by an ACCU-CAL 50-LED(DYMAX). The swelled hydrogel films were imaged using an epi-fluorescence microscope (DMI3000B, Leica).

3. RESULTS AND DISCUSSIONS

First, we attempted to determine the temperature increase in the NPs under light irradiation due to the photothermal effect. The NPs used in the work are superparamagnetic magnetite coated with a double surfactant layer (SO/SDBS), and the average diameter is found to be 18.7 nm (Figure S1, Supporting Information). Figure 1 shows the temperature changes for an
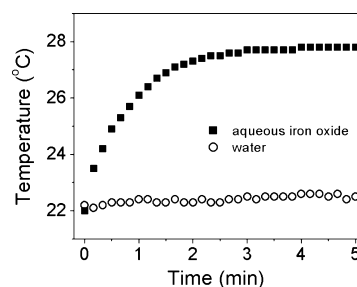

Figure 1. Temperature change for pure water and 2.3 mg/mL of aqueous iron oxide nanoparticles (NPs) under illumination with blue light of 43.5 mW/cm^2.

aqueous dispersion of NPs (with the same concentration as the hydrogel/NPs composites used in this work) exposed to 43.5 mW/cm^2 of visible light irradiation. Pure water is employed as a control. We found that the NPs dispersed in water absorbed visible light and consequently generated heat. As seen in Figure 1, the temperature of the aqueous dispersion of NPs increased from 22.2 to 27.7 °C over 3 min under illumination with visible light, while the pure water did not undergo a significant temperature change under the same conditions. These results indicate that sufficient heat is produced under visible light irradiation to cause a substantial temperature increase, confirming that the NPs convert the photo energy of visible light into thermal energy, which increases the temperature of the water loaded with NPs. As described above, it is reported that the NPs in the thermally responsive hydrogel matrix

absorbed visible light and converted the photo energy into thermal energy, heating up the hydrogel network and causing a decrease in volume.

The light-responsive hydrogels we developed were prepared from the temperature-responsive monomer N-isopropylacrylamide (NIPAm), the cross-linker N,N-methylene bis-(acrylamide) (BisAA), and NPs dispersed in water. Figure 2a
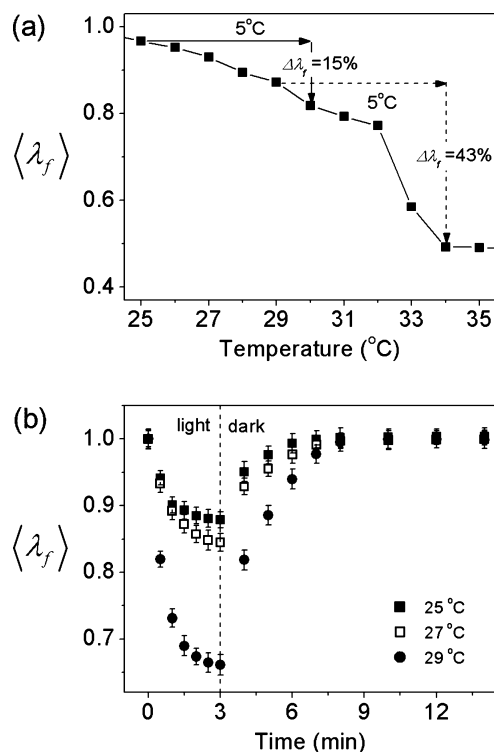

Figure 2. (a) Temperature-dependent linear swelling ratio λ_f during heating for poly(N-isopropylacrylamide) (PNIPAm) hydrogel containing NPs. Arrows indicate degree of λ_f changes for PNIPAm containing NPs for temperature increase of 5 °C at 25 and 29 °C. (b) Normalized linear swelling ratio $\langle \lambda_f \rangle$ for PNIPAm containing NPs exposed to 43.5 mW/cm^2 blue light for 3 min at 25, 27, and 29 °C.

