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PAPER

An infrared-light responsive graphene-oxide incorporated poly(*N*-isopropylacrylamide) hydrogel nanocomposite

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We demonstrate a new light-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel nanocomposite incorporating glycidyl methacrylate functionalized graphene oxide (GO–GMA) instead of metallic nanoparticle fillers. GO–GMA is synthesized by esterification with glycidyl methacrylate. GO–GMA incorporated hydrogels are synthesized by photopolymerization of NIPAAm including 4-dimethylaminopyridine (DMAP) and *N*,*N*′-methylenebisacrylamide (NMBA) in GO–GMA dispersed dimethyl sulfoxide (DMSO) solution. Results show that such a nanocomposite hydrogel can undergo a large volumetric change in response to infrared (IR) light illumination, due to the highly efficient photothermal conversion of GO–GMA. It also exhibits significantly larger water uptake compared to conventional PNIPAAm hydrogel by 3 times. Based on the developed IR-responsive nanocomposite hydrogel, we have also realised a microvalve that controls the fluidic flow within a microfluidic channel through remote IR light actuation.

1. Introduction

Responsive hydrogels which have the capability to respond to external stimuli, such as temperature,[1] pH,[2] photons,[3,4] and antigens,[5] have attracted much attention because such hydrogel systems can serve as functional materials with potential applications in the areas of drug/gene delivery,[6] microlenses,[7] sensors,[8] and so forth. Light-responsive hydrogels are promising ones because the activation process *via* light can be remote and noninvasive.[9] For example, thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels have been shown to possess light responsiveness for microfluidic applications when incorporating gold nanoparticles (AuNPs).[10] The light response is realized by combining the reversible hydration–dehydration transition of NIPAAm and plasmonic absorption band in the near-infrared (IR) region of AuNPs.[11] However, the volumetric change does not seem to be significantly more than the conventional responsive hydrogel, thus limiting the application as actuators.

Recently, graphene oxide (GO) has been demonstrated to exhibit extraordinary physical properties when mixed with polymers to form nanocomposites.[12] GO is an attractive precursor for the production of functional composite materials because of its easy processability in solution, scalability from graphite,[13] as well as rich colloidal properties.[14] We here report on a new IR-light responsive hydrogel which is based on thermo-responsive PNIPAAm hydrogels incorporating glycidyl methacrylate functionalized graphene-oxide (GO–GMA). We took advantage of the giant-IR-absorption band in GO[15] and its superior thermal conductivity to absorb IR and trigger the hydration–dehydration transition within the hydrogel networks. In addition, the superior thermal conductivity and photothermal conversion capability of GO[16,17] can enhance the performance of the IR-light responsive hydrogel. Thus, we were able to realize an IR-responsive PNIPAAm hydrogel without adding metallic nanoparticles. The resultant hydrogel nanocomposite demonstrated significant, three times larger uptake of water compared to PNIPAAm hydrogel itself. Its lowest critical solution temperature (LCST) is also lowered by 10 °C as compared to PNIPAAm. As an example of the applications, we also demonstrated a microvalve in a microfluidic channel that could be remotely actuated by IR light.

2. Experimental

2.1 Materials

Graphite powder was obtained from Fisher Scientific. Isobornyl acrylate (IBA) was from Surface Specialties UCB (Smyrna, GA, USA). Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), 4-dimethylaminopyridine (DMAP), *N*,*N*-dicyclohexylcarbodiimide (DCC), glycidyl methacrylate (GMA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 90%) were obtained from Sigma-Aldrich (St Louis, MO, USA). *N*-Isopropylacrylamide (NIPAAm), *N*,*N*′-methylenebisacrylamide (NMBA; electrophoresis grade), and dimethyl sulfoxide

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(DMSO, 99.6+%) were from Acros Organics (Morris Plains, NJ, USA). All reagents were used as received.

