Fast Self-Healing of Graphene Oxide-Hectorite Clay-Poly(*N,N*-dimethylacrylamide) Hybrid Hydrogels Realized by Near-Infrared Irradiation

Enzhong Zhang, Tao Wang, Lei Zhao, Weixiang Sun, Xinxing Liu, and Zhen Tong*

Research Institute of Materials Science and State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

S *Supporting Information*

ABSTRACT: Self-healing hydrogels were proposed to be used as biomaterials, because of the capability of spontaneously healing injury, but most of the reported self-healing hydrogels do not possess high mechanical strength and fast self-healing at the same time. Herein, we prepared graphene oxide (GO)-hectorite clay-poly(*N,N*-dimethylacrylamide) (PDMAA) hybrid hydrogels with enhanced mechanical properties and fast self-healing capability realized by near-infrared (NIR) irradiation. The physical cross-linking between clay sheets and PDMAA chains provided the hydrogel with mechanical strength to maintain its stability in shape and architecture. GO sheets in the hybrid hydrogels acted as not only a collaborative cross-linking agent but also as a NIR absorber to absorb the NIR irradiation energy and transform it to thermal energy rapidly and efficiently, resulting in a rapid temperature increase of the GO containing gels. The chain mutual diffusion and the reformation of physical cross-linking occurred more quickly at higher temperature; consequently, the damaged hydrogel was almost completely recovered in a few minutes upon irradiation. We also demonstrated a potential application of the hybrid hydrogel as a self-healing surgical dressing.

KEYWORDS: *self-healing, hybrid hydrogel, graphene oxide, near-infrared, PDMAA*
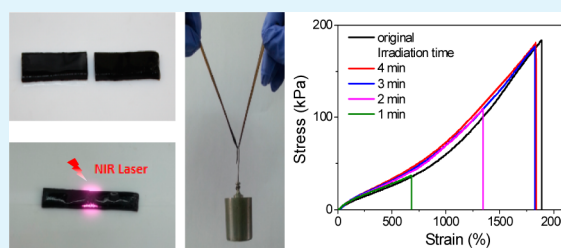
1. INTRODUCTION

Self-healing materials possess an important capability of repairing themselves from damage.[1-4] This is a striking property that can increase reliability of the device made from these self-healing materials and prolong the lifetime of the material components.[5,6] Most living creatures have this fascinating capability in the nature by activating a regeneration process to recover destroyed functions to a certain extent.[7,8] This striking feature has inspired researchers to design self-healable synthetic materials. Recently, great progress has been achieved in development of self-healing hydrogels capable of response to the external stimulus, such as pH,[9-11] light,[12] electricity,[13] and redox potential.[14,15] The self-healing of hydrogels is mostly realized by reversible interactions between polymer backbones and/or functional groups on the polymer chains in the hydrogels. The interaction used for healing includes supramolecular assembly,[16-18] host-guest inclusion,[10,15,19] freezing-thawing process,[20] dynamic covalent bonding,[21] hydrogen bonding,[22,23] and ionic bonding of polymer chains with Ca^{2+} ions.[24]

There are still several challenges in application of the self-healing hydrogels: First, only a few self-healing hydrogels have showed actually available mechanical properties up to now. Haraguchi et al. reported the hectorite clay-poly(*N,N*-dimethylacrylamide) (PDMAA) nanocomposite (NC) gels with high self-healing efficiency, high tensile strength (up to

0.13 MPa), and high elongation (900-1200%).[25] Zhao et al. found the self-repairing capability from the poly(vinyl alcohol) (PVA) hydrogel prepared by the freezing-thawing process with the highest tensile strength of ~0.20 MPa.[20] Wang et al. prepared a self-healing composite hydrogel containing graphene oxide (GO) with tensile strength up to 0.35 MPa and elongation up to 4900%.[26] Second, most reported self-healing hydrogels do not meet the demands of fast repairing and high recovery degree. The self-healing NC hydrogel, PVA hydrogel, and GO-containing hydrogel mentioned above required a long time for the healing (up to 24 h). Okay et al. fabricated the hydrogel via hydrophobic interaction with fast self-healing (within several seconds) and high recovery degree (up to 100%), but the self-healing needed external force and the tensile strength was lower than 25 kPa.[27] Varghese et al. reported the acryloyl-6-aminocaproic acid (A6ACA) hydrogel with rapid self-healing ability (within several seconds) based on the optimal balance of hydrophobic and hydrophilic interactions, but its tensile strength was lower than 50 kPa.[28]

