Thermal-responsive nanocomposite hydrogel based on graphene oxide-polyvinyl alcohol/poly (N-isopropylacrylamide)

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Abstract. A novel graphene oxide-polyvinyl alcohol/poly (N-isopropylacrylamide) hydrogel (GO-PVA/PNIPA hydrogel) with temperature sensitivity is prepared through in situ free-radical polymerization and freezing–thawing cyclic process. In this study, mechanical property and temperature sensitive property of GO-PVA/PNIPA hydrogel are investigated. The results show that the mechanical strength of GO-PVA/PNIPA hydrogels are enhanced with the increasing content of GO and also keeps good temperature sensitivity. Graphene oxide acting as a multi-functional crosslinker between PVA and PNIPA is responsible for the improving strength. Furthermore, this GO-PVA/PNIPA hydrogel with excellent mechanical strength holds a great promise as candidate for temperature sensitive material.

1. Introduction
Graphene oxide (GO), as a 2D nanocarbon material [1], has attracted great interest due to its extraordinary mechanical, electronic and thermal properties [2]. Plenty of hydrophilic oxygenated functional groups of GO are helpful to be easily exfoliated into monolayer sheets [3], which can disperse in water [4]. Recently, some functional nanocomposites have been synthesized from GO and polymers to exhibit extraordinary physical properties [5].

Intelligent hydrogels are able to respond to external stimuli, such as temperature, pH, solvent composition, light and magnetic fields [6], which is helpful to develop the functional materials for the applications of drug delivery, micro lenses, sensors and artificial organ[7]. It is noted that pH and temperature are two important factors for human body so that pH- and temperature-responsive hydrogels are most widely investigated [8]. As we know, poly(N-isopropylacrylamide) (PNIPA) is one of the common temperature-responsive hydrogels, which has a volume phase transition temperature (VPTT, approximately 32 °C) in aqueous solution [9].

Polyvinyl alcohol (PVA) hydrogel has good biocompatibility which is synthetized with widely used freezing–thawing cyclic process [10], because physical crosslinking can be formed in concentrated PVA solution via numerous crystalline areas [11]. Liu reported that a small amount of GO could effectively reinforce poly(vinyl alcohol) (PVA) film due to the uniform dispersion of GO sheets in a PVA matrix and the strong interaction between these two components [12]. Zhang et al. found that the addition of GO can lead to significant reinforcement of the tensile strength of boron-cross-linked GO/PVA hydrogels [13]. Kong et al. found that improved swelling ratios of PVA/GO hydrogels illustrate the enhanced macromolecular chain mobility [14]. Despite enormous reports on
the graphene/polymer composites, it is a challenge to synthesize temperature-responsive GO-hydrogel.[15].

In this paper, we successfully prepared a novel temperature-responsive hydrogel based on PNIPA and PVA using GO sheets as crosslinkers. Compared with the conventional PNIPA hydrogel, this kind of nanocomposite presents high tensile strength and temperature sensitivity.

2. Experimental section

2.1. Materials
Natural graphite powers were bought from Beijing Invention Biology Engineering & New Material Co. Ltd. N-isopropylacrylamide (NIPAM) and N, N', N'-tetraacetylenediamine (TEMED) were purchased from Sigma-Aldrich Chemical Reagent Co., polyvinyl alcohol (PVA), potassium persulfate (KPS), sodium nitrate (NaNNO₃), potassium permanganate (KMnO₄) and sulfuric acid (H₂SO₄) were obtained from Beijing Chemical Factory, China. In all of the experiments, deionized water was used.

2.2. Preparation of graphene oxide (GO) sheets
GO was prepared from natural graphite powder by a modified Hummers method[16]. Graphite (2 g) was mixed with H₂SO₄ (50 mL) at 0 °C for 2 h. Then, NaNO₃ (1 g) and KMnO₄ (4 g) were added and the mixture was stirred at room temperature for 1 h. Distilled water (100 mL) was slowly added to the reaction, the temperature was kept at 90 °C for 3 h. Subsequently, the mixture was further treated with 5% H₂O₂ (50 mL) to terminate the reaction. Finally, the GO was obtained via freeze drying procedure after being filtered and washed with water.

2.3. Preparation of GO-PVA/PNIPA hydrogels
Firstly, an appropriate amount of GO, PVA (10% in aqueous solution) and H₂O (10 g) were added into a vial, and then the solution was sonicated for 30 min and stirred for 20 min. Subsequently, a certain amount of NIPAM and initiator KPS (2% in aqueous solution) were added into the mixture. Then the O₂ in the solution was removed by vacuum filtration. Finally, the catalyst of TEMED (8 μL) was added while stirring. The solution was injected into a mold and free-radical polymerization was carried out in a water bath at 20 °C for 24 h. Tree freezing–thawing cyclic process was taken to the resulting hydrogel. The detail of precursor solutions is listed in Table 1.

Table 1. The compositions of GO-PVA/PNIPA hydrogel precursor solutions.

| Samples       | PVA(g) | GO(mg) | NIPAM (g) | KPS (mg) | TEMED (μL) | H₂O (g) |
|---------------|--------|--------|-----------|----------|------------|---------|
| GO1-PVA1/PNIPA| 0.25   | 10     | 1.1318    | 10       | 8          | 10.0    |
| GO1-PVA2/PNIPA| 0.50   | 10     | 1.1318    | 10       | 8          | 10.0    |
| GO1-PVA3/PNIPA| 0.75   | 10     | 1.1318    | 10       | 8          | 10.0    |
| GO2-PVA2/PNIPA| 0.50   | 20     | 1.1318    | 10       | 8          | 10.0    |
| GO3-PVA2/PNIPA| 0