2.2 Graphene oxide (GO) synthesis

Fig. 1 shows the synthesis route of the glycidyl methacrylate functionalized GO *via* esterification and incorporation with PNIPAAm hydrogel. First, GO was prepared from natural graphite powder by a modified Hummers method.[18] Graphite (5 g) and $NaNO_3$ (2.5 g) were mixed with a 95% sulfuric acid (H_2SO_4, 120 mL) in a 500 mL flask. The mixture was stirred for 30 min in an ice bath. Under vigorous stirring, 15 g of $KMnO_4$ was added to the suspension. The rate of addition was controlled to keep the reaction temperature lower than 20 °C. The ice bath was then removed, and the mixture was stirred at 35 °C overnight. As the reaction proceeded, the mixture gradually became pasty, and the color turned into light brown. Afterwards, 150 mL of deionized (DI) H_2O was slowly added to the pasty mixture still under vigorous agitation. The reaction temperature was observed to rapidly increase to 98 °C with effervescence, and the color changed to brown yellow. The diluted suspension was then stirred for 1 day. Next, 50 mL of 30% hydrogen peroxide (H_2O_2) was added to the mixture. For purification, the mixture was washed with 5% of hydrochloric acid (HCl) and then with DI water for several times to obtain the graphite oxide sample. The exfoliation was carried out by sonication of GO in aqueous solution for 40 min. The as-produced GO sheet was observed under scanning electron microscopy (SEM).

2.3 Synthesis of glycidyl functionalized GO (GO–GMA)

The as-synthesized GO has many carboxylic groups within its molecular structure which is perfect for esterification to anchor methacrylate groups onto GO. The synthesis of GO–GMA is also shown in Fig. 1, leveraging the methods published by Salavagione *et al.*[19] First, GO (0.5 g), DCC (1.85 g, 9 mmol) and DMAP (0.14 g, 1.2 mmol) were dissolved in dimethyl sulfoxide (DMSO, 60 ml) at the room temperature. After dissolution of DMAP, GMA (0.5 g, 3.52 mmol) was added. The mixture was stirred at 45 °C for 24 hours in ambient condition. To quench the reaction, an equimolar amount of HCl was added to the solution to neutralize DMAP. The neutralized GO–GMA was then precipitated with isopropanol (IPA) and GO–GMA powder was obtained. The GO–GMA powder was further dispersed in DI water and reprecipitated out with IPA for three times. The precipitates were obtained in a centrifuge at 2500 rpm for 30 min. Centrifugation was performed with Centra Biofuge Primo equipped with a rotor (Thermo Electron Corp., Model 854, Marietta, OH). The product was dried in vacuum at the room temperature for 24 hours and redispersed in DMSO for further use. The GO–GMA stayed well dispersed without precipitation in DMSO for several weeks.

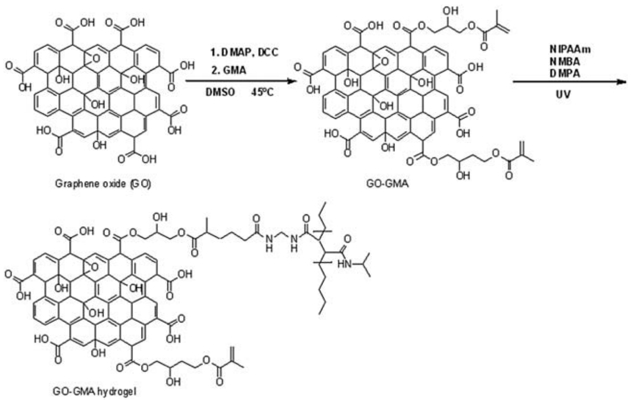

Fig. 1 Synthesis of glycidyl methacrylate functionalized GO *via* esterification and incorporation with PNIPAAm hydrogel.

