Materials Research Express

PAPER

The role of graphene oxide in dramatically enhancing the mechanical and photoresponsive self-healing properties of poly(N, N-dimethylacrylamide) hybrid hydrogels

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Keywords: PDMA, graphene oxide, NIR photoresponse, mechanical properties, self-healing

Abstract
A fast self-healing hydrogel system with high strength and excellent response to the near infrared light (NIR) was proposed. The effect of graphene oxide (GO) on the mechanical and self-healing properties of poly(N,N-Dimethylacrylamide) (PDMA) hydrogels was studied. The results indicated that the self-healing efficiency of pure PDMA hydrogels was lower than that of PDMA-GO hydrogels. Especially, when the content of GO was more than or equal to 3 mg ml\(^{-1}\), the self-healing efficiency can reach to approximately 100\% after 2 h. It is due to that the increase in the content of GO could induce a rapid temperature rise of the hydrogel, which was benefit for improving the fast self-healing capacity. Most notably, PDMA-GO hydrogels still exhibited the excellent mechanical properties and the stable loading-unload behavior after the damage parts were healed. It can be contributed that GO forms hydrogen bonds with the three-dimensional network structure of the hydrogel matrix.

Introduction
Self-healing soft materials have some fascinating capability like the living creatures by activating regeneration process to healing itself from physical damage to certain extent [1]. The striking property of these self-healing materials can increase reliability of the device and prolong the lifetime of the material components [2]. Therefore, the self-healing materials have many potential applications in the tissue engineering [3], wound healing [4], soft actuators [5], biomedical devices [6] and so on. The self-healing hydrogels as a fascinating soft material have aroused researchers’ wide concern. In recent years, great research focus on the development of self-healing hydrogels with the capability of the response to the external stimulus, such as pH [7], light [8], electricity [9], and pressure [10]. The self-healing action of hydrogels is primarily achieved by reversible interactions between functional groups on the polymer backbone and/or polymer chains in the hydrogels. Interactions for healing include hydrogen bonding [11], supramolecular assembly [12], host-guest inclusion [13], dynamic covalent bonding [14], freeze-thaw cycles [15], and metal-ligand coordination [16]. The PDMA hybrid hydrogels have been greatly attractive to the application of the self-healing hydrogels. PDMA is a very useful hydrophilic biocompatible polymer with associative properties [17]. The PDMA hydrogels have a good self-healing property due to the continuous movement of the polymer segment inside it, under the wet condition, the hydrophobic segment is recombined, and the hydrogel destroyed network structure is healed. However, PDMA hydrogels generally exhibit rather low mechanical strength due to the lack of an efficient energy dissipation mechanism in the chemically crosslinked PDMA network [18]. Haraguchi [19] demonstrated self-healing behavior of hybrid PDMA hydrogels prepared using Laponite clay nanoparticles. The hydrogels
sustain up to about 1500% strain and the damage created in the gels could be healed at 50 °C within 10 h. The mechanical properties of PDMA hydrogels were improved, but the self-healing time was longer.

In fact, the self-healing hydrogels have several obstacles to the application, e.g. available mechanical properties, recovery degree and the speed of response and healing. Many recent efforts to improve these properties of hydrogels are proceed, for examples, nanosize carbon materials of carbon nanotube, graphene and GO have been used as the response to the versatile stimulus-responsibility [20]. GO as a two-dimensional nanomaterial is prepared from natural graphite. GO possesses exceptional optical, electrical and mechanical properties due to the fact that the GO sheets possess many functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl groups, which are capable of forming hydrogen bonds with polymer chains. Especially, some studies [21] have found that GO possess an extraordinary capability of photo-thermal energy transformation due to its high absorbance to the NIR and superior conversion to heat. The GO sheets in the hydrogel as the NIR absorbent can induce the fast temperature increase of the hydrogel. In addition, GO can also improve the strength of hydrogel and produce robust hydrogels. Therefore, with the view of the above merits, the light-controlled functional hydrogels with excellent mechanical properties can be prepared through the addition of GO as a NIR absorbing agent. Chen [22] et al reported a hybrid supramolecular hydrogel (HSH) displaying rapid self-healing, tunable bioadhesive, and stimuli-responsive properties. GO has been reported as an effective building block to enhance the mechanical and stimuli-responsive properties of nanocomposite hydrogels. Wang [23] et al synthesized a high tensile strength (0.35MPa) GO-containing self-healing hydrogel by using GO as the polyfunctional initiating and cross-linking center. Lee [24] et al demonstrated a hydrogel actuator made of reduced GO(rGO)-elastin that exhibits rapid motion that can be adjusted by near-infrared laser position.