Recently, nanosize carbon materials of carbon nanotube, graphene, and GO become most attractive for their versatile stimulus-responsibility, possibly available in many areas, such as

electronic devices,[29,30] biomedical apparatus,[31,32] and energy storage materials.[33,34] The near-infrared (NIR) irradiation has been suggested as a noninvasive, harmless, and highly efficient skin-penetrating biomedical technique.[35,36] GO is a two-dimensional nanomaterial prepared from natural graphite. There are many functional groups at the GO sheets, such as hydroxyl, epoxy, carbonyl, and carboxyl groups, which are capable of forming hydrogen bonds with polymer chains. Therefore, GO is efficient to enhance the mechanical property of hydrogels. Wang et al. synthesized a high tensile strength (0.35 MPa) GO-containing self-healing hydrogel by using GO as the polyfunctional initiating and cross-linking center.[26]

In the previous study, we obtained the GO-poly(N-isopropylacrylamide) (PNIPAm) NC gels with high strength, high extensibility, and excellent reversible thermosensitivity.[37] The GO-PNIPAm hydrogel without hectorite clay became very weak with the storage modulus about 1 order of magnitude lower than that containing only 1 wt % clay, because the clay acted as a cross-linking agent to increase mechanical strength in the NC gels.[37] GO was also found to possess an extraordinary capability of photothermal energy transformation due to its high absorbance to the NIR light and superior conversion to heat.[38,39] Consequently, GO was utilized not only in producing robust hydrogels but also in preparing light-controlled functional hydrogels as a NIR absorbing agent. Lo et al. used a glycidyl methacrylate functionalized GO (GO-GMA) in PNIPAm hydrogel to build a microvalve switched by external IR irradiation.[40] Lee et al. demonstrated a hydrogel actuator made of reduced GO (rGO)-elastin exhibiting a rapid motion tunable by the NIR laser position.[41] Li et al. reported the NIR laser-triggered self-healing hydrogel of rGO-PDMAA with much low strength and long healing time about 2 h.[42]

PDMAA has been used in self-healing hydrogels already.[25,42] The GO sheets in the hydrogel act as the NIR absorbent to induce a fast temperature increase of the hydrogel.[39] Here, we attempt to fabricate a fast self-healable and highly stretchable hydrogels using hectorite clay as the cross-linking agent and GO as the energy-transformation agent. Our GO-clay-PDMAA hybrid hydrogels prepared with strength of 184 kPa and elongation at break of 1890% can be self-healed rapidly and efficiently up to 96.0% strength recovery by simply irradiated with NIR for no longer than 3 min. In the present paper, we report the effect of healing time, GO content, and clay content on the recovery degree of the hybrid hydrogels. We also demonstrate the potential application of the hydrogel as a self-healable surgical dressing.

2. EXPERIMENTAL SECTION

2.1. Materials. Monomer N,N-dimethylacrylamide (DMAA, stabilized with 500 ppm MEHQ) was purchased from J & K Technology Co. Ltd. Synthetic hectorite clay of gel-forming grade LAPONITE XLG [$Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4$] with 30 nm diameter and 1 nm thickness, a layered silicate of low heavy metal content, was kindly provided by Rockwood Ltd. and used after being dried at 125 °C for 4 h. Raw graphite was purchased from Alfa Aesar (325 mesh, 99.8%). Initiator potassium peroxydisulfate (KPS) was recrystallized from deionized water and dried in vacuum at room temperature. Catalyst N,N,N′,N′-tetramethylethylenediamine (TEMED, Sinopharm Group Chemical Reagent Co. Ltd.) was used as received. All other chemicals were analytical grade reagents and purified by the standard method prior to use. Pure water was obtained by deionization and filtration using a Millipore purification apparatus (resistivity >18.2 MΩ·cm).