2.4 Preparation of GO–GMA hydrogel microactuators

Our GO–GMA hydrogel can be photopatterned *via* liquid-phase photopolymerisation.[20] In our experiments, the composite gel was prepared by photopolymerisation of NIPAAm in the presence of GO–GMA well dispersed in DMSO solution. The GO laminates are covalently modified and crosslinked within the hydrogel network by using the previously described esterification reaction. Fig. 2 shows the schematic of the fabrication process of a GO–GMA hydrogel structure within a microfluidic channel. First, the microfluidic channel was defined. A polycarbonate cartridge cavity (HybriWells, Grace Bio-Labs, Bend, OR) was filled with isobornyl acrylate (IBA) prepolymer solution. The thickness of the cavity was defined by a 200 μm thick spacer. A film photomask was aligned on top of the cartridge followed by an ultra-violet (UV) radiance (intensity, $I = 9$ mW cm^{-2}; time, $t = 20$ s). The IBA was photopolymerised in this step and thus formed the microfluidic channel. Afterwards, another glass slide was placed onto the IBA channel structure. A pregel solution was prepared by mixing NIPAAm, NMBA, GO–GMA DMSO solution, water and DMPA in the weight ratio of 2.18 : 0.124 : 3.0 : 1.0 : 0.154. The concentration of GO–GMA in DMSO solution is 50 mg ml^{-1} which makes the GO–GMA 2.3 wt% of the overall hydrogel composition. This GO–GMA pregel solution was then injected into the channel and was subsequently photopatterned under UV light (intensity $I = 28$ mW cm^{-2}; time $t = 25$ s). Non-crosslinked gel precursor was then flushed away using DI water and a rectangular GO–GMA hydrogel structure was formed in the microchannel. The patterned composite

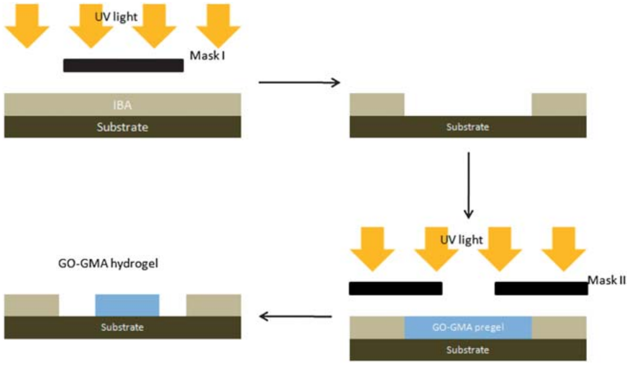

Fig. 2 Photopatterning of GO–GMA hydrogel within a microfluidic channel. The microchannel is first formed through a masked photolithography step, with IBA as the structural material forming the channel. Then, GO–GMA pregel solution is flowed into the channel, followed by photopatterning *via* a second mask.

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GO–GMA hydrogel was brown in color due to the presence of incorporated GO.

2.5 Measurement

The presence of pendant glycidyl methacrylate groups in GO–GMA is confirmed by the FT-IR spectra (Bruker Equinox 55 FTIR with diamond ATR accessory, Billerica, MA). Strong volumetric change of the GO–GMA hydrogel when exposed to IR-light irradiance was observed (see later sections). A charge coupled device (CCD)-coupled stereoscope was placed above a piece of fabricated hydrogel film submerged in DI water to monitor and record the images of the film when it underwent volumetric change. An IR light source (Hotspot, Model H. S. 250.3, I^{2}R, Cheltenham, PA) was irradiated from the side at an oblique angle and the power intensity at the plate of the IR-responsive hydrogel was measured by a power meter (Field Max II, Coherent Inc., Santa Clara, CA) to be 1.21 W cm^{-2}.

The photothermal conversion efficiency of GO–GMA was measured by irridiating identical IR light to GO–GMA DMSO, pure DMSO, and pure DI water solution with the power intensity of 1.2 W cm^{-2} and exposure area of 2 cm^2 for 2 min. The temperature was recorded using a thermocouple every 5 seconds.

