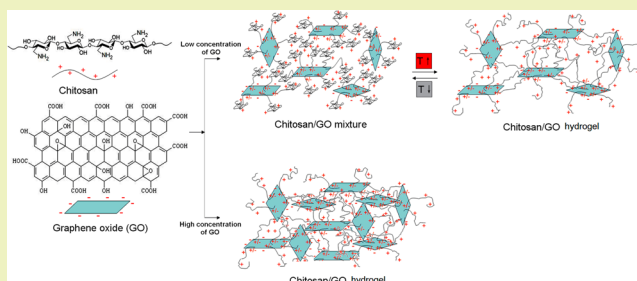


Supramolecular Hydrogel of Chitosan in the Presence of Graphene Oxide Nanosheets as 2D Cross-Linkers

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ABSTRACT: Biomass-based materials are attractive due to their renewability, biodegradability, and biocompatibility. Chitosan is a typical biomacromolecule that can be used as feedstock for novel materials. Here, the self-assembly of chitosan chains with graphene oxide (GO) nanosheets has been studied, where GO works as the two-dimensional cross-linker due to its multifunctional groups on both sides. Supramolecular hydrogels of chitosan and GO have been prepared by controlling the concentration of GO, ratio of chitosan to GO, and temperature. It was found that at high GO concentration, hydrogel can be obtained at room temperature, and the as-prepared hydrogel showed a self-healing performance. However, at low GO concentration, the supramolecular hydrogel formed only at high temperature (95 °C). The driving force for the hydrogel is believed to be the noncovalent interactions. The reversible hydrogels have potential applications in fields of biomaterials, wastewater treatment, and smart materials.

KEYWORDS: Chitosan, Hydrogel, Graphene oxide (GO), Cross-linker, Supramolecular



■ INTRODUCTION

Polymeric gels are typical fascinating and versatile soft materials with wide potential applications,¹ which can be prepared using covalent or noncovalent cross-linking. Hydrogels that are capable of autonomous healing upon damage have also been paid much attention because of their potential applications.^{2,3} Generally, covalently cross-linked gels lack the ability to self-heal. More recently, self-healed gels have been prepared through reconstruction of the 3D network of gels by reversible cross-linking.^{4,5} Dynamic covalent and adaptive chemistry have been developed for the preparation of reversible gels.^{6,7} An alternative route to prepare reversible gels relies on noncovalent interactions, which are the driving force for the formation of a supramolecular network.⁸ However, the supramolecular gels based on noncovalent interactions are typically fragile. Aida et al. recently synthesized a new hydrogel that possesses remarkable mechanical strength with self-healing properties using a well-defined branched molecule, which is a dumbbell-shaped dendrimer with multiple guanidinium groups capable of forming multiple noncovalent interactions with clay.⁹ The study also revealed that it causes no gelation when a linear polymer with two guanidinium end groups was utilized, indicating that multiple interactions between polymeric chains and cross-linkers are key factors for supramolecular hydrogel formation.

Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to its novel electronic and mechanical properties.¹⁰ Graphene is usually

prepared by the reduction of its precursor graphene oxide (GO),^{11,12} and GO is a typical pseudo-two-dimensional oxygen-containing solid in bulk form that possesses multiple functional groups, including hydroxyls, epoxides, and carboxyls,^{13,14} which has been used as fillers for the next generation of nanocomposite materials.^{15–18} However, there are few studies on the preparation of a supramolecular hydrogel using GO as a 2D cross-linker. Recently, Xu et al. prepared a hydrogel of GO and DNA through 3D self-assembly.¹⁹ Shi et al. prepared a pH-sensitive GO composite hydrogel using poly(vinyl alcohol) as a cross-linker,²⁰ and Han et al. prepared a supramolecular hydrogel using reduced GO with a nonionic Pluronic copolymer (poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)), PEO-*b*-PPO-*b*-PEO) under the assistance of α -cyclodextrin.²¹

Chitosan (CS), a linear natural polysaccharide, is made up of glucosamine and N-acetylglucosamine units linked by a β (1–4) glycosidic bond, capable of forming hydrogels that have potential applications in biomaterials by cross-linking or blending.^{22,23} However, there is still a challenge to prepare a chitosan hydrogel using a simple method.^{24,25} Chitosan is a polymer with multiple amino groups, which can be protonized in an acid aqueous solution and has the potential to form composites with negatively charged molecules or materials,

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such as GO nanosheets. Recently, GO nanosheets were reported as being used as reinforced material to blend with chitosan for nanocomposite preparation.^{26,27}

Here, the supramolecular hydrogels of chitosan and GO have been prepared by noncovalent interactions. The effects of the concentration and ratio of them on the gelation are discussed, and the self-healing properties of the as-prepared materials are also studied.