In the present paper, a PDMA-GO hybrid hydrogel with fast self-healing, high strength and excellent response to NIR is proposed. We systematically report the effect of GO content on tensile strength, healing time and the recovery degree of the PDMA hybrid hydrogels using the method of hanging weight, infrared image device and load-unload capability.

**Experimental**

**Preparation of PDMA-GO composite hydrogels**

GO was synthesized by the Hummers Method [25]. A certain amount of GO nanosheets as additives was dispersed in the deionized water (25 ml) and GO was evenly dispersed in water with a high-speed shear (10,000 r min⁻¹, 3 min) and ultrasonic treatment. Sodium chloride (NaCl, 0.5M) and ammonium dodecyl sulfate (ADS, 7% w/v) were dissolved in the aqueous solution of GO at 35 °C to obtain a transparent solution. Then, hydrophobic monomer octadecyl methacrylate (SMA, 0.85 mmol) was dissolved in the solution under stirring for 2 h at 35 °C. After addition and dissolving N,N-dimethylacrylamide (DMAA, 0.15V/V) for 1 h, N,N,N',N'-tetramethylenelethlyenediamine (TEMED, 0.0025 V/V) was added into the solution. Finally, 3 mM of potassium persulfate (KPS) was added to initiate the reaction. The solution was transferred into glass tubes of 13 mm internal diameters and the polymerization was conducted for 16 h at 50 °C. The obtained hydrogel was expressed as PDMA-GOₓ, in which X represented the concentration of GO as Xmg ml⁻¹. The reaction mechanism of PDMA-based hydrogels is shown in figure 1. As shown in figure 1(a), micellar hydrogels including NaCl are prepared by copolymerization of hydrophobic monomer SMA with hydrophilic monomer DMAAm in micellar solution formed by dodecyl ammonium sulfate. Figures 1(b) and (c) show the principle diagrams of pure PDMA hydrogels and PDMA-GO composite hydrogels, respectively. PDMA-based hydrogels are crosslinked by hydrophobic interaction in the micelles of ADS. GO nanosheets are connected with the three-dimensional reticular matrix of the hydrogels in the form of hydrogen bonds.

**FTIR characterization of hydrogel**

The hydrogel samples were washed and swollen by an excess of deionized water for over 5 days. To prepare freeze-dried samples, the swollen hydrogels in deionized water were rapidly frozen in liquid nitrogen for 5 min and then freeze-dried by a freeze drier (FD-1C-50, Beijing BoYiKang) at −48 °C for 72 h. The FTIR spectra was recorded from 400 to 4000 cm⁻¹ at room temperature (Thermo Fisher Scientific, Nicolet iS 10).

**Swelling behavior tests**

The hydrogel samples were cut into discs with thickness of 5 mm and diameter of 13 mm, and then washed and swollen by an excess of deionized water for over 5 days. The hydrogel discs were dried completely at 50 °C and the weight was recorded as m₀. Finally, the hydrogel was swollen sufficiently in a deionized-water bath at 20 °C and the weight was recorded as m₁. The equilibrium swelling ratios were defined as (m₁-m₀)/m₀.
Mechanical properties tests
The mechanical properties of the as-prepared hydrogels were measured by hanging the load in the room-temperature condition and the relative humidity is about 70%. The water content of the hydrogel is about 80%. The hydrogel samples were cut into cylinders with 13 mm in diameter and 50 mm in length. Then, the hydrogel samples were folded and hanged weights of 0 g, 10 g, 20 g, 50 g, 100 g, 200 g and 500 g. The length of the hydrogel after loading was measured and the changes of the hydrogel were recorded in real time by camera. The load was increased slowly until the hydrogel broke, which was the maximum load of the hydrogel and defined as M. At least three specimens were measured to obtain statistical data for each test.