Measurement of the GO–GMA hydrogel was following the method published by Wu *et al.*[21] The swelling ratios of GO–GMA hydrogel and conventional PNIPAAm hydrogels, as comparison, were measured gravimetrically in the controlled temperature range of 10–50 °C in water bath. The conventional NIPAAm hydrogel prepolymer mixture consists of NIPAAm, NMBA, DMSO, DI water and DMPA in the weight ratio of 2.18 : 0.124 : 3.0 : 1.0 : 0.154 followed by photopolymerization under the same condition as GO–GMA hydrogel. Gel disc samples were incubated in DI water for at least 24 h at room temperature and the weight of the gel was recorded at 5 °C intervals after blotting the excess surface water with moistened Whatman #1 filter paper. The swelling ratio (S_r) was calculated *via* eqn (1)

$$S_r = (W_w - W_d)/W_d \tag{1}$$

where S_r is equilibrium swelling ratio, W_w and W_d are swollen weight of the gel after equilibration in DI water and dry weight of the gel dried in vacuum overnight, respectively. The swelling ratio was measured after the gel was incubated at the new temperature in DI water for 1 hour to reach equilibrium. The measurements were carried out as the temperatures were raised.

3. Results and discussion

The dispersion of the sheets can be seen from the SEM image shown in Fig. 3. In order to functionalize GO with methacrylate groups which could facilitate crosslinking with PNIPAAm polymers, we employed the Steglich esterification process to make GO sheets crosslinkable to the PNIPAAm hydrogel network.[23] GO sheets have chemically reactive oxygen functional groups, such as carboxylic acid groups at their edges and epoxy and hydroxyl groups on the basal planes. Our approach to the chemical modification of GO is to utilize esterification reactions of carboxylic acid groups to glycidyl methacrylate. In our case, esterification with glycidyl methacrylate using DMAP and DCC was performed successfully and an increased solubility of functionalized GO in DMSO compared to the non-functionalized one was observed.

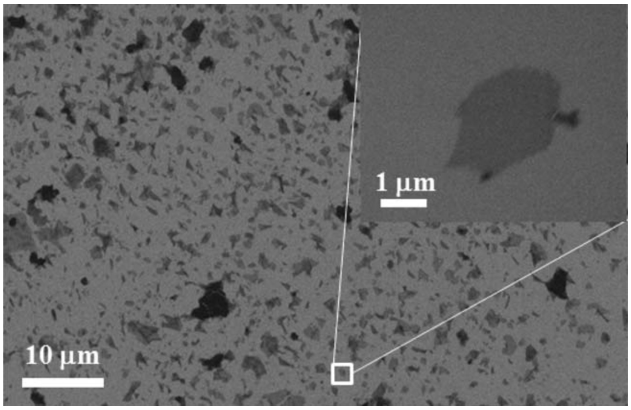

Fig. 3 SEM images of as synthesized GO sheet on a silicon substrate. The low contrast is due to the thinness of the GO sheet.[22] The black sheets are flakes which consist of several layers of GO sheets.

The presence of pendant glycidyl methacrylate groups in GO–GMA is confirmed by the FT-IR spectra, as shown in Fig. 4. The FT-IR spectra of GO were also obtained for comparison. In the spectra, some peaks changed in intensity due to the modification, and new bands were present. The development of the band at 1718 cm^{-1} suggests the presence of new carbonyl species in both GO and GO–GMA. This band is most often related to the C=O stretching motions of COOH groups situated at the edges of the GO sheets and has low intensity due to the high aspect ratio of GO which makes the relative amount of edge sites very small. Vibration modes of epoxide (C–O–C) (1230–1320 cm^{-1}) and C–OH (1137 cm^{-1}) are also shown in the spectrum, consistent with the observation reported in M. Acik *et al.*[15] In addition, a broad band centered at 3000 cm^{-1} in the spectra of both GO and GO–GMA is due to the OH group of COOH; it contains a significant contribution from the skeletal vibration of oxidized graphitic domains. Similarly, in our case the band at 1567 cm^{-1}

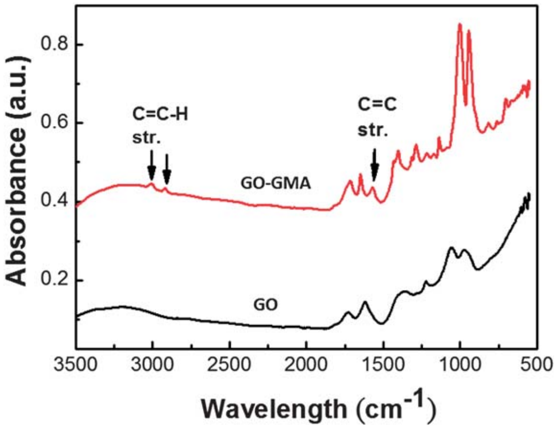

Fig. 4 FT-IR of GO and GO–GMA. The absorption peaks of GO–GMA that are distinct from GO are marked with arrows and labelled with vibration modes.