EXPERIMENTAL SECTION

Materials. Chitosan was obtained from Sinopharm Chemical Reagent Co. Ltd. in China (degree of deacetylation: 90%, $M_w = 8000$ – 20000) as a matrix material. Graphite powder, natural briquetting grade, 99.9995% (metals basis) was purchased from Alfa Aesar. The other reagents (HAc, NaOH, NaNO₃, and KMnO₄) of analytical grade, 98% H₂SO₄, and 30% H₂O₂ were purchased from Sinopharm Chemical Reagent Co. Ltd. in China and were used as received without further purification. Ultrapure water with resistivity of 18 M Ω cm was produced by a Milli-Q (Millipore, U.S.A.) and was used for solution preparation.

Preparation of GO and Supramolecular Hydrogel of Chitosan and GO. GO was prepared from natural graphite by the well-known Hummers method with some modification,^{10,27,28} and the characteristic of the as-prepared GO in a single layer can be found in our previous studies.^{11,12} Highly oxidized GO, especially synthesized from natural graphite, can be easily dispersed in water. On the basis of this, a desired amount of GO powder (0.1–0.3 g) was dispersed into 100 mL of ultrapure water and was treated by mild ultrasound for 15 min in a 250 mL beaker, forming a homogeneous suspension. The size of the GO nanosheet is about several micrometers with a wide polydispersity as reported previously.¹² A total of 1.0–3.0 mL of acetic acid (HAc) and 1.5–8.0 g of chitosan were added into the GO suspension sequentially under stirring. Then the mixture was settled down at room temperature or treated by heating at 95 °C to see whether hydrogel formed or not.

Characterization. Dynamic rheological analysis was performed to obtain information on interactions among HAc, CS, and GO. Tests of the rheological properties of the samples at different temperatures were carried out with a rheometer (Haake Mars II). The maximum resulting strain of all samples was less than 0.01. Fourier transform infrared (FT-IR) spectra of the samples were recorded by a Bruker vector-2 spectrophotometer (Germany), and the gels were freeze-dried and triturated for the FT-IR measurement using the KBr method. The test specimens were prepared by the KBr-disk method. Wide-angle X-ray diffraction (XRD) analyses were carried out by employing a X-ray diffractometer (D/MAX-1200, Rigaku Denki Co. Ltd., Japan). The X-ray diffraction patterns with Cu K α radiation ($\lambda = 1.5406$) at 40 kV and 100 mA were recorded in the range of $2\theta = 5^\circ$ – 70° . For the XRD measurement, the sample was prepared by freeze-drying of the hydrogel followed by it being crushed into a fine powder. The section structures of the hydrogel were measured using a Shimadzu SEM (Superscan SSX-550, Japan). The hydrogels were frozen in liquid nitrogen and immediately snapped and then vacuum-dried. DTG curves of the samples were obtained by a Shimadzu TGA-50 thermogravimetric instrument. The temperature range is employed from 20 to 700 °C with a ramp rate of 10 °C min⁻¹.

RESULTS AND DISCUSSION

Chitosan is a well-known cationic polymer with multi-hydroxyl and amino groups, while GO is negatively charged with plenty of hydroxyls and epoxides. It has the potential to form complex interactions between them. Figure 1 shows the FT-IR spectra of chitosan, GO, and the mixture of them with different ratios of chitosan/GO. The concentration of chitosan is fixed at 8.0 wt %, while a little amount of GO was added in concentration from 0.1 wt % to 0.3 wt %. For GO, a strong –OH peak at 3368 cm⁻¹ and other C–O functionalities such as COOH

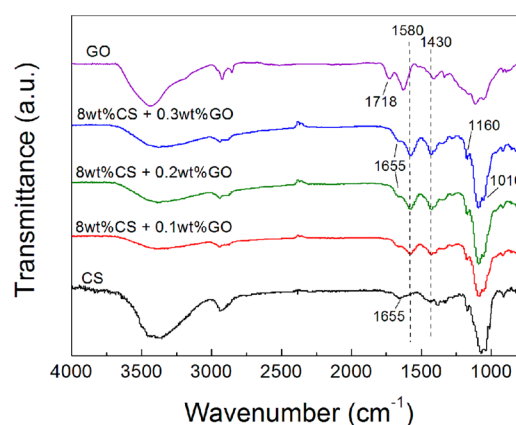


Figure 1. FTIR spectra of GO, chitosan, and chitosan/GO composites at different ratios.