The hydrogel samples were cut into cylinders with 13 mm in diameter and 30 mm in length. The hydrogel samples were pulled to 30 cm, and then restored for 2 min. The length of the restored hydrogel was measured. Each hydrogel sample was repeated five times, and the changes of the hydrogel were recorded with a camera in real time.

Self-healing property tests
The hydrogel samples were cut into discs with thickness of 5 mm and diameter of 13 mm, which were cut off two parts from the middle with a blade. The cut samples were healed through two ways. One was self-healed for 2 h at room temperature 25 °C, and the other was self-healed for 2 h under NIR (808 nm, 2 W) with spacing of 10 cm. The changes of incision were observed by stereoscopic microscope, and the temperature change of the hydrogel was recorded by infrared thermal imager. The original hydrogel discs, the hydrogel discs after self-healing for 2 h at room temperature and the hydrogel discs after self-healing for 2 h under NIR were hanged the load separately, and the load was slowly increased until the hydrogel broke. The maximum loads were recorded.
Results and discussion

Figure 2 shows the FTIR spectra of hydrogels with different content GO. Figures 2(b)–(f) displayed that the position of the characteristic peaks in the infrared spectra of hydrogels did not change significantly with the addition of GO. It is contributed that GO network and PDMA network in self-healing hydrogels are intertwined by hydrogen bonding between the PDMA chains and the oxygen-containing functional groups of GO nanosheets. The wider absorption peak at 3090–3660 cm\(^{-1}\) is corresponded to the vibration of –OH. The peaks at 2930 and 2850 cm\(^{-1}\) were related to the anti-symmetric and symmetric stretching vibration of –CH\(_2\)– respectively. The characteristic peak at 1620 cm\(^{-1}\) is the absorption peak of C=O stretching vibration. The absorption peaks at 1500 cm\(^{-1}\) are assigned as the bending vibration of –C–H in –CH\(_2\) and –CH\(_3\). The characteristic peak at 1250 cm\(^{-1}\) belongs to the tensile vibration of –C–N–. Moreover, PDMA-GO\(_x\) hydrogel exhibits a peak of C=O at 1627 cm\(^{-1}\) indicating the presence of GO in the composites. Furthermore, the PDMA-GO\(_x\) hydrogels exhibit a stronger peak at 3069–3697 cm\(^{-1}\) than pure PDMA hydrogel, indicating the existence of van der Waals forces and hydrogen bonding interactions between hydrogel and GO sheets [26]. It is related to the graphene oxide dispersed and interacted in polymer matrix. On the one hand, GO reduction is probably present in PDMA-GO\(_x\) preparation process. As-prepared GO nanosheets as additives were dispersed in the deionized water by the high energy shear and ultrasonic treatment, respectively. The high-speed and long-
time shear and ultrasonic treatments play a key role in GO reduction during the whole processing. Studies were reported on direct synthesis of aqueous graphene sheets from graphite using ultrasonic exfoliation method \[27-29\]. The high-energy shear and sonication generated the most stable homogeneous aqueous RGO dispersion. Moreover, the morphology of graphene sheets is also altered due to the intense ultrasonic cavitation energy. On the other hand, the probability of GO reduced to some extent depends mostly on the interaction between GO basal functionalities and monomeric segments inside the gel matrix. Especially, the abundant oxygen-containing functional groups \(\text{–COOH and –OH}\) of GO nanosheets react with PDMA chains by the interchain hydrogen bonding during the \textit{in situ} polymerization process.