2.2. Preparation of Graphene Oxide. Graphite oxide (GO) was prepared according to the modified Hummers method,[43] similar to that used in our previous work.[37] For example, 2 g of graphite powder and 1 g of $NaNO_3$ were added to 46 mL of cold (~0 °C) concentrated H_2SO_4 in a 250 mL flask. The mixture was stirred in an ice water bath for 30 min, and then 6 g of $KMnO_4$ was slowly added under vigorous stirring. The reaction was kept at a temperature lower than 20 °C for 2 h. Then, the ice water bath was removed, and the reaction mixture was maintained at 35 °C for 0.5 h. Afterward, 30 mL of deionized water was gradually added into the mixture, and the reaction flask was transferred into a 98 °C water bath for 15 min. Finally, 20 mL of 30% H_2O_2 was added to the mixture. For purification, the mixture was washed with 5% of HCl and deionized water several times. The GO was dried at 60 °C in vacuum for 24 h.

2.3. Synthesis of GO-Clay-PDMAA Hybrid Hydrogels. The GO-clay-PDMAA hybrid hydrogel was synthesized by in situ free radical polymerization of monomer DMAA in the clay suspension containing GO. First, the desired amount of GO was dispersed in 10 mL of water by ultrasonic radiation for about 1 h, and then the required amount of clay was added into the GO suspension, which was stirred for 30 min and ultrasonically dispersed for about 1 h. The suspension with specified GO and clay concentration was obtained. Then, 1.05 mL of monomer DMAA was added into the suspension, which was degassed and nitrogen-saturated under continuous and vigorous stirring in an ice water bath for another 2 h. Finally, 0.5 mL of KPS solution of 20 mg/mL and 10 μL of catalyst TEMED were added under stirring. The mole ratio of DMAA monomer to initiator to catalyst in all suspensions was kept at 100:0.370:0.638, and the DMAA content was fixed at 1.0 mol/L. The suspension was rapidly injected into a laboratory made mold of 60 mm × 60 mm × 1 mm, which consisted of two glass substrates with a rubber spacer of 1 mm thickness, and the mold was put into an oven filled with N_2. The polymerization was conducted at 20 °C for 24 h to produce the GO-clay-PDMAA hybrid hydrogel.

In this paper, the GO-clay-PDMAA hybrid hydrogels were designated as GOmD1Cn, where m and n stood for the concentration of GO (mg/mL) and clay (wt %), respectively, and D1 for the DMAA concentration of 1.0 mol/L. For the clay-PDMAA hybrid hydrogel without GO, the GO0 was omitted. For example, the GO2D1C2 gel consisted of 2 mg/mL of GO, 1.0 mol/L of DMAA, and 2 wt % of clay. The gel samples were cut into different shapes for test.

2.4. Characterization. The healing of damaged GO hybrid hydrogels (blade cut) was carried out by keeping the cut surfaces in contact and irradiated with a NIR laser (808 nm, 1.6 w) for different times (1−4 min) in atmosphere. The energy density delivered to the sample was 2.54 Wcm^{-2}.

Tensile strength was measured with a Shimadzu autograph AG-Xplus 50N system at ambient temperature on the as-prepared and self-healed GO hybrid hydrogels of 6 mm width and 1 mm thickness. The sample length between the jaws was 30 mm, and the crosshead speed was 100 mm/min. The tensile strain was taken as the length change related to the original length, and the tensile stress was evaluated on the cross section of the original sample.

Dynamic mechanical property was detected with a strain controlled rheometer ARES-RFS using parallel plates of diameter of 25 mm. Silicone oil was laid on the edge of the fixture to prevent water evaporation. The frequency sweep was performed over the angular frequency ω range of 0.01−100 rad/s at strain amplitude $γ_0$ of 0.5% within the linear viscoelasticity regime determined previously by the dynamic strain sweep at 5 rad/s. Dynamic temperature sweep was performed from 10 to 80 °C with heating rate of 5 °C/min at $γ_0$ = 0.5% and ω = 6.28 rad/s.