(1718 cm⁻¹), C–OH (1398 cm⁻¹), and C–O–C (1063 cm⁻¹) are clearly visible. The spectrum also shows a C=C peak at 1620 cm⁻¹ corresponding to the remaining sp² character. For chitosan, the peaks at 3400 cm⁻¹ are corresponding to the N–H stretching vibration, and the absorption peaks at 1010 and 1160 cm⁻¹ are attributed to the primary alcoholic group of C₆–OH and the secondary alcoholic group of C₃–OH. The peak at 1655 cm⁻¹ is assigned to the carbonyl stretching vibration of the acetylated amino group. Clearly, compared with pure chitosan and GO, both the peaks at 1655 cm⁻¹ belonging to the N–H stretching vibration of chitosan and 1718 cm⁻¹ related to the C=O stretching vibration of GO decreases hugely for the chitosan/GO composites. In addition, two new peaks appear at 1580 and 1430 cm⁻¹, indicating the formation of hydrogen bonding and an electrostatic interaction between chitosan and GO.^{22,23} The noncovalent interactions are the driving force for the formation of hydrogel.

The noncovalent interactions between chitosan and GO are the driving force for the formation of the supramolecular structures. At lower chitosan concentration, the addition of GO could increase the viscosity of the solution, resulting in the formation of strong films after drying.²⁶ It is possible to form supramolecular CS/GO hydrogels if the concentration of chitosan is high enough. Figure 2 shows the photographs of a pure 8.0 wt % chitosan solution and 8.0 wt % chitosan solutions with 0.1–0.3 wt % GO at room temperature or 95 °C. Apparently, both the chitosan solutions with or without 0.1 wt % GO are in sol state at both room and high temperature, indicating deficient interactions among them. However, there forms a stable hydrogel when 8.0 wt % chitosan was mixed with 0.3 wt % GO at room temperature. For the system containing of 8.0 wt % chitosan and 0.2 wt % GO, there appears to be thermo-reversible gelation behavior. The mixture is in sol state at room temperature, while it becomes gel at 95 °C, and it can return to the sol state again when cooled to room temperature. So, a self-healing hydrogel can be designed. When a broken hydrogel was treated by a gel–sol–gel transition, the shape of the hydrogel can be renewed to its origin state. The concentration of chitosan in solution is a key factor in the formation of a hydrogel, and there exists a critical gelation concentration of chitosan c_g in aqueous solution, 8.0 wt %. Below the c_g , it could not form hydrogel even if the concentration of GO in the mixture arrives at its maximum value, 0.3 wt %. Above the c_g , it is possible to form a hydrogel.

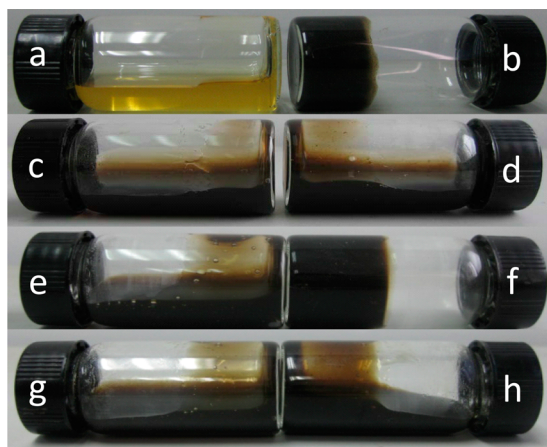


Figure 2. Photographs of the 8.0 wt % chitosan aqueous solution with or without GO at room temperature or 95 °C: (a) without GO at RT, (b) 0.3 wt % GO at RT, (c) 0.1 wt % GO at RT, (d) 0.2 wt % GO at RT, (e) 0.1 wt % GO at 95 °C, (f) 0.2 wt % GO at 95 °C, (g) 0.1 wt % GO at RT, and (h) cooling the gel in (f) back to RT.