The swelling properties of PDMA-based hydrogels are shown in figure 3. PDMA hydrogels doped with different content of GO after drying and swelling equilibrium displayed that the volume and transparency of the hydrogel have changed dramatically (see figure 3(a)). The equilibrium swelling ratio of the PDMA-based hydrogels is indicated in figure 3(b). The equilibrium swelling ratio of the pure PDMA hydrogels is 51, while the addition of a small amount of GO \(1 \text{ mg ml}^{-1}\) causes the reduction of the equilibrium swelling ratio of the hydrogel \(\sim 43\). The high equilibrium swelling ratio of the pure PDMA hydrogels demonstrated that a certain amount of hydrophobic segments are present in the three-dimensional network structure. On the contrary, the hydrogen bond is combined between the slight GO nanosheets and the three-dimensional network structure with the addition of GO, which make the expansion of the molecular chain difficulty, and then have a certain hindrance to the swelling of the hydrogel. Surprisingly, as the content of GO increases from \(1 \text{ mg ml}^{-1}\) to \(7 \text{ mg ml}^{-1}\), the equilibrium swelling ratio of hydrogel is gradually increased. It can be explained that the presence of amount of GO nanosheets increases hydrophilicity of hydrogels, which caused the equilibrium swelling ratio gradually increases.

As as reported by Gibas et al \[30\], the equilibrium swelling of hydrogels is directly affected by the flow and equilibrium expansion of the internal water molecules, including that primary bound water affected by hydrophilic groups, so-called hydrophobically bound water or secondary bound water interact with hydrophobic groups and the absorbed free water driven by the covalent or physical crosslinking, which fills the space between the network chains and the centres of larger pores, macropores or voids. The total amount of water absorbed by a hydrogel depends on the temperature and the specific interaction between water molecules and polymer chains, which can be explained by the Flory-Huggins solution theory \[31\]. Thus, it can be seen that the equilibrium swelling of hydrogels is related to hydrophilic-hydrophobic groups and the covalent or
physical crosslinking. The addition of GO improved the crosslinking and have a certain hindrance to the swelling of the hydrogel, but it can induce amount of the absorbed free water into the network structure by the osmotic driving force of the network towards infinite dilution [30]. In addition, the hydrophilicity of GO nanosheets increases the adsorption of the primary bound water. Here the PDMA hydrogel network filled with different GO improves the strength of the hydrogel network, and while maintains a rubber-like elasticity on the hydrogels [26]. As mentioned in the literature, graphene nanosheets as the nanobuilding blocks can withstand external stress and exhibit reversible ductility. Therefore, the PDMA hydrogel network filled with different amounts of GO not only improves the strength of the hydrogel network, but also affect the adsorption and swelling of the water molecules on the hydrogel chains and increase the equilibrium swelling ratio of hydrogel gradually.

To evaluate the mechanical properties of the GO modified hydrogels, the load-elongation properties of PDMA-based hydrogels were performed in figures 4 and 5. Figures 4(a)–(e) show the optical images of the load test of hydrogels doped with different content of GO nanosheets (1 mg ml$^{-1}$ 7 mg ml$^{-1}$) at the weights of 10 g, 20 g, 50 g, 100 g, 200 g, and 500 g, respectively. The measurement results are shown in figure 5. The mass of the load of the pure PDMA hydrogels exhibits little changes when the load is less than 50 g, while as the load increases, the length of the hydrogel has a linear increase from 3.7 cm at 50 g to 31.7 cm at 500 g. With the doping of GO nanosheets, the stretch trend of hydrogels is similar. When the concentration of GO was 1 mg ml$^{-1}$, the load elongation of the hydrogel changed significantly. Compared with the pure hydrogel, the length at the load of 20 g has no any change, while the load increases to 500 g, the length of the PDMA-GO1 hydrogels reduces to 27.5 cm, indicated in figure 5. It is contributed that there are substantial portions of polymer chains physically adsorbed to the GO platelets by forming hydrogen bonds with the amide groups at the PDMA chains, because there are plentiful hydroxyl, carbonyl and epoxy groups on the GO surface containing 80% water content in hydrogels. These hydrogen bonds form the cross-linking points to build the three dimensional network in the hybrid hydrogels [32]. The hydrogen bonds limit the molecular-chain stretch [33]. With the increase of GO content from 1 to 7 mg ml$^{-1}$, the length of the hydrogel at the load of 500 g gradually lengthens due to that the
increase of GO content will hinder the copolymerization of SMA and DMAAm to a certain extent and the relative reduction of chemical-bond content will be beneficial for the hydrogel stretch.