The photothermal transformation efficiency was measured by irradiating NIR laser to the GOmD1C2.5 gels at the energy density of 2.54 Wcm^{-2}. Thickness of the GOmD1C2.5 gels was 1 mm, the irradiation area was 1.6 cm^2, and exposure time was 180 s. The temperature was recorded every 10 s using a thermocouple.
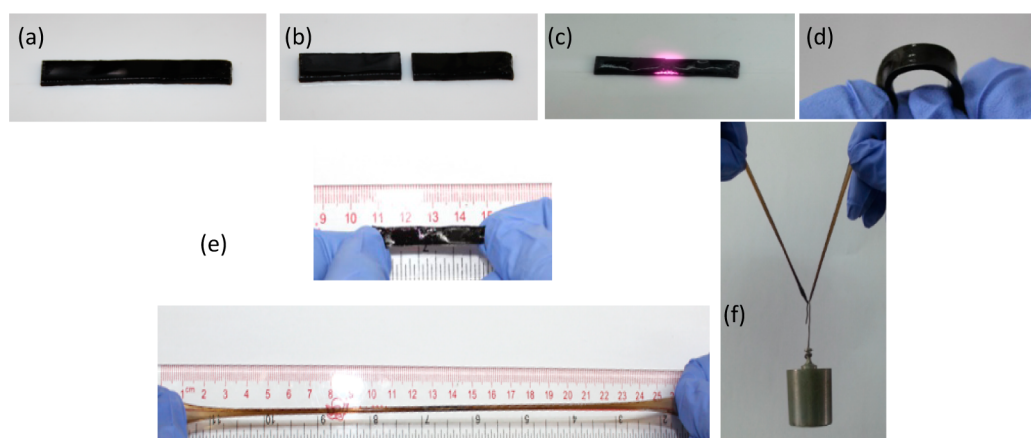
Figure 1. Photographs of the GO2D1C2.5 hybrid hydrogel: (a) original; (b) after cutting; (c) contacted and irradiated with a NIR laser; (d) after irradiation for 1 min; (e) stretch of healed gel to ∼650%; (f) loaded with 200 g after irradiation for 3 min.

3. RESULTS AND DISCUSSION

3.1. Fast Self-Healing. All hydrogel samples were shaped into 5 mm width and 1 mm thickness for the self-healing test. Photos in Figure 1 illustrate a GO hybrid hydrogel cut and self-healed. The damaged gel is self-healed very fast by keeping the cut surfaces in contact and irradiated with a NIR laser under ambient condition (Figure 1a−c). The GO hybrid hydrogel containing 2.5 wt % of clay is chosen in the self-healing test because the clay is easy to aggregate when mixed with GO if its concentration is higher than 2.5 wt %. On the other hand, the GOmD1Cn hybrid hydrogels with lower clay content are too weak to be stretched. The GO2D1C2.5 gel healed for 1 min can be bent 180° or even more and can withstand a large deformation for a long time (Figure 1d). After healing, no obvious vestige of the damage is left at the junction. The self-healed hydrogel is able to be stretched up to ∼650% of its original length (Figure 1e). Moreover, the GO2D1C2.5 gel healed for 3 min can withstand an external bending load of 200 g (Figure 1f). The self-healed gel breaks still at the junction position under excessive stretch, and the ratio of elongation for the irradiated part to the unirradiated part is about 4:5.

Interestingly, this fast self-healing performance has been also found from the samples containing different GO contents and even from the connection of hybrid hydrogels with and without GO. For example, GO2D1C2.5 and D1C2.5 gels are combined together by joining two cut surfaces and irradiating with a NIR laser beam. The combined GO2D1C2.5-D1C2.5 sample is depicted in Figure 2(a−d), which can also withstand a large deformation for a long time. The combined hybrid hydrogel can be stretched up to ∼1800% of its original length, and the external bending load is higher than 100 g. Figures 2e and 2f demonstrate the combined gel of three blocks of GO2D1C2.5, GO1D1C2.5, and D1C2.5 under stretch.

In order to explore this self-healing behavior systematically, first we studied the healing time t dependence of the hybrid hydrogels. The recovery degree is defined as the tensile strength ratio of the healed gel to the original one. Figure 3a presents the stress−strain curves for the GO2D1C2.5 gel after self-healing for different times. The tensile strength increases with increasing healing time, and about 60% of the original strength is recovered after 2 min irradiation. After 3 min, the recovery degree of the GO2D1C2.5 gel achieves 96%, signifying almost full recovery. Further extending healing time to 4 min does not lead to a significant increase in the strength
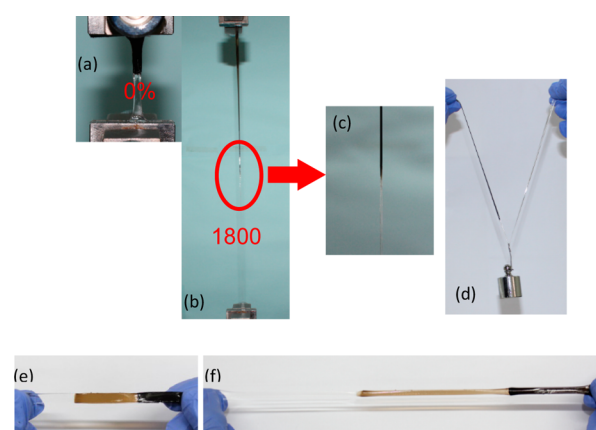

