Mechanically Strong Janus Poly(*N*-isopropylacrylamide)/Graphene Oxide Hydrogels as Thermo-responsive Soft Robots[*]

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Abstract   Simple preparation of stimuli-responsive hydrogels with good mechanical properties and mild stimuli-responsiveness is essential for their applications as smart soft robots. Mechanically strong Janus poly(*N*-isopropylacrylamide)/graphene oxide (PNIPAM/GO) nanocomposite hydrogels with stimuli-responsive bending behaviors are prepared through a simple one-step method by using molds made of a Teflon plate and a glass plate. Residual oxygen in the air bubbles on the Teflon plate surface affects the polymerization and hence the cross-linking density, leading to the different swelling/deswelling rates of the two sides of the gels. Therefore, the hydrogels exhibit bending/unbending behaviors upon heating/cooling in water. The incorporation of GO nanosheets dramatically enhances the mechanical properties of Janus hydrogels. Meanwhile, the photo-responsive property of the GO nanosheets also imparts the hydrogels with remote-controllable deformation under IR irradiation. The application of the Janus PNIPAM/GO hydrogels as thermo-responsive grippers is demonstrated.

Keywords   Stimuli-responsive hydrogels; Soft robots; Poly(*N*-isopropylacrylamide); Graphene oxide; Mechanical properties

INTRODUCTION

Stimuli-responsive hydrogels that can perform anisotropic shape deformations under external stimuli (such as temperature[1−7], light[8, 9], pH[10−12], moisture[13−15] and ionic strength[16]) have drawn rapidly increasing attention in the last two decades, since the transformation of external stimuli into mechanical motions of the hydrogels allows the manufacturing of smart soft robots.

Structural inhomogeneity across the thickness or in plane is critical for the anisotropic shape deformation of the hydrogels. Bi-layer hydrogels with heterogeneous structures across the thickness have been widely used to fabricate soft robots[1−4, 17−19]. Hu *et al.* first reported the preparation of bi-layer hydrogels by assembling a poly(*N*-isopropylacrylamide) (PNIPAM) gel layer and a poly(acrylamide) (PAAm) gel layer, and the manufacture of a gel "hand" that bends and catches an object in hot water[1]. Yao *et al.* prepared bi-layer PNIPAM-clay nanocomposite hydrogels with different cross-linking densities, and demonstrated their applications as encapsulants and manipulators[2]. To overcome the drawbacks of bi-layer hydrogels, such as complicated and time-consuming preparation as well as weak interactions between the two layers, hydrogels

with gradient distributive components across the thickness are prepared by one-step method with assistance of the gravity[9], an applied electric[20] or magnetic field[21]. On the other hand, hydrogels with structural inhomogeneity in plane, especially with locally changed components or cross-linking densities, are also prepared by photolithographic[22−24] and ion-printing methods[25−27].

PNIPAM hydrogels are the most common and extensively studied thermo-responsive hydrogels, since the sharp volume change of PNIPAM systems can be actuated at a mild LCST (lower critical solution temperature) around 33 °C. Recently, light-absorbing nanoparticles, such as gold nanorods[28], carbon nanotubes[29−31], graphene[16, 32] and graphene oxide (GO) nanosheets[8, 33, 34], as well as magnetite nanoparticles[35], that can transform visible and more often infrared (IR) light to thermal energy are incorporated into PNIPAM hydrogels to endow them with photo-(essentially thermal) responsive performance, which realizes the remote control of the deformation and hence movement of soft robots. For example, Zhang *et al.* prepared bi-layer hydrogels by assembling a PNIPAM/GO hydrogel and a PNIPAM hydrogel, which can lift an aluminium dish or a glass plate upon irradiation of IR light[8], by remote control.