shows the equilibrium linear swelling ratio (λ_f) changes of PNIPAm containing NPs as a function of temperature. λ_f is defined as the amount a gel swells in each dimension at the equilibrium state when immersed in water, meaning that the volume-swelling ratio is equal to λ_f^3. The measurements of λ_f were performed by incrementally raising the temperature by 1.0 °C over 10 min and subsequently holding for an additional 10 min prior to determining the degree of swelling. PNIPAm gel undergoes a reversible volume phase transition from a swollen hydrated state to a shrunken dehydrated state with an increase in temperature.[19,20] As seen in Figure 2a, PNIPAm gel shows almost linear variation in the swelling from 25 to 32 °C, while rapid volume shrinkage due to the volume phase transition was found at ~33 °C. Above 34 °C, no change in λ_f was observed. We note that the hydrogel containing NPs shows nearly the same thermal behavior as that of the pure hydrogel of the same chemical composition, indicating that the NP contents used in this work have little influence on the thermosensitivity of the composite hydrogels (Figure S2, Supporting Information).

First, we estimated light-induced volume shrinkage of the PNIPAm gel irradiated at RT. On the basis of the temperature increase of 5 °C due to the photothermal effect for the NPs

under light irradiation, light-induced λ_f change is estimated at about 15% which corresponds to a volume shrinkage of 38%. Then, we also estimated the light-induced volume change when the temperature of the medium was 29 °C. In this case, the temperature of the hydrogel can be increased to 34 °C, resulting in an increase in λ_f to 43% (an 82% volume shrinkage). If the temperature increase due to the photothermal conversion of the NPs is preserved regardless of the temperature of the medium, the degree of light-induced shrinkage of the hydrogel can be different depending on the temperature of the medium. We assumed that light-induced volume shrinkage can be maximized with hydrogels of identical chemical composition and identical exposure conditions when the LCST of the hydrogel is in the temperature increase range of the photothermal effect.

To validate our conclusion for light-induced volume shrinkage depending on the temperature of the medium, the λ_f change for PNIPAm containing NPs under visible light irradiation was measured with the medium at various temperatures. The linear swelling ratios of the gels are normalized by the swelling ratios of the gels at the equilibrium swelling state before illumination. As shown in Figure 2b, the normalized linear swelling ratio ($\langle \lambda_f \rangle$) measured at 25 °C decreases to 0.88, while the $\langle \lambda_f \rangle$ is 0.84 after 3 min of irradiation at 27 °C. Light irradiation at 29 °C led to a decrease of the $\langle \lambda_f \rangle$ to 0.66, which corresponds to approximately 71% decrease in the volume compared to the initial equilibrium state. These measurements indicate that the degree of volume change of the hydrogels under light irradiation can be controlled by adjusting the temperature of the medium. We found that light-induced volume change was maximized when the temperature of the medium is just below the LCST of the hydrogels.

On the basis of the temperature-responsive swelling ratio curve and measured volume shrinkage of the hydrogels, we estimated the temperature increases of the hydrogels containing NPs due to photothermal conversion after 3 min irradiation at each temperature point. They ranged from 4.2 to 4.4 °C, revealing that the temperature increase of the hydrogels is independent of the temperature of the medium in this temperature range.

To maximize volume shrinkage in response to light irradiation, we next consider the control of the thermal behavior of the hydrogels loaded with NPs. As described above, light-induced volume shrinkage is maximized when the temperature of the medium is just blow the LCST of the hydrogels. As shown in Figure 2b, we changed the temperature of the medium to maximize volume shrinkage. However, for real-world applications operated at RT, controlling the temperature of the medium is not realistic. In this situation, adjusting the thermal behavior of the hydrogels can maximize the light-induced volume shrinkage. If the LCST of the hydrogel is reduced by 4 °C, the light-induced λ_f decrease is estimated to be 43%, even at RT, as shown in Figure 3a.