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(as marked in Fig. 4) can be attributed to $C{=}C$ stretching of methacrylate groups which are distinct from unfunctionalized GO. Indeed, this band suggests that esterification is also taking place in our system. The methacrylate group is also confirmed by the marked increase in the band around 3006 cm^{-1} and 2921 cm^{-1}, which appears weak in methacrylate and has been assigned to alkene C–H stretches.

It has been shown that GO is capable of converting photo-energy into thermal energy effeciently.[17] The temperature changes caused by the photothermal conversion of GO–GMA in DMSO solution are shown in Fig. 5. The comparison with pure water and DMSO under identical IR light irradiation conditions clearly demonstrates the high performance of GO–GMA for photothermal energy conversion. The pure water and DMSO solution did not undergo significant temperature change upon irradiation of IR light for 2 min. However, the temperature of the GO–GMA DMSO solution rose from the room temperature to 41 °C within 2 min under the same irradiation condition. Using the molar heat capacity of DMSO (153.27 J mol^{-1} K^{-1}), the amount of heat transfer to 2 mL of DMSO causing 16.1 °C of temperature change can be estimated to be 63.27 J. With the irradiation power of 1.2 W cm^{-2} over 2 cm^2 of exposure area, we can then estimate the overall efficiency of the photothermal conversion process in DMSO solution to be 22%. The high efficiency of heat transfer to DMSO solution is attributed to the extremely high value of thermal conductivity of graphene which has been reported to be up to 5300 W m^{-1} K^{-1} at the room temperature.[16,24] The superb thermal conduction of GO is beneficial to our IR light responsive hydrogel because faster heat conduction may facilitate faster response from the hydrogel.

Fig. 6 shows the equilibrium swelling ratio (S_r) which is defined as the water uptake over the dry weight of a hydrogel *vs.* temperature under controlled heating environment. This illustrates the LCST and water absorbing behavior of GO incorporated and conventional PNIPAAm hydrogels. Results in Fig. 6 show that introduction of GO sheets can dramatically increase the swelling ratio below LCSTs by approximately 3 fold; the phase transition temperature is lowered by 10 °C and the volume collapses more gradually within a broader temperature range compared to conventional PNIPAAm hydrogel. The possible reason is that the incorporated GO–GMA sheets within hydrogel networks produce a less dense gel network than the conventional PNIPAAm hydrogel and thus extra volume in the precipitating water uptake. This interesting phenomenon may be due to that many immobile water molecules interact with the GO structure.[25] Within the hydrogel networks, these GO sheets provide more interactions with water molecules, create more hydrogen bonding between water and hydrogel network, and thus holds more water molecules than traditional PNIPAAm hydrogels.[26] These GO–GMA hydrogels have fast macromolecule permeation rates, high swelling ratios, and rapid volumetric changes in response to temperature rise or fall through the LCST.

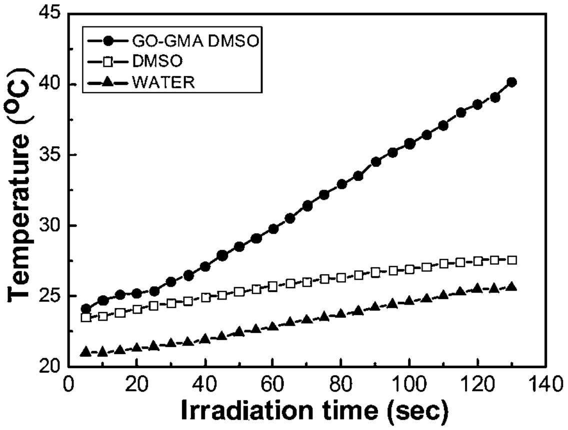

Fig. 5 Temperature response of GO–GMA upon IR light irradiation. The overall exposure duration is 2 min with power density of 1.2 W cm^{-2}.