In this work, PNIPAM/GO nanocomposite hydrogels are prepared with structural inhomogeneity across the thickness through a simple one-step method by using molds made of two different hydrophilic/hydrophobic plates[27, 36, 37]. Mechanical properties of the hydrogels are enhanced by incorporation of GO nanosheets owing to their formation of hydrogen bonds with PNIPAM chains[38−41]. In addition, the photo-responsive property of GO nanosheets also imparts the hydrogels with remote-controllable deformation.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM) (Tokyo Chemical Industry Co., Ltd., Japan) was recrystallized from *n*-hexane and dried at 30 °C. Potassium persulfate (KPS), *N,N,N′,N′*-tetramethylenediamine (TEMED) and *N,N′*-methylenebisacrylamide (BIS) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene oxide (GO) solution was prepared according to the modified Hummers[42] method accompanying with dialysis purification and mild ultrasonication. Fe_3O_4 (nanoparticles, 10−50 nm, 25 wt% solution) was purchased from Aladdin Reagents, Inc. (Shanghai, China).

Hydrogel Preparation

Poly(*N*-isopropylacrylamide) (PNIPAM) and PNIPAM/GO hydrogels were prepared by *in situ* free radical polymerization. NIPAM (1.5 mol·L^{-1}), BIS (1.5 × 10^{-3} mol·L^{-1}), KPS (0.01 mol·L^{-1}), GO (0, 1, 3 and 5 mg·mL^{-1}), and in some cases Fe_3O_4 nanoparticles (0.5 wt%), were thoroughly dissolved in deionized water. After being deaerated by bubbling with high-purity nitrogen for 15 min in an ice-water bath, TEMED (0.01 mol·L^{-1}) was added into the solution. And then the solution was injected into molds made of a Teflon plate and a glass plate (as well as two Teflon or two glass plates) with a silicone-rubber spacer (1, 2 or 3 mm thickness). Finally, the molds were sealed and then kept at 20 °C for 48 h to ensure the completion of polymerization. In addition, to avoid the influence of residual air on the surfaces of the Teflon and glass plates, the molds were also vacuum evacuated and filled with high-purity nitrogen before their use.

Swelling/Deswelling and Thermosensitive/Photosensitive Deformable Behaviors of the Janus Hydrogels

The as-prepared hydrogels were equilibrium swollen in 20 °C deionized water for 48 h, or deswelled at 40 °C water-bath for 60 s. The swelling/deswelling behaviours of the hydrogels were measured from the change of swelling ratio (SR), defined as SR = $(m_s − m_d)/m_d$, where m_s and m_d are the weights of swollen and dried samples, respectively.

Thermosensitive deformation of the hydrogel strips soaked in a 40 °C water-bath was recorded with a digital camera. Their bending angles were measured according to our previous work[27]. On the other hand, the deformation of the PNIPAM/GO hydrogels could be driven by light in air. The light source was a halogen tungsten lamp (with a filter having cut off < 600 nm, 2.8 W·cm^{-2}).

Mechanical Tests

The as-prepared hydrogel samples were tested with an Instron 3366 electronic universal testing machine (Instron Corporation, Norwood, MA, USA). Uniaxial compression tests were performed on cylindrically samples with a thickness of 3 mm and a diameter of 20 mm at a crosshead speed of 1 mm·min^{-1}. The compressive stress (σ_c) was calculated by σ_c = load/(πr^2) (r, the original radius of the specimen). The strain (ε_c) under compression was defined as the change in the thickness relative to the original thickness. Stress-strain data between ε_c = 1%–5% were used to calculate initial tensile elastic modulus (E). Tensile tests were performed on dumbbell-shaped specimens, in accordance to DIN-53504 S3 (inner width: 2 mm; gauge length: 10 mm; thickness: 2 mm) at a cross-head speed of 400 (%)·min^{-1}. The tensile stress σ_t was calculated as follows: σ_t = load/(tw) (t and w were the initial thickness and width of the dumbbell-shaped hydrogel sample). The tensile strain ε_t was defined as the change in the grip separation relative to the gauge length. Stress-strain data between ε_t = 10%–35% were used to calculate initial tensile elastic modulus (E). A thin layer of silicon oil was coated on hydrogels to prevent the evaporation of water. And three specimens per experimental point were tested to ensure the reliability of the data.