As described previously, adjustment of the LCST of PNIPAm can be achieved by copolymerizing NIPAm with hydrophilic or hydrophobic comonomers.[28,29] The alteration of the LCST of PNIPAm is attributed to a change in the critical hydrophilic/hydrophobic balance in the side group of PNIPAm and the resultant change in the polymer's interaction with water molecules. Copolymerization of PNIPAm with more hydrophilic or hydrophobic monomers allows the optimization of the overall hydrophilicity of the PNIPAm side group.
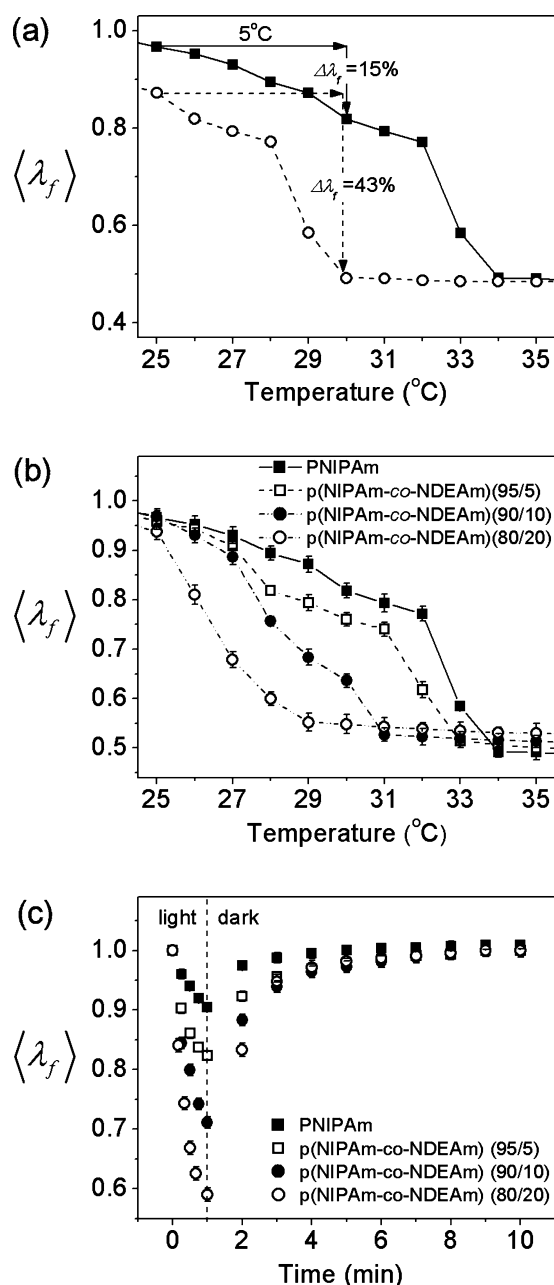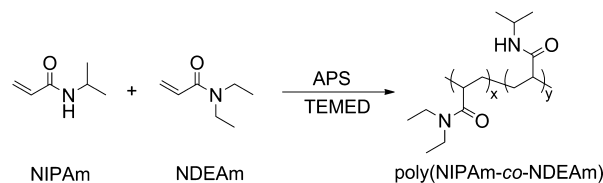
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Scheme 1. Synthesis of Poly(N-isopropylacrylamide-co-N,N-diethylacrylamide) through Free-Radical Polymerization

the PNIPAm copolymer exhibiting a decreased LCST. In p(NIPAm-co-NDEAm), the existence of hydrophobic diethyl groups near the polymer backbone retards the hydration of polymer chains. Accordingly, polymer aggregation can be promoted, inducing the LCST to shift to lower temperature. As the hydrophobic surface of the polymer increases, the LCST will decrease.

The temperature-dependent linear swelling ratios for the p(NIPAm-co-NDEAm) hydrogels containing NPs were measured and plotted in Figure 3b. These copolymer hydrogels were found to exhibit characteristic temperature-dependent phase transitions. As expected, the resultant copolymers show lower LCSTs than the PNIPAm homopolymer due to the incorporation of hydrophobic NDEAm into the polymer backbone. Figure 3b demonstrates that the p(NIPAm-co-NDEAm) hydrogels show a phase transition temperature of 26−32 °C depending on NDEAm content, which lies in between the phase transition temperature of the homopolymers PNIPAm (~33 °C)[3] and PNDEAm (25−28 °C).[29] We found that the temperature range for rapid volume decrease shifted to lower temperature with increased NDEAm composition of the hydrogel.