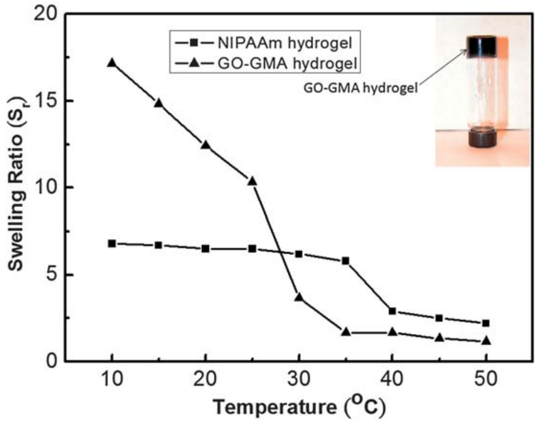

Fig. 6 Swelling ratio dependence on temperature for GO–GMA and conventional PNIPAAm. The inset shows the synthesized GO–GMA hydrogel.

When exposed to IR light, the nanocomposite hydrogel underwent significant volumetric change. Fig. 7(a) shows the photographs recording such changes in size as time proceeds. From the time instant of 1 s, IR light was turned on and the rectangle-shaped GO–GMA hydrogel film started to shrink in all directions. At 75 s, the GO–GMA hydrogel shrunk to its minimum size and remained unchanged after that. This result further confirms the photothermal conversion through GO–GMA sheets within the hydrogel network can trigger the hydrophobic–hydrophilic transition effectively.

As an application of our GO–GMA hydrogel, we also demonstrated a microvalve based on this hydrogel in a microfluidic channel (Fig. 8). The rectangular hydrogel structure as the microvalve was phototopatterned using the same method described above. Initially at its OFF state, with the IR light turned off, the GO–GMA hydrogel microvalve completely blocked the fluidic flow in the microfluidic channel (Fig. 8a). When the IR light was turned on, the GO–GMA sheets absorbed IR light, triggered the hydrogel to contract to allow for fluidic flow (from the left side to right in Fig. 8b), thus the ON state. The GO–GMA hydrogels shrunk in every dimension. As the IR light was turned off, the heat dissipated to the surrounding environment and the hydrogel absorbed water and expanded back to its original volume, preventing the fluidic flow (OFF state again). Note that in this experiment, the function of the GO–GMO hydrogel microvalve was remotely controlled by IR light.

The main reason for the distinctive property of our GO–GMA hydrogel is attributed to its inherent rapid transition in

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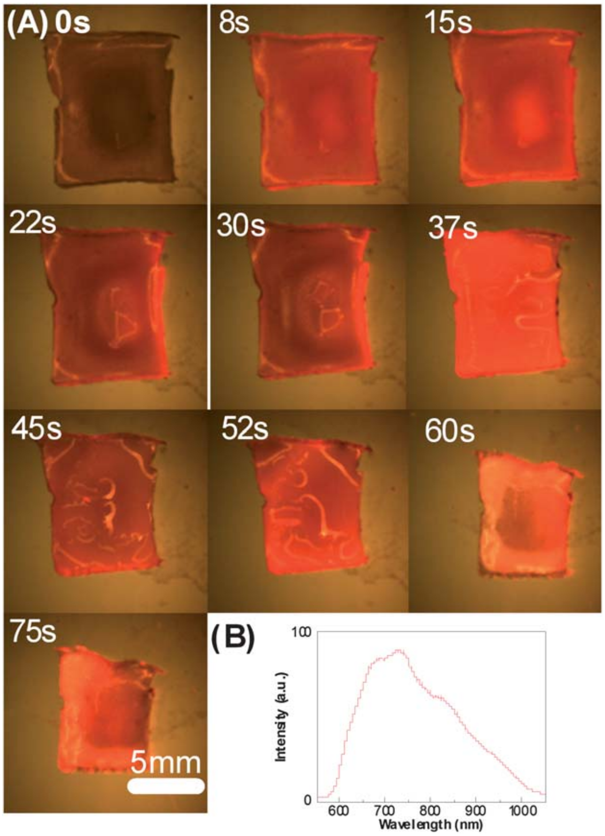