RESULTS AND DISCUSSION

Preparation of Janus PNIPAM Hydrogel Matrix

To introduce structural inhomogeneity, molds made of a hydrophobic Teflon plate and a hydrophilic glass plate (T-G mold) were used to prepare the hydrogels used in this work, termed as T-G hydrogels. The two sides of the gels are termed as T side and G side according to the plates used. The equilibrium swollen hydrogel strip bends to the G side, showing a bending angle of −150°. When the gel strip is immersed in 40 °C water, the bending is reversed to the T side very quickly in only about 1 s, and the bending angle increases almost linearly to 460° in 6 s, then at a lower increasing rate to about 760° at 30 s (Fig. 1a). When the bended hydrogel strip is immersed in 20 °C water, it unbends and reverts to its original shape, though at a much lower rate.

For comparison, hydrogels were also prepared by using molds made of two Teflon plates (T-T mold) and two glass plates (G-G mold), termed as T-T hydrogels and G-G hydrogels, respectively. However, the T-T and G-G hydrogels do not show bending-unbending deformations when immersed in hot and cool water (Fig. S1 in supporting information, SI).

To understand the difference in the structure of the hydrogels, the swelling/deswelling behaviours of the hydrogels were firstly measured. From the deswelling curves of the hydrogels shown in Fig. 1(b), it was found that the T-T and G-G gels showed the fastest and the lowest deswelling rates, respectively, and the T-G gel showed an intermediate deswelling rate. Figure 1(c) shows that the equilibrium swelling ratios (ESR) of the hydrogels were in the order of T-T gel (32) > T-G gel (30) > G-G gel (29). In addition, the compressive elastic moduli of the T-T, T-G and G-G hydrogels were 4.2, 9.5 and 15 kPa (Fig. 1d), respectively. The difference in the swelling/deswelling behaviour and elastic modulus of the hydrogels suggests that the use of Teflon plate induced a lower cross-linking density in the hydrogels, which will be discussed in the next part. Therefore, the use of a T-G mold led to a higher cross-linking density in the hydrogel close to the G side and a lower cross-linking density close to the T side. The different cross-linking densities across the gel thickness caused the different swelling/deswelling behaviours of the two sides of the T-G hydrogels, leading to the bending/unbending deformations.
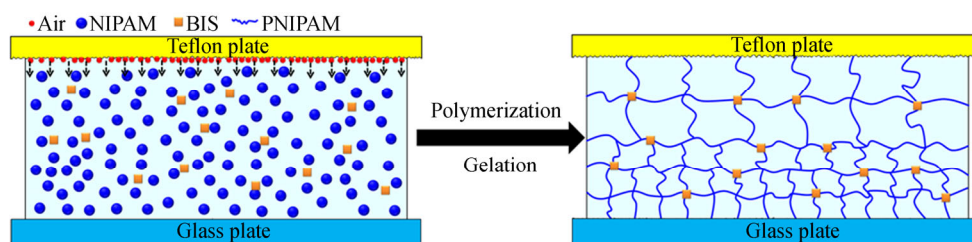
The presence of air bubbles on the Teflon plate surface is believed to be the main reason for the lower cross-linking of the hydrogel close to it[43, 44]. When the aqueous solution was filled into the mold, the aqueous monomer solution could not freely spread, and hence air bubbles were trapped between the Teflon plate surface and the solution due to the low surface tension of the hydrophobic Teflon plate and its rough surface. On the contrary, the hydrophilic and smooth glass plate surface was completely covered by the aqueous solution without air bubbles trapped. Although the solution in the mold had been deaerated by bubbling high-purity nitrogen, the air bubbles were not totally removed. As depicted in Scheme 1, during the polymerization and gelation process, the oxygen in the air bubbles on the Teflon plate surface gradually migrated into the solution and hence retarded or inhibited the polymerization, leading to the lower polymerization efficiency and hence cross-linking density in