To confirm that light-induced volume change is affected by the thermal behavior of the hydrogels, we investigated the swelling and shrinking for various chemical compositions of p(NIPAm-co-NDEAm) hydrogels loaded with NPs when exposed to visible light irradiation for 1 min. When exposed to blue light of 43.5 mW/cm², the copolymer hydrogels containing NPs underwent significant volume changes depending on their NDEAm content. As can be seen in Figure 3c, the degree of λ_f change induced by light irradiation ranged from 9.5% to 38% for 1 min exposure in proportion to the NDEAm composition (from 0 to 20 mol %). For the PNIPAm homopolymer hydrogel, the linear swelling ratio decreases to 0.90, while the linear swelling ratios of the p(NIPAm-co-NDEAm) copolymer hydrogels incorporating 5 and 10 mol % of NDEAm are 0.82 and 0.71 after 1 min of irradiation, respectively. Irradiation of the 20 mol % NDEAm hydrogel led to a decrease in the linear swelling ratio to 0.62, which corresponds to approximately 76% decrease in the volume compared to the initial equilibrium state before light exposure.

These measurements indicate that the decrease in volume under light irradiation is proportional to the NDEAm content of the copolymer hydrogels, suggesting that the degree of volume change can be easily manipulated by chemically controlling the thermal behavior of the hydrogel matrix. An increase in the NDEAm composition of the hydrogel leads to a decrease in the material's LCST, which, in turn, yields a hydrogel that contracts more under identical irradiation conditions at RT.

Upon removing the visible light, the hydrogels containing NPs recovered their original volumes in 6−7 min, regardless of the hydrogel compositions. These results are consistent with

Figure 3. (a) Temperature-dependent linear swelling ratio λ_f during heating for poly(N-isopropylacrylamide) (PNIPAm) hydrogel containing NPs. Symbols indicate supposed temperature-dependent λ_f for PNIPAm of 4 °C lower LCST. Arrows indicate degree of λ_f changes for PNIPAm and the supposed curve with a temperature increase of 5 °C at 25 °C. (b) Temperature-dependent normalized linear swelling ratio $\langle\lambda_f\rangle$ during heating for PNIPAm and poly(N-isopropylacrylamide-co-N,N-diethylacrylamide) (p(NIPAm-co-NDEAm)) of various NDEAm compositions summarized in Table 1. (c) Normalized linear swelling ratio $\langle\lambda_f\rangle$ for PINPAm and p(NIPAm-co-NDEAm) of various NDEAm compositions containing NPs exposed to 43.5 mW/cm² of blue light for 1 min at 25 °C.

To shift the LCST of the PNIPAM hydrogel to a lower temperature, we have prepared various compositions of poly(N-isopropylacrylamide-co-N,N-diethylacrylamide) (p-(NIPAm-co-NDEAm)) loaded with NPs through free-radical polymerization as shown in Scheme 1. Details of the synthetic conditions are summarized in Table 1. The existence of hydrophobic NDEAm as a comonomer is expected to lead to

the theory for hydrogel swelling kinetics, which is dependent only upon their dimensions.[27]

With this relationship between light-induced volume change and thermal behavior, we could minimize light irradiation time to achieve specific aimed volume decrease. We irradiated p(NIPAm-co-NDEAm) hydrogels with visible light at RT until λ_f changes reached about 10%, which corresponds to volume shrinkage of 27%. Figure 4 shows the light-induced λ_f decreases
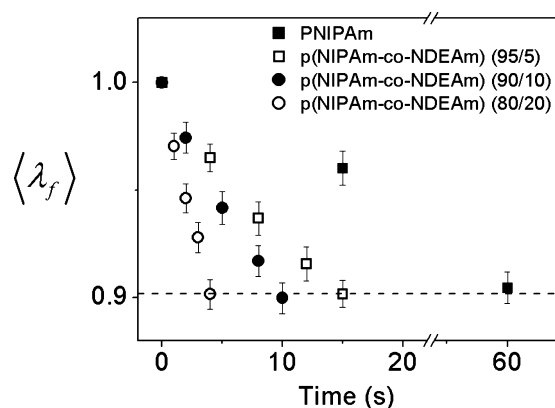