Figure 2. Photos of connected hybrid hydrogels of GO2D1C2.5 (black) and D1C2.5 (transparent): (a, b, c) damaged and combined hybrid hydrogels stretched up to 1800%; (d) loaded with 100 g; (e, f) healing and stretching of combined D1C2.5, GO1D1C2.5, and GO2D1C2.5 gels (left to right).

of the healed gel. To our knowledge, the healing efficiency of ∼96% within such a short time is a remarkable result for an intrinsic self-healing hydrogel material.

By carefully looking in Figure 3a, a little increase in the modulus is found for the healed gels. The water loss from the gel during healing is possibly attributed to this because there is a weight loss of 5.1% from the GO2D1C2.5 gel after 4 min irradiation (Figure S1 in the Supporting Information). The stress−strain curve of the GO2D1C2.5 gel tested immediately after self-healing by 3 min irradiation almost overlaps that of 1 h after irradiation (Figure S2), indicating that this amount of water loss influences the recovery degree slightly.

Next, we varied the GO content in the hybrid hydrogels, which significantly changed their mechanical and self-healing properties. The tensile stress−strain curves of the GOmD1C2.5 hybrid hydrogels are plotted in Figure 4a. For the original samples, the strength obviously increases and the elongation at break decreases with increasing GO content due to the increase in the cross-linking density caused by GO in the hydrogels.[37] For example, the strength and final elongation for GO2D1C2.5 is 184 kPa and 1890%, but they become 36 kPa and 2120% for D1C2.5. This implies that the strong hydrogen bonding between the GO sheets and PDMAA chains acts as the physical cross-linking for the hybrid hydrogels.
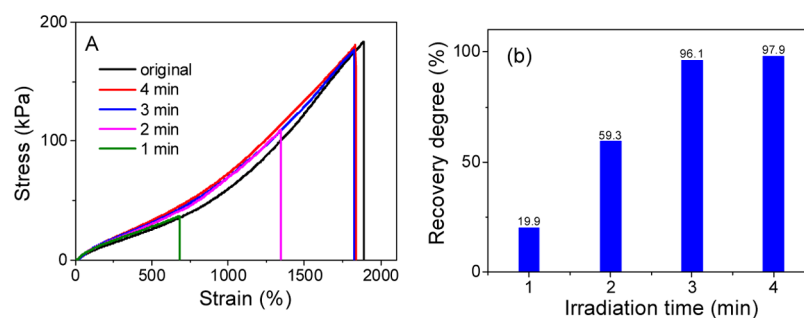
Figure 3. Tensile property of the GO2D1C2.5 gel: (a) stress−strain curves of the original and self-healed gels after irradiation for the indicated times; (b) recovery degree of tensile strength varying with irradiation time for the self-healed gels.
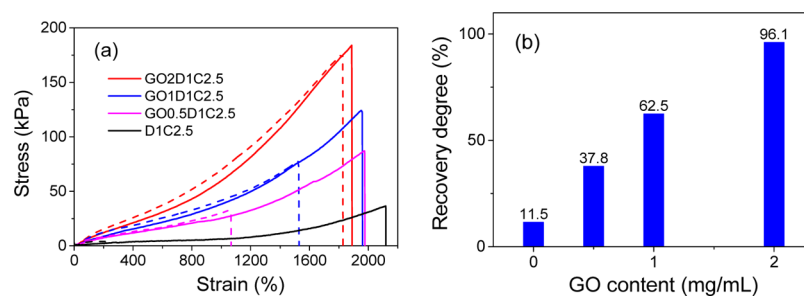