Fig. 7 (a) Dynamic change of a piece of IR-responsive GO–GMA-hydrogel film in one illumination cycle as a function of time. The IR is on at 1 s. The intensity of the IR light reaching the hydrogel sample is 1.21 W cm^{-2}. (b) Spectrum of the used IR light source.

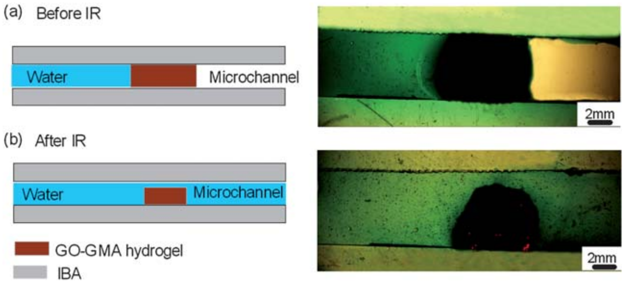

Fig. 8 A microvalve made of GO–GMA IR-responsive hydrogel. Top-views of the microvalve are on the left. Respective images taken under a microscope are on the right. (a) GO–GMA hydrogel microvalve before actuated by IR irradiation (OFF state) and (b) after exposure to IR light (ON state). The valve exhibits significant change in dimensions before and after IR actuation. Initially, the fluid flow is blocked by the valve at its OFF state. Then, at its ON state, the flow is able to pass through the microvalve.

hydrophilicity and hydrophobicity of PNIPAAm hydrogel.[27,28] The hydrophilic groups in the side chains of the PNIPAAm hydrogel connect with water molecules through hydrogen bonds. There are also numerous C–OH, and C–O–C groups on the GO–GMA sheets either on the edges or the planes that can also serve as hydrogen bonding sites and provide extra hydrogen bonding with water molecules.[25] These extra hydrogen bonds act cooperatively to form a stable hydration shell around the hydrophobic groups, which should lead to greater volumetric change of the GO–GMA hydrogel as compared to PNIPAAm hydrogel without GO incorporation. This is consistent with our observation.

The incorporated GO–GMA sheets within the hydrogel network absorb the IR irradiation and convert the energy into heat which heats up the vicinity within the hydrogel network. It has been reported that efficient heating of water can take place because of the high photothermal conversion efficiency of GO.[17] The heat generation through the photothermal conversion of GO caused by IR light irradiance and superior thermal conduction raises the temperature above the LCST and triggers the hydrophilic–hydrophobic transition. Thus, the hydrophobic interactions among the hydrophobic groups become relatively stronger above the LCST, which induces the release of the entrapped water molecules from the network until the hydrophobic interactions become fully dominant. With a rapid water release, the polymer chains collapse abruptly and the phase separation of the hydrogel network system occurs.

4. Summary

In summary, we demonstrated an IR-light-responsive GO–GMA incorporated hydrogel nanocomposite that undergoes significant volumetric change when irradiated by IR light. Results show that the GO–GMA hydrogel not only exhibits strong response to IR light irradiance but carries a large swelling ratio as well. In addition, the transition temperature is lowered by 10 °C due to the incorporation of GO. We also realized a microvalve in a microfluidic channel implementing such a hydrogel nanocomposite. The microvalve can control the fluidic flow within the microchannel through remote IR light actuation. This material potentially has many applications as actuators, such as in microelectromechanical systems, microfluidic devices and lab on chips. The synthesis procedure could be extended to other responsive hydrogels bearing pendant hydroxyl and amino groups. Future work includes comprehensive characterization of the GO–GMA hydrogel and study of the light responsive mechanism.

Acknowledgements

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