Figure 4. Normalized linear swelling ratios $\langle \lambda_f \rangle$ for p(NIPAm-co-NDEAm) containing NPs exposed to 43.5 mW/cm^2 of blue light at 25 °C. A dotted line is drawn at $\langle \lambda_f \rangle = 0.9$, corresponding to a volume shrinkage of 27%.

for various compositions of p(NIPAm-co-NDEAm) hydrogels. As shown in Figure 4, with the increase of NDEAm content in the copolymer, the irradiation time required for a 10% linear swelling ratio decreases. For the PNIPAm homopolymer, irradiation for 1 min led to a 10% decrease of the linear swelling ratio, while 4 s of irradiation is sufficient for a 10% decrease in the linear swelling ratio for the 20 mol % NDEAm hydrogel. These results indicate that a shorter irradiation time is needed for volume decrease in hydrogels with a LCST close to RT. Since the temperature of hydrogels rapidly approaches the LCST, at which point the polymer exhibits a large volume change, as the content of NDEAm increases, a fast light-induced volume decrease can be achieved by incorporating the hydrophobic NDEAm moiety into the hydrogel matrix.

On the basis of the fast light-responsive volume decrease of p(NIPAm-co-NDEAm) hydrogel containing NPs, a liquid microvalve was fabricated to control flow in a microfluidic channel by visible light irradiation. Microvalve control by light irradiation is attractive as it enables on-demand remote operation with independent local control and rapid triggering. Since p(NIPAm-co-NDEAm) hydrogels loaded with NPs show fast volume decrease, the operation time for opening the microvalve is decreased.

To fabricate microchannels equipped with hydrogel microvalves, cylindrical fragments of p(NIPAm-co-NDEAm) hydrogel loaded with NPs were inserted into plain capillary tubes with a 1.1 mm inner diameter, as shown in Figure 5. Rhodamine B solution was introduced to the capillary on the left side of the microvalve in order to visualize the effect of the microvalve on the fluidic flow.

Initially, in its "off" state, the hydrogel microvalves completely blocked the fluidic flow in the microfluidic channels (Figure 5a). When the hydrogel microvalve in the lower microchannel was irradiated with visible light for 9 s, the hydrogel microvalve absorbed the visible light and contracted
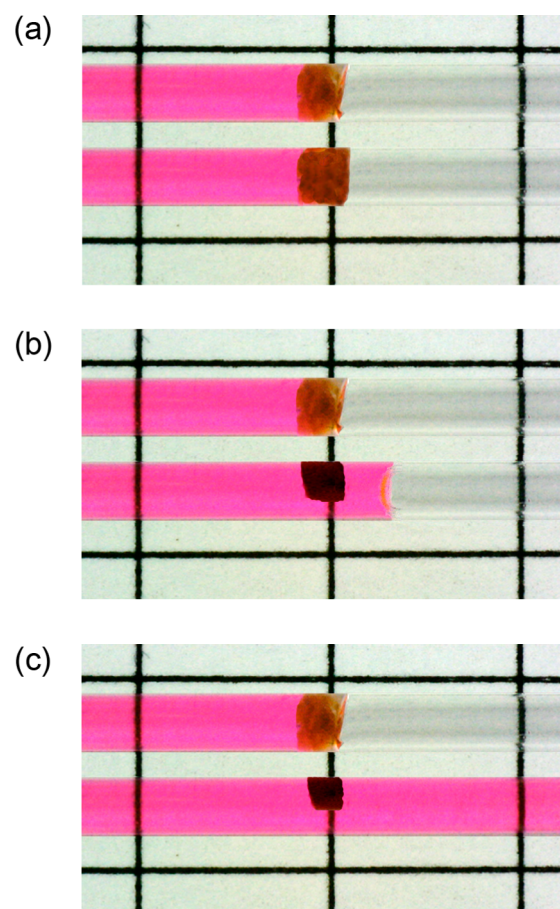