Figure 4. Tensile property of the GOmD1C2.5 gels: (a) stress−strain curves of the original samples (solid lines) and the self-healed ones after irradiation for 3 min (dashed lines); (b) recovery degree of the self-healed samples after irradiation for 3 min.
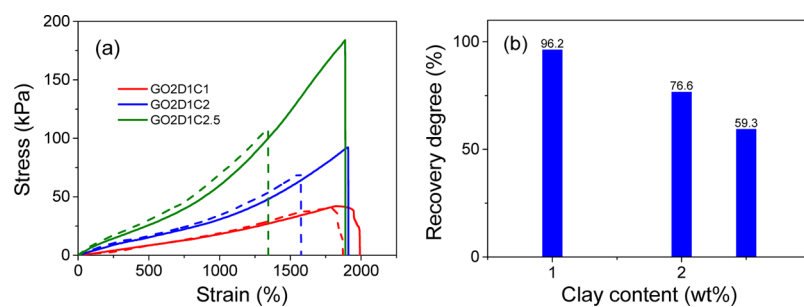

Figure 5. Tensile property of the GO2D1Cn gels: (a) stress−strain curves of the original gels (solid lines) and self-healed gels after irradiation for 2 min (dashed lines); (b) recovery degree after irradiation for 2 min varied with clay content.

The recovery degree of the self-healed GOmD1C2.5 gels after irradiation for 3 min (Figure 4b) increases obviously with increasing the GO content. For example, the recovery degree is 11.5% for the D1C2.5 gel, 62.5% for the GO1D1C2.5 gel, and 96.1% for the GO2D1C2.5 gel, respectively. Besides, the hybrid hydrogel with lower GO content requires more time to recover. In contrast, the hybrid hydrogel with higher GO content exhibits a faster and better self-healing performance. This behavior is induced by the high efficiency of the photothermal energy transformation of the GO in the hybrid hydrogel, which results in higher temperature of the GOmD1C2.5 gels with higher GO content (discussed in Section 3.2). Further increasing GO content higher than 2 mg/mL does not enhance the energy transformation efficiency efficiently[39] and causes difficulty in preparation of uniform GO and clay suspension.

Finally, we assessed the effect of the hectorite clay content on the self-healing efficiency of the hybrid hydrogels. As displayed in Figure 5, the gel containing less clay exhibits a higher recovery degree with lower strength. The recovery degree and strength of the GO2D1C1 gel containing 1.0 wt % of clay healed for 2 min are 96% and 42 kPa, respectively. In contrast, for the GO2D1C2.5 gel containing 2.5 wt % of clay healed for 2

min, the recovery degree and strength become 59.3% and 109 kPa, respectively. The self-healing capability of the hybrid hydrogel drastically decreases with increasing clay content. When the clay content is lower than 1 wt %, the strength of the hydrogel just healed for 2 min is comparable to that of the original one. The hybrid hydrogel GO2D1 without clay behaves as a viscous paste, lack of mechanical strength due to its low cross-linking density, though the healing efficiency is about 99%. The above results suggest that the mobility of the polymer chains would be essentially important for the self-healing and that the physical cross-linking formed by the clay platelets suppresses this mobility and in turn declines the self-healing efficiency. Thus, the elongation at break is higher for the gel containing 1.0 wt % of clay than that containing 2.5 wt % of clay. An optimal clay and GO content should enhance the mechanical strength and maintain a reasonable self-healing efficiency synergistically. The tensile stress-stain curves of the GO2D1C1 and GO2D1C2 gels containing 1.0 and 2.0 wt % of clay, respectively, are summarized in Figure S3 for comparison of different irradiation times. The recovery degree increases for longer irradiation time, similar to that in Figure 3 for the

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GO2D1C2.5 gel with 2.5 wt % clay, but the strength is lower due to lower clay content.

The clay-PDMAA gel has been reported as a physically cross-linked hydrogel with good mechanical properties due to the strong interaction between the polymer chains and the clay platelets.[44,45] For the GOmD1C2.5 hydrogels, the clay and GO platelets act as the collaborative cross-linking agents. There are substantial portions of polymer chains physically adsorbed to the GO platelets by forming hydrogen bonds with the amide groups at the PDMAA chains, because there are plentiful hydroxyl, carbonyl, and epoxy groups on the GO surface. These hydrogen bonds form the cross-linking points to build the three-dimensional network in the hybrid hydrogels.

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.[46] As the number of the hydrogen bonds grows up to a certain extent, the network is rebuilt across the damaged fracture, and the tensile strength is recovered. Similar to the reported GO-poly-(acrylamide) gels,[26] the self-healing of the GO and clay hybrid hydrogels arises from the reformation of the physically cross-linked network at the interface. The chain mutual diffusion is the key step for the self-healing of the gel, which is affected by temperature, healing time, GO content, and clay content. With increasing healing time, the polymer chains diffuse deeper across the interface, and hence stronger bonding is formed to cause a higher recovery degree as seen in Figure 3b. High clay content in the gel increases the cross-linking density and thus suppresses the chain mobility. Finally, the recovery degree decreases with increasing clay content as shown in Figure 5b.