the region close to the Teflon plate. Therefore, Janus PNIPAM hydrogels with a gradient or heterogeneous distribution of cross-linking density across the thickness were prepared.
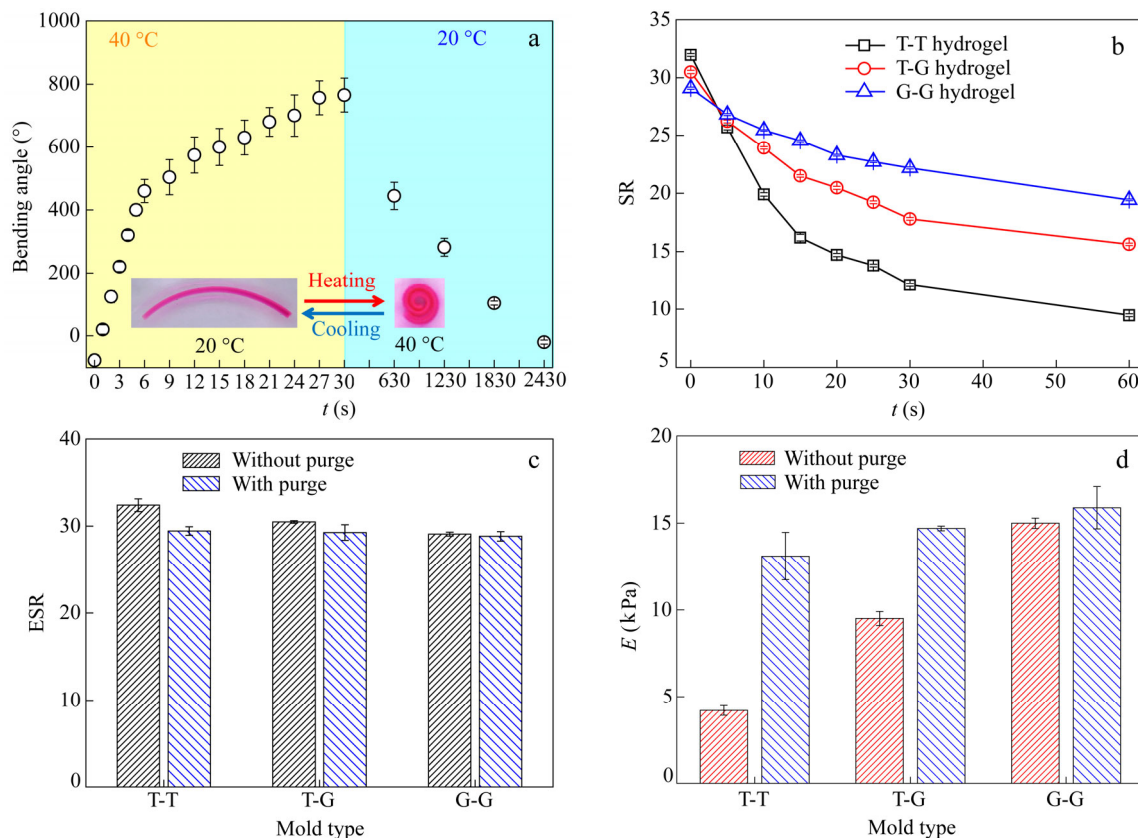
Fig. 1 (a) Bending-unbending behavior of the T-G strip in 40 and 20 °C water (The insets are the T-G hydrogel strip in the 20 and 40 °C water.); (b) Deswelling behaviours of the hydrogels in 40 °C water; (c) Equilibrium swelling ratios and (d) compressive elastic moduli of the hydrogels prepared with or without purge pre-treatment
All experiments were conducted in triplicate and the error bars represent standard deviations. The online version is colorful.


Scheme 1 The proposed formation mechanism and microstructure of the Janus PNIPAM hydrogels
(The online version is colorful.)

To verify the influence of the residual air bubbles on the Teflon and glass plates, the molds were purged by vacuum evacuation followed by exchanging with high-purity nitrogen before the addition of the solution. The ESR and elastic moduli of the hydrogels were also measured. As shown in Figs. 1(c) and 1(d), the hydrogels prepared this way showed lower ESRs and higher moduli than the hydrogels prepared without purge. The difference was significant in the case of T-T mold, while for the G-G mold the difference was very small. These results proved that the residual air on Teflon plate surface played a critical role in altering the cross-linking density across the thickness and hence the formation of deformable hydrogels.