The maximum loading capabilities of the GO modified PDMA hydrogels were carried out in figure 6. The pure PDMA hydrogel has a maximum load mass of 1190 g. The addition of GO nanosheets significantly improve the strength of the PDMA hydrogels. The maximum loading mass of the PDMA-GO1 hydrogels is 1440 g, which is 21% higher than that of the pure PDMA hydrogels. As the GO content increases, the loading strength of the PDMA hydrogel also evidently increases. When the concentration of GO reaches 5 mg ml\(^{-1}\), the maximum loading mass (1520 g) has an increase of 27.7% compared to the PDMA hydrogels. More unexpected is when the concentration of GO is 7 mg ml\(^{-1}\), the loading strength of hydrogel displays a slight decrease and the maximum load mass drops to 1490 g. It can be explained that the presence of a large number of GO nanosheets reduce chemical bond content generated by the copolymerization of SMA with DMAAm so that the loading strength of the PDMA hydrogel has a slight drop [34].

The tensile-recovery performance were analyzed in order to study the cycle mechanical properties of the GO modified PDMA hydrogels in figure 7. Figure 7(a) indicated that the hydrogel cylinder with a length of 3 cm is stretched to 30 cm and then naturally recovered to 4 cm after 2 min. After repeated stretching for 5 times, the recovery length averages 4.2 cm. Compared with the pure PDMA hydrogels, the tensile-recovery properties of the doping with GO hydrogel have been significantly improved. After the first stretch of PDMA-GO1 hydrogels to 30 cm, the natural recovery reaches 3.5 cm after 2 min shortened by 12.5%. After repeated stretching for 5 times, the recovery length averages 3.7 cm, and the results are shown in figure 7(b). As the GO content increases,
the recovery length becomes shorter, e.g. the PDMA-GO3 hydrogel is 3.3 cm and the PDMA-GO5 hydrogel is 3.2 cm. After repeated stretching for 5 times, the recovery length of the PDMA-GO1 hydrogel is 3.4 cm on average and the recovery length of the PDMA-GO5 hydrogel is 3.3 cm on average (see figures 7(c)–(d)). With the further increase of GO content, the recovery length of PDMA-GO7 hydrogel becomes 3.5 cm, which is 5.7% longer than that of PDMA-GO5 hydrogel after repeated stretching for 5 times. The recovery length is 3.6 cm on average, shown in figure 7(e). After doping an appropriate amount of GO, GO forms a strong hydrogen bond with the three-dimensional network structure of the PDMA hydrogel matrix, which can effectively prevent the stretching of the hydrogel molecular chain and can be quickly recovered after being stretched [33]. However, excessive GO will affect the copolymerization of SMA and DMAAm to a certain extent, which can lead to the reduction of molecular segments, thus it is unbene

Figure 7. The loading-unloading test of hydrogels, (a) PDMA, (b) PDMA-GO1, (c) PDMA-GO3, (d) PDMA-GO5, (e) PDMA-GO7, (f) contrast diagram.

The increase in graphene content can cause the additional crosslinking point generation by the graphene sheets, and thus with graphene content the toughness value was also increased. According to the above analysis, the addition of GO can not only strengthen the three-dimensional...
network structure of the PDMA hydrogel matrix, but also maintain the corresponding toughness. Meanwhile, it is found that after the first or multiple stretch, the natural-recovery length of the hydrogel doped with GO was shorter than that of the undoped hydrogel, and the recovery of the hydrogel in PDMA-GOx was the shortest, which was close to the original length of 3 cm. Meanwhile, the hydrogels retain little change with increasing GO content after the multiple loading-unloading stretch, showing the remarkable rapid self-recoverability of the PDMA-GOx hydrogel. The results reveal the similar with the research [26]. GO also acts as stress dissipation in the PDMA-GOx hydrogel. The available dissipated energy can destruct the hydrogen bonding in the first stretch, but then the energy of the hydrogel was no change after the multiple stretch, indicating that the hydrogel had significant fatigue resistance. This finding indicated that GO can not only effectively prevent the stretching of the hydrogel molecular chain, but also can be quickly recovered after being stretched.