3.2. Accelerated Temperature Increase. The chain diffusion is accelerated by heating; therefore, the strength recovery by self-healing is enhanced by increasing temperature. Increasing GO content in the gel increases the heating rate and thus improves the recovery degree as shown in Figure 4b. Direct evidence of the higher GO content causes higher temperature is manifested in Figure 6. The temperature of the
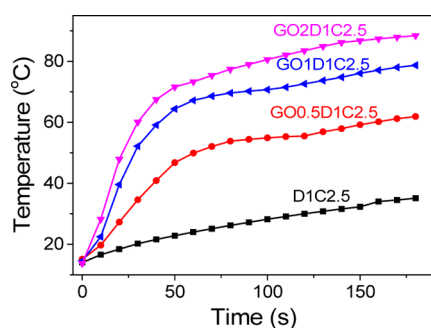

Figure 6. Temperature of the GOmD1C2.5 gels varying with NIR irradiation time.

GOmD1C2.5 gels is increased by the NIR laser irradiation as a function of irradiation time. The GO containing gels exhibit a fast temperature rise than that without GO, demonstrating high efficiency of the photothermal energy transformation by GO. The higher the GO content, the faster the temperature increases. For example, the temperature of the GO2D1C2.5 gel is increased from 14 to 80 °C within 100 s. The heating rate is higher at the beginning and then declines possibly due to the

fast heat dissipation at higher temperature. To maintain the healing temperature below 50 °C, the self-healing behavior of the GO0.5D1C2.5 gel is observed and presented in Figure S4, where the recovery degree is only 0.19% for 2 min irradiation. For the other gels with more GO, the temperature surpasses 50 °C too fast to be monitored.

The hybrid hydrogels are considered to be self-healed at high temperature even without NIR laser irradiation because it is heating that enables the polymer chains to diffuse mutually across the cut interface. For example, a column of the GO2D1C2.5 gel is reshaped into a disc after compression at 80 °C for only 5 s (Figure 7a, b). Furthermore, the chopped
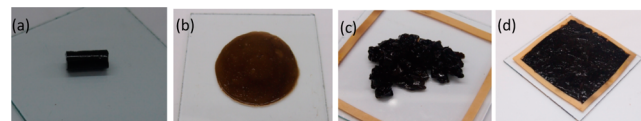

Figure 7. A column of the GO2D1C2.5 gel (a) is reshaped into a disc after compression at 80 °C for 5 s (b); the chopped GO2D1C2.5 debris (c) is connected through molding compression at 80 °C for 2 min (d).

GO2D1C2.5 gel debris is connected into a square sheet by molding compression at 80 °C for 2 min (Figure 7c, d). This phenomenon confirms that the mutual diffusion of the polymer chains across the interface can be promoted by heating, which causes the cross-linking by hydrogen bonds and heals the broken network. In contrast, the traditional chemically cross-linked hydrogels, without reversible linkages, cannot form new cross-linking junctions after polymerization, so that they are not healable by heating.[25] When the cut surface layer is precoated with a layer of water, the self-healing capability of the hybrid hydrogels almost vanishes. This water layer forms a block to the polymer chain diffusion.

In order to detect the change in the cross-linking density induced by heating, the frequency sweep of the GO2D1C2.5 gel was performed at several temperatures (Figure 8a). Storage modulus G' is always higher than loss modulus G'', and both moduli show a weak dependence of the angular frequency ω within the tested frequency range, suggesting the existence of network in the hydrogel to support its solid-like behavior. On the other hand, G' of the GOmD1C2.5 gels decreases obviously with increasing temperature (Figure 8b). It is interesting that the hybrid hydrogel containing more GO behaves more obvious decrease in the storage modulus G'. When heated from 10 to 80 °C (the same range as that induced by the NIR irradiation, Figure 6), G' of the GO2D1C2.5 gel decreases to 48.6%, while that of the D1C2.5 hydrogel without GO only decreases to 68.6%. GO in the hybrid hydrogels plays the role of an additional cross-linking agent to join the PDMAA chains, resulting in an increase in G'.[37] The present results indicate that the cross-linking formed by the GO becomes weaker at higher temperature in favor of the polymer chain diffusion to heal the damaged fracture. Thus, the GO in the present gels has two roles: photothermal energy transformation and reversible cross-linking sensitive to heating.