The cross-linked structure of the as-prepared hydrogel can be directly observed by SEM. Figure 3 shows the SEM image of

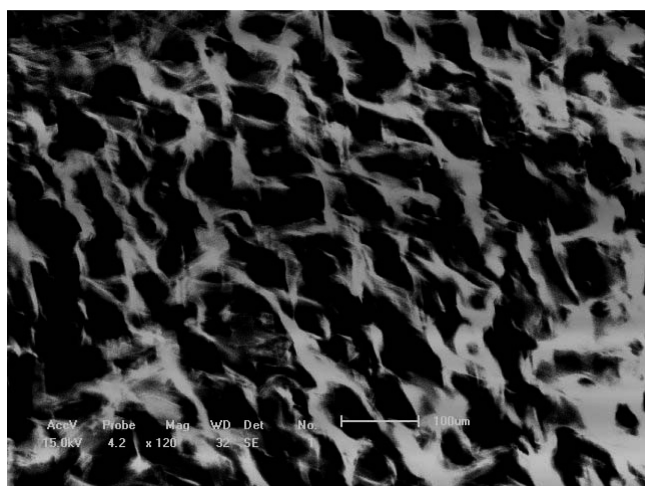


Figure 3. SEM image of the cross-section of 8.0 wt % chitosan/0.3 wt % GO hydrogel.

the cross-section of the CS/GO hydrogel prepared from 8.0 wt % chitosan and 0.3 wt % GO at room temperature. Apparently, porous structures with pores in size of tens of micrometers can be found.

Figure 4 shows the XRD patterns of the chitosan/GO hydrogel and pure chitosan. The characteristic peaks of chitosan around $2\theta = 8.3^\circ$, 11.3° , 18.1° , and 22.8° can be clearly seen for pure chitosan.²³ However, the intensity of all the peaks decreases after formation of a complex hydrogel of chitosan and GO, indicating that the addition of GO decreases the crystalline degree of chitosan. The decrease in the interactions among chitosan chains is believed to be due to the formation of new interactions between GO and chitosan. In addition, for the hybrid hydrogel, the peak at 22.8° was broadened, indicating enrichment of an amorphous structure of chitosan.^{24,28}

The thermal behavior of the dried hydrogel was also studied, and Figure 5 shows the DTG curves of pure chitosan and dried

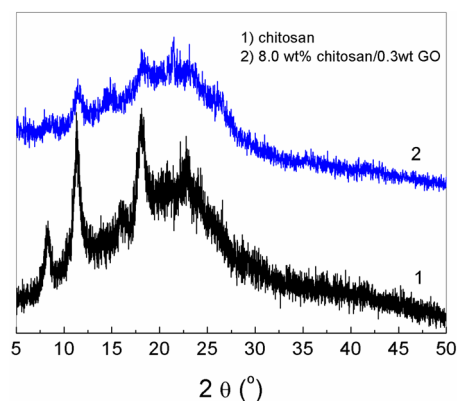


Figure 4. XRD patterns of chitosan and chitosan/GO hydrogel.