Figure 5. Microvalve made with the p(NIPAm-co-NDEAm) (80/20) hydrogel containing NPs. The photographs show the microvalves (a) before and after exposure to 43.5 mW/cm^2 of blue light on only the lower microchannel for (b) 9 s and (c) 17 s.

to allow for fluidic flow from the left side to the right side as shown in Figure 5b. To the best of our knowledge, this is the fastest opening of a hydrogel microvalve for a microfluidic device reported in the literature.[12,15,16] For the hydrogel microvalve incorporating chromophores such as spirobenzo-pyran, chromophores are immediately isomerized under light irradiation, thus the volume of hydrogel decreases due to the osmotic pressure change.[12] The hydrogel microvalve fabricated with PNIPAm functionalized containing the spirobenzopyran group was opened after 18−30 s of blue light irradiation with the intensity of 20 mW/cm^2. Even though operating with low light intensity, the hydrogel microvalve recovered its initial size in 3 h after stopping light irradiation due to the very slow reverse isomerization for spirobenzopyran. Also, this system includes the acidic environment, which may be harmful to biomolecules. On the other hand, photothermal materials in the hydrogel matrix efficiently generated heat without any environmental change and immediately cool down after turning light off. According to the previous report regarding hydrogel microvalve containing photothermal materials such as graphene oxide, near IR irradiation of several Watts for 1−2 min is needed to open the hydrogel valve through photothermally triggered volume change of the valve.[15,16]

Additional irradiation resulted in further shrinking of the microvalve, allowing higher fluidic flux (Figure 5c). In contrast, during this time the nonirradiated microvalve in the upper microchannel maintained its volume and blocked the flow. This

result indicates that individual microvalves can be controlled independently by local light irradiation.

After the visible light was turned off, the heat dissipated into the surrounding environment, and the hydrogel expanded back to its original volume, preventing the fluidic flow in the lower channel. As described in a previous report, light-induced volume changes in these thermally responsive hydrogel materials are fully reversible and repeatable, allowing for repetitive cycling of the valve.[19,20] Furthermore, the degree of valve opening (i.e., the shrinkage of the hydrogels) at specific fluidic temperatures can be tuned by adjusting the chemical composition of the hydrogels, the concentration of the NPs, and the light dose. If required, faster responses can be obtained with higher light intensities. According to our previous work, the temperature increase due to the photothermal effect is proportional to the light intensity.[19] A rapid increase in temperature can induce a faster opening of the hydrogel microvalve. We have attempted to use a stronger light source to minimize the operation time for opening the microvalve. When exposed to visible light of 380 mW/cm^2, fluidic flow allowed by the opening of the valve was detected in just ~5 s.

4. CONCLUSION

We can conclude that the thermal behavior of hydrogel matrices plays a crucial role in light-induced volume change of hydrogels loaded with photothermal materials. We found that the light-induced volume change of a hydrogel composite was maximized when the temperature of the medium is just below the hydrogel's LCST. By copolymerization with hydrophobic NDEAm, the LCST of PNIPAm could be lowered to maximize light-induced volume change at RT. Knowing this relationship between light-induced volume change and thermal behavior, we could minimize the required light irradiation time to achieve a specific aimed volume decrease in the hydrogel. This enhanced performance allowed the effective fabrication of a liquid microvalve for microfluidic devices. We demonstrated remote control of the fluidic flow utilizing a microvalve fabricated from light-responsive hydrogels that showed a significantly reduced response time and improved volume decrease.

ASSOCIATED CONTENT

Ⓢ Supporting Information

TEM image, size analysis data, X-ray diffraction profile, and magnetization curve of NPs and temperature-dependent swelling behavior for the pure and composite hydrogels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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