Mechanical Properties of PNIPAM/GO Hydrogels

Although the Janus PNIPAM hydrogels exhibit bending deformation upon thermo-stimulus, their weak mechanical properties should restrict their practical applications. To enhance the mechanical properties of the hydrogels, graphene oxide (GO) nanosheets, as polyfunctional cross-linking centers by forming many H-bonds with PNIPAM chains, were added to increase the cross-linking densities and hence the elastic moduli (E) of the hydrogels[45–47]. And the easy breakage of H-bonding would provide the hydrogels with an effective energy-dissipating mechanism, leading to their higher tensile strengths (σ_b) and elongations (ε_b). Hydrogels were prepared at a fixed c_{NIPAM} (1.5 mol·L^{-1}) but varying GO concentration (c_{GO}) (0, 1, 3 and 5 mg·mL^{-1}) and their tensile mechanical properties were measured. Figure 2(a) shows the typical tensile stress-strain (σ_t-ε_t) curves of the PNIPAM/GO nanocomposite hydrogels; σ_b and E of the hydrogels are summarized in Fig. 2(b). The hydrogel without GO exhibits poor mechanical properties; its σ_b, E and ε_b were 17 kPa, 9 kPa and 445%, respectively. As expected, the addition of GO nanosheets significantly improved the mechanical properties of the hydrogels, as indicated by the enhanced σ_b, E and ε_b. E increased almost linearly with increasing c_{GO}, while σ_b and ε_b of the hydrogels increased with c_{GO} until 3 mg·mL^{-1}. The highest σ_b, E and ε_b of the PNIPAM/GO hydrogel obtained at c_{GO} = 3 mg·mL^{-1} were 184 kPa, 24 kPa and about 788%, respectively, much higher than those of the hydrogel without GO. The decreased σ_b and ε_b at c_{GO} of 5 mg·mL^{-1} was possibly due to the uneven distribution of GO nanosheets at this concentration. Hereafter, this study was conducted with the PNIPAM/GO hydrogels prepared with a c_{GO} of 3 mg·mL^{-1}.
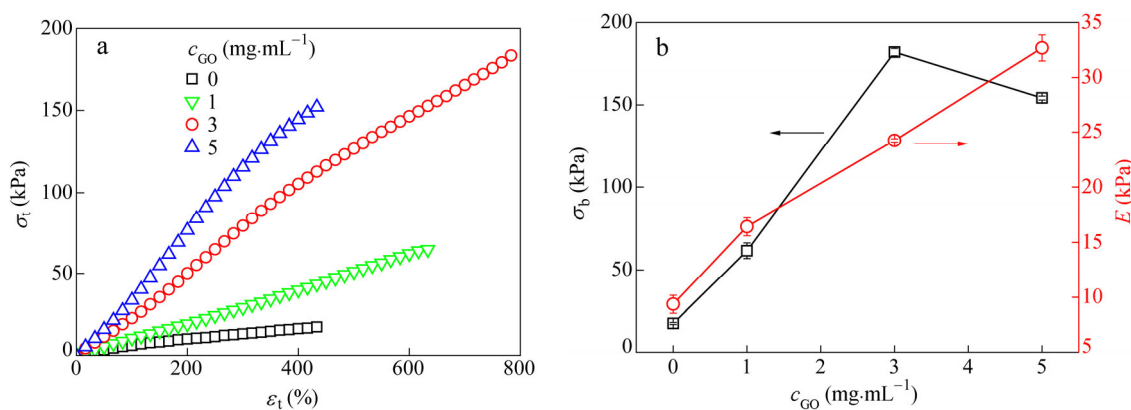

Fig. 2 (a) Typical tensile stress-strain curves and (b) tensile strengths and elastic moduli of the PNIPAM/GO hydrogels prepared with a fixed c_{NIPAM} (1.5 mol·L^{-1}) but varying c_{GO} (0, 1, 3 and 5 mg·mL^{-1})
All experiments were conducted in triplicate and the errors bars represent standard deviations. The online version is colorful.

Bending Deformation of Janus PNIPAM/GO Hydrogels

PNIPAM/GO hydrogels prepared in different molds without purge exhibited deswelling behaviours very similar to those of PNIPAM hydrogels (Fig. S2, in SI). Similar to the PNIPAM T-G hydrogels, the Janus PNIPAM/GO hydrogel prepared in the T-G mold also bended to the T side in 40 °C water and returned to its original state after being immersed in 20 °C water (Fig. 3a), indicating that it also had a heterogeneous distribution of cross-linking density across the thickness. Note that the bending degree of the PNIPAM/GO hydrogel was lower than that of the PNIPAM hydrogel, due to its higher cross-linking density.