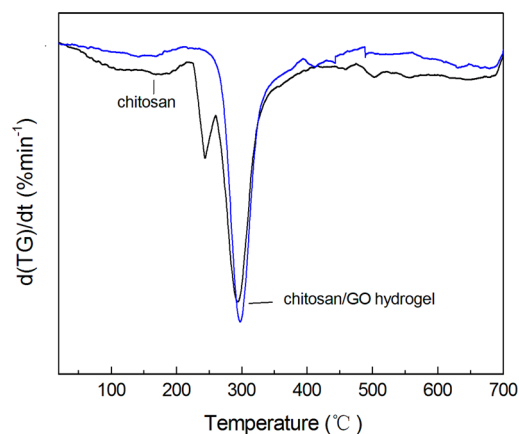
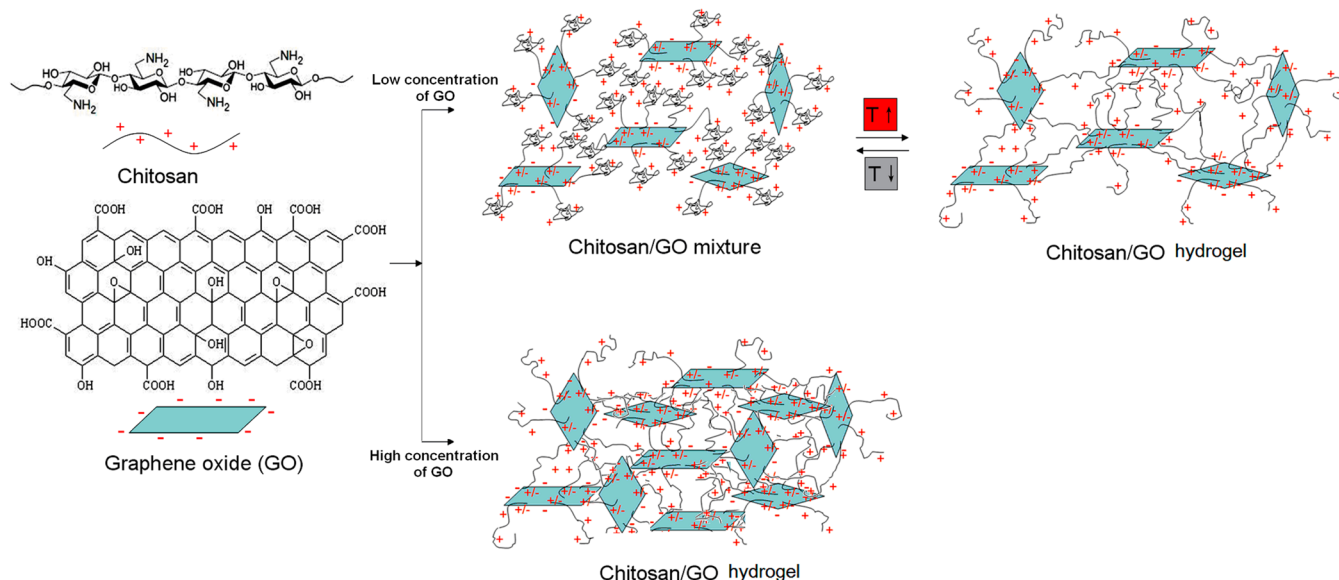


Figure 5. DTG curves of pure chitosan and dried chitosan/GO hydrogel.

chitosan/GO hydrogel. Compared to pure chitosan, the decomposition temperature of the hydrogel is about 300 °C, indicating a strong interaction between chitosan and GO.

Scheme 1 shows the possible concise mechanism for formation and damage of the supramolecular hydrogel of CS/GO. Both chitosan and GO are multiple groups for the noncovalent interactions, and this will result in the formation of hydrogels while the ratio of chitosan to GO is 27–40 where GO works as a 2D cross-linker. The noncovalent interactions drive the formation of a complex network of chitosan and GO. However, there are still many unknowns of the mechanism of thermo-induced formation of hydrogels. In this system, there exists three kinds of molecules: water, chitosan, and GO. The interactions among them include F_{w-w} , F_{w-cs} , F_{cs-cs} , F_{w-go} , F_{cs-go} , and F_{go-go} , and the hydrogel formation is believed to suppress interactions between chitosan and GO with water, especially at high temperature. The process includes two steps. First, chitosan interacts with GO by an electrostatic interaction after they are mixed together at room temperature, and the chitosan chains are in a compressed state due to the complex intra- and inter-molecular hydrogen bonding. Second, upon heating, the hydrogen bonding interactions among chitosan chains are weakened, and the free motion of the chitosan chain and GO nanosheets increase, resulting in more interaction among them.^{25,26} As a result, the stretched chains have many chances to interact with other GO sheets, and the possibility of entanglement of chains also increases, forming a network of

Scheme 1. Schematic Mechanism for the Supramolecular Hydrogel Formation at Different Conditions



them at the end.²⁹ Details about the mechanism should be studied next.

Figure 6 shows the rheological properties of the chitosan aqueous solution with or without GO as a function of

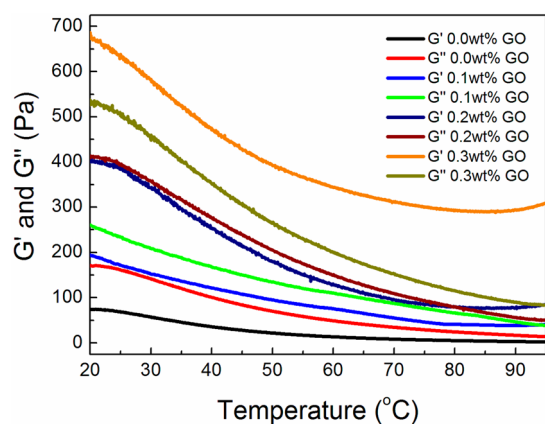


Figure 6. Storage (G') and loss (G'') moduli of the mixture of chitosan and GO with different concentrations as a function of temperature.