The self-healing performance of the PDMA-based hydrogels is compared under the condition of room temperature and the near-infrared irradiation. Figure 8 shows the optical image of the self-healing performance for the PDMA-based hydrogels. The self-healing micrographs of pure PDMA hydrogels at different times under NIR are shown in figures 8(a–3)–(a–7). After 2 h of near-infrared irradiation, the gap in the hydrogel has an obvious healing sign due to that the increase of the surface temperature of the hydrogels induced by the near-infrared light accelerates the self-healing efficiency. Compared with the PDMA hydrogels, the self-healing efficiency of PDMA-GOx hydrogels is obviously improved as the concentration of GO increase (figures 8(b) to (e)). After 2 h of near-infrared irradiation, the gap in the PDMA-GOx hydrogels has more obvious healing sign than the pure PDMA hydrogels due to that the temperature of the hydrogel is significantly increased in the near-infrared light with the doping with graphene oxide. GO is one of the sp2 carbon materials and has good photothermal stability. When the photothermal conversion effect occurs, the material can absorb the light energy (especially near-infrared light) and then convert into electron or hole resonance kinetic energy or electronic transition to generate energy through surface localized plasmon resonance (LSPR). The phenomenon increases the ambient temperature by transmitting the vibration energy of the lattice scattering to the surrounding environment [36]. Thereby, the increase in temperature significantly accelerates the self-healing rate of the hydrogel.

The self-healing efficiencies of the PDMA-based hydrogels were studied through the measurement of the self-healing loading properties. Figures 9(a)–(e) show the self-healing loading properties of the hydrogel at 25 °C and the near-infrared irradiation for 2 h. The maximum loading value of the original PDMA hydrogel disc is 430 g. The maximum load of the self-healing hydrogel at 25 °C for 2 h is 100 g, while the near-infrared irradiation can obviously improve the maximum load, approximately 280 g. The self-healing process is shown in the figure 10(a). Meanwhile, the self-healing results of PDMA-GOx hydrogels can be obtained. The original PDMA-GOx hydrogel disc has a maximum load of 470 g and the self-healed hydrogel has a maximum load of 110 g at 25 °C for 2 h due to the recombination of the hydrophobic segments in the internal hydrogel and the strong physical bond between the GO and the molecular chain [32]. The self-healing process is shown in the
Figure 9. The maximum load of the original hydrogel wafer, the wafer self-healed at 25 °C for 2 h and the wafer self-healed for 2 h under NIR. The load of hydrogels, (a) PDMA, (b) PDMA-GO1, (c) PDMA-GO3, (d) PDMA-GO5, (e) PDMA-GO7, (f) The self-healing efficiency of hydrogels. The error bar represents the standard deviation of the sample. The error bars stand for the standard deviation of the samples.

Figure 10. Schematic diagram of self-healing of hydrogels (a) PDMA, (b) PDMA-GOx.
figure 10(b). When the gel is cut, the network is destroyed. The polymer chains move across the interface of the cut gel to the opposite side by mutual diffusion when contacted. Then, new hydrogen bonds are formed between the polymer chains and clay and GO platelets within the thin layer of two cut surfaces [37]. The maximum load of the self-healed PDMA-GO$_1$ hydrogel after the near-infrared irradiation for 2 h (350 g) was 218.2% higher than that at 25 °C. Similarly, the original PDMA-GO$_3$ hydrogel disc have a higher maximum load (500 g) than the pure PDMA hydrogel (430 g). Compared with PDMA and PDMA-GO$_1$ hydrogels, the maximum load of the self-healed hydrogels (130 g) increased by 30% and 18.2%, respectively. Especially, the maximum load under the near-infrared irradiation can have the same the loading capabilities as the original hydrogels. The self-healing performance induced by the near-infrared irradiation can be significantly improved by 276.9%, compared to the self-healing properties at 25 °C. As the GO content further increase, the maximum loads of self-healed PDMA-GO$_3$ and PDMA-GO$_7$ hydrogels at 25 °C for 2 h are 130 g and 140 g, respectively. Meanwhile, the maximum loads of the self-healed hydrogels under the near-infrared irradiation for 2 h reach 500 g and 530 g, respectively. The increase in GO content in the PDMA-GO$_3$ and PDMA-GO$_7$ hydrogels do not significantly improve the self-healing properties of the hydrogel compared to the PDMA-GO$_3$ hydrogel.