Moreover, the bending deformation of the Janus PNIPAM/GO hydrogel can be remote-triggered by IR light, as the additive GO nanosheets can absorb IR light and transform it to thermal energy. In this work, the IR light-driven bending of the Janus PNIPAM/GO hydrogels was observed in air. Under the irradiation of IR light, the temperature of the gel sample increased gradually and the gel underwent volume phase transition when the temperature reached the LCST of PNIPAM. The higher volume shrink of the T side than that in the G side of the hydrogels would lead to the bending of the gel strip toward the T side. As demonstrated in Fig. 3(b), no matter which one of T and G surfaces was irradiated, the hydrogel strip bended toward the T side. However, a slower bending rate with a lower bending degree toward the T side was observed when the G surface was irradiated due

to the slow heat transfer rate of the hydrogels. The bended hydrogel strip returned to its original shape after being immersed in 20 °C water (Fig. S3, in SI).
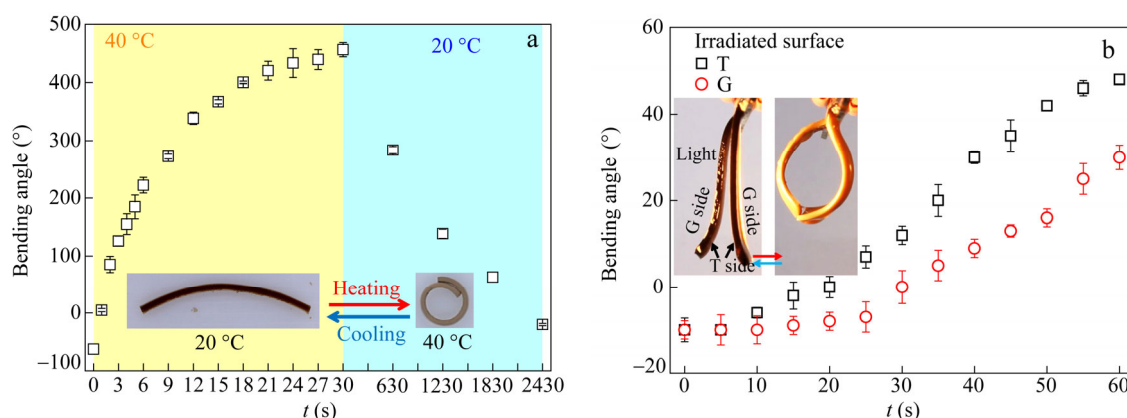
Fig. 3 (a) Bending/unbending behaviours of the Janus PNIPAM/GO hydrogel strips (length = 2.5 cm, width = 2 mm and thickness = 1.6 mm) in 40 and 20 °C water; (b) Bending behaviours of the Janus PNIPAM/GO hydrogel strips (length = 5 cm, width = 3 mm and thickness = 1.6 mm) actuated by IR light (The insets are original and bended states of the strips.) All experiments were conducted in triplicate and the errors bars represent standard deviations. The online version is colorful.