temperature. Clearly, for the pure chitosan solution, the storage moduli (G') is smaller than the loss moduli (G'') for the entire temperature range, indicating that the system retains its sol state even at high temperature. Similar results can be found for the 8.0 wt % chitosan/0.1 wt % GO system, but both values of G' and G'' increase. However, for the 8.0 wt % chitosan/0.2 wt % GO system, the value of G' is larger than G'' above 82 °C, indicating the gelation of the system. For the 8.0 wt % chitosan/0.3 wt % GO system, the value of G' is always larger than G'' throughout the temperature range, indicating the formation of hydrogel at room temperature.

Figure 7 shows the G' and G'' of the chitosan/GO systems as functions of the angular frequency at a fixed strain. For the pure chitosan aqueous solution (1.5 wt % and 8.0 wt %) and 1.5 wt % chitosan/0.3 wt % GO system, the G' values are always smaller than the G'' values over the entire range of frequencies, indicating the sol states of the systems. However, for the 8.0 wt

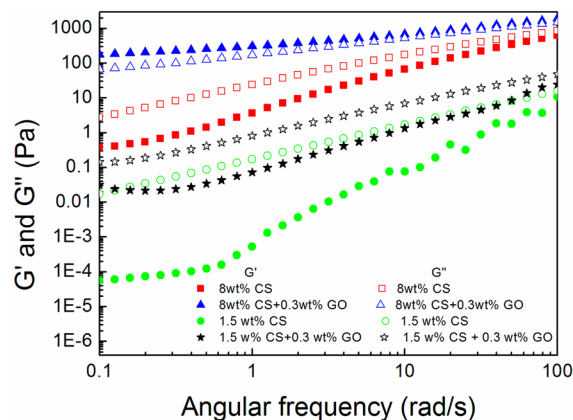


Figure 7. Storage (G') and loss (G'') moduli of the mixture of chitosan and GO with different concentrations as a function of frequency sweep.

% chitosan/0.3 wt % GO system, the G' values are always larger than the G'' values over the entire range of frequencies. Combined with the result of Figures 6 and 7, it can be concluded that both the concentration of chitosan and temperature are the two key factors for the formation of supramolecular hydrogel.

The as-prepared CS/GO hydrogel could not only take the place of the thermo-induced sol–gel–sol transition, but also can self-heal after it was broken. As shown in Figure 8, the as-prepared CS/GO hydrogel (8.0 wt % chitosan/0.3 wt % GO) is stable at room temperature and can be stretched or compressed. After it was cut by a knife and two parts were obtained (Figure 8b), they could be combined together again after stacking for 1 min through the reconstruction of the network between chitosan and GO at the interface. The repaired hydrogel also shows a similar mechanical property to its original, and it can be stretched as shown in Figure 8. This reveals that the CS/GO hydrogel can be self-healed.

CONCLUSIONS

Supramolecular hydrogels of chitosan and GO have been prepared by the noncovalent interactions between them while

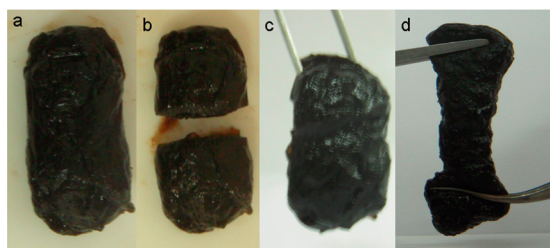


Figure 8. Photo images of the self-healing of the CS/GO hydrogel after breaking at room temperature. (a) As-prepared CS/GO hydrogel. (b) Cut by a knife. (c) Two parts stacked together for 1 min. (d) Stretching of the self-healed hydrogel.

GO nanosheets work as 2D cross-linkers. The hydrogel shows a thermo-reversible sol–gel transition when it was prepared by 8.0 wt % chitosan and 0.2 wt % GO. It is also possible to prepare a CS/GO hydrogel at room temperature by controlling the concentration and ratio of chitosan and GO (8.0 wt % chitosan/0.3 wt % GO), which showed a self-healing property after it was damaged. These new kinds of hydrogels have potential applications in both biomaterials and environmental science as a smart soft material.

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Notes

The authors declare no competing financial interest.

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