Figure 9(f) indicated the self-healing efficiency of pure PDMA-based hydrogels at 25 °C and near-infrared irradiation for 2 h. The self-healing efficiency of pure PDMA hydrogel at 25 °C and under the near-infrared irradiation for 2 h is 23.3% and 65.1%, respectively. The temperature of the hydrogels increased by a dozen Celsius degrees due to the near-infrared irradiation, which is benefit for the movement of the polymer segment. Under the wet condition, the hydrophobic segment is recombined and the destroyed network structure of the hydrogel can be healed to a certain extent [32]. After doping with 1 mg ml$^{-1}$ of GO, the healing efficiency of the hydrogel at 25 °C for 2 h was almost unchanged (23.4%), while the self-healing efficiency under the near-infrared irradiation can reach 74.5%, significantly improving the self-healing efficiency of the pure PDMA hydrogels. It can be contributed that graphene oxide, as a sp$^2$ carbon material, exhibits a excellent photothermal stability, which converts the near-infrared energy into heat energy and causes the rise in the temperature of the hydrogel (about 40 °C) to accelerate the self-healing behavior. Moreover, the recombination of the hydrophobic segments in the hydrogel occurs and a strong physical bond between the GO and the molecular chain is reformed. When the doping concentration of GO is 3 mg ml$^{-1}$, the hydrogel has a healing efficiency of 26% at 25 °C for 2 h, which is 2.6% higher than that of pure PDMA and PDMA-GO$_1$ hydrogels. The number of hydrogen bonds increases between GO and the molecular chain. The self-healing efficiency of PDMA-GO$_3$ hydrogel under the near-infrared irradiation is 98%, which is close to the performance of the original hydrogel. Compared with the pure PDMA and PDMA-GO$_3$ hydrogels, the self-healing efficiency is significantly improved. With the further increase in GO content, the self-healing efficiencies of PDMA-GO$_3$ and PDMA-GO$_7$ hydrogels at 25 °C for 2 h have no any change. The self-healing efficiencies of PDMA-GO$_5$ and PDMA-GO$_7$ hydrogels under the near-infrared irradiation were 98.1% and 100%, respectively, similar to that of PDMA-GO$_3$ hydrogels. It means that further increasing GO content higher than 3 mg ml$^{-1}$ does not enhance the energy-transformation efficiency efficiently [38].

Conclusions

In summary, a novel photoresponsive hydrogel with rapid self-healing responsivity and stable load-unload capability was successfully prepared through cross-linked PDMA-based hydrogels using the copolymerization between the hydrophilic monomer DMAAm and the hydrophobic monomer SMA in the ADS micelle solution. The hydrogel exhibited excellent photo-responsive behavior and mechanical properties after the self-healing under the irradiation of NIR, which can reach to approximately 100% at the time of 2 h. Moreover, the self-healing hydrogels could undergo reduplicative load-unload process without any damage. Interestingly, the addition of GO improve the photo-thermal transformation effect of PDMA hydrogel. Based on our studies, the low-cost, high loading capability, and rapidly photo-responsive hydrogel would be widely utilized in artificial intelligence system, wearable device, flexible visual display and optical storage device.

Acknowledgments

Hongyan Wu and Ke Huang contributed equally. This project is supported by the Six Talent Peaks Project of Jiangsu Province, China (No. GDZB-046), Natural Science Foundation–Outstanding Youth Foundation of Jiangsu Province of China (No.BK20160091) and Student Innovation Training Program of Jiangsu Province (No. 202110300075Y).
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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