Application of Janus PNIPAM/GO Hydrogels

The mechanically strong Janus PNIPAM/GO hydrogels with outstanding thermal responsive bending/unbending behaviour can be used in manufacturing various soft robots. For example, a single PNIPAM/GO hydrogel strip can be used as a gripper to snatch up an object in 40 °C water, and then release it in 20 °C water (Fig. 4a). Moreover, the hydrogel gripper unbends in 20 °C water and snatches up another object in 40 °C water again (Fig. S4, in SI). The grabbing process can also be carried out in air under IR irradiation. When two hydrogel strips are assembled with their T surfaces facing each other, another type of gripper is obtained. Under IR
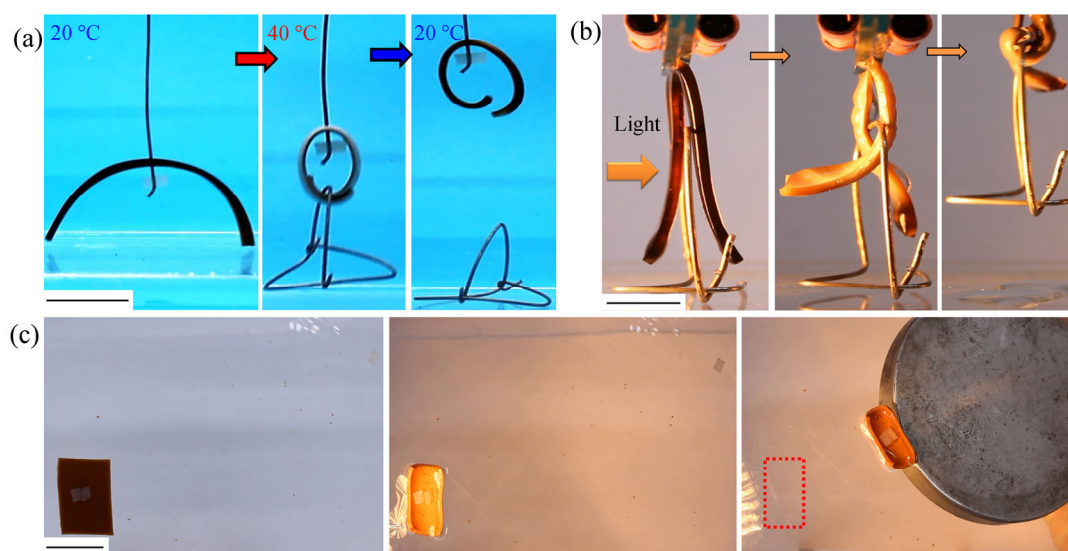
Fig. 4 (a) A hydrogel strip (length = 8 cm, width = 5 mm and thickness = 1.6 mm) in its original state, its bending and grabbing an object in 40 °C water, and its unbending and releasing of the object in 20 °C water; (b) Two hydrogel strips (length = 5 cm, width = 5 mm and thickness = 1.6 mm) assembled into a gripper, which bends under IR irradiation to grab, hold and transfer an object; (c) Deformation of a hydrogel sheet into a "boat" and the movement of the boat driven by a magnet (The red dotted frames indicate the initial position of the hydrogel sample. All scale bars are 1 cm. The online version is colorful.)

irradiation, the bending towards the T sides of the two strips can grab, hold and transfer the object (Fig. 4b).

In addition, magnetic Fe_3O_4 nanoparticles were also introduced into the PNIPAM/GO hydrogels. The magnetic hydrogels also show thermal responsive bending/unbending behaviour. A rectangular hydrogel sheet deforms into a "boat" under IR irradiation, and the boat loaded with two small objects moves under the attraction of a magnetic field. This demonstrates that these hydrogels would be an ideal candidate for carriers (Fig. 4c).

CONCLUSIONS

In summary, PNIPAM/GO nanocomposite hydrogels with structural inhomogeneity across the thickness that exhibit outstanding bending behaviours and good mechanical properties are prepared through a simple one-step method by using a mold made of a Teflon plate and a glass plate. The residual oxygen in the air bubbles on the Teflon plate surface affects the polymerization reaction and hence the cross-linking density, leading to the different swelling/deswelling rates of the two sides of the gels. Therefore, the hydrogels exhibit bending/unbending behaviors upon heating/cooling. Since the polymerizing processes in the molds made of two different hydrophilic/hydrophobic plates are inhomogeneous, many other inhomogeneous hydrogels can be obtained through this one-step method by properly selecting solvents and monomers. To enhance the mechanical properties of the Janus hydrogels, GO nanosheets are incorporated into the Janus hydrogels. Meanwhile, the photo-responsive property of GO nanosheets imparts the hydrogels with remote-controllable deformation under IR irradiation. The incorporation of other light-absorbing nanoparticles can also impart the hydrogels with remote-controllable deformation. We also demonstrated the applications of the Janus PNIPAM/GO hydrogels as soft robots, such as grippers and a "boat". And the introduced magnetic Fe_3O_4 nanoparticles allow the boat moving under the attraction of a magnet. We believe that the applications of the Janus hydrogels prepared by this one-step method can be explored further for applications such as micro-fluidics, soft machines and biomimetic devices.

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