These GO hybrid hydrogels can withstand and recover from substantial damage with good biocompatibility.[42,47,48] To demonstrate the possible application of the hydrogel as a self-healing surgical dressing, a sponge is covered with the GO2D1C2.5 gel (Figure 9a). After irradiated with NIR laser for 30 s (Figure 9b), a syringe needle is penetrated into the
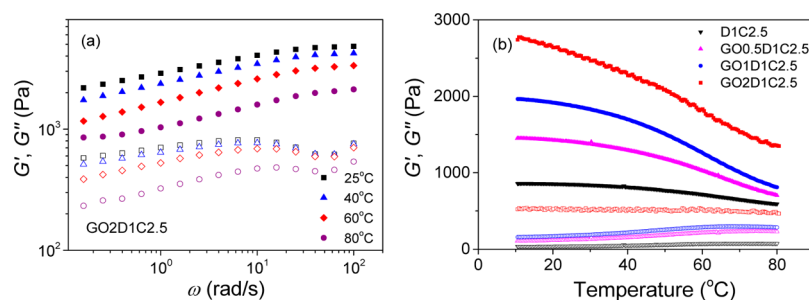
Figure 8. (a) Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of angular frequency ω for the GO2D1C2.5 gel at indicated temperatures; (b) temperature sweep of the GOmD1C2.5 gels at $\omega = 6.28$ rad/s.
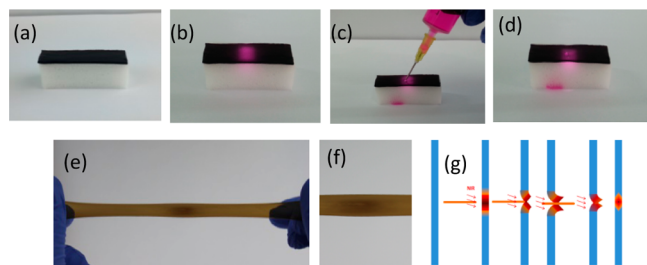

Figure 9. (a) A sponge covered with the GO2D1C2.5 gel; (b) irradiated with NIR laser for 30 s; (c) injection of a pink liquid into the sponge; (d) the punched hydrogel irradiated for 90 s; (e) the punched hydrogel after healing under stretch; (f) enlarged photo of the punched hydrogel after healing under stretch; (g) schematic illustration for the healable surgical dressing.

hydrogel to inject pink liquid into the sponge (Figure 9c). The punched hydrogel is irradiated for another 90 s after removing the needle (Figure 9d). After this treatment, the damaged hole is completely healed without a trace (Figure 9e), even in the enlarged photo under stretch (Figure 9f). Figure 9g illustrates the whole self-healing process for the hybrid hydrogel used as a healable surgical dressing.

4. CONCLUSIONS

In summary, we have prepared fast self-healable GO-clay-PDMAA hybrid hydrogels with high extensibility and mechanical strength contributed by both hectorite clay and GO as cross-linking agents. The fast self-healing is obviously realized by the NIR laser irradiation for only 2−3 min up to the strength recovery of ~96%. The GO platelets in the hybrid hydrogels absorb the NIR irradiation energy and transform it to thermal energy to promote the mutual diffusion of the polymer chains across the cut interface. At the same time, the GO platelets form the thermally breakable linkages with polymer chains, which is favorable for the chain movement at high temperature. Therefore, increasing the GO content enhances the self-healing efficiency of the hybrid hydrogels. On the other hand, increasing the clay content declines the self-healing efficiency because the clay suppresses the chain movement by enhanced cross-linking. A potential application of the hybrid hydrogels is demonstrated as a self-healable surgical dressing, which is capable of repairing itself from physical damage. This self-healing hybrid hydrogel may find applications in smart dressing, coating, soft actuator, and biomedical devices.

■ ASSOCIATED CONTENT

S **Supporting Information**

The water loss of the GO2D1C2.5 gel and the stress−strain curves of the GO0.5D1C2.5, GO2D1C2.5, GO2D1C1, and GO2D1C2 gels are included. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 86-20-87110273. E-mail: mcztong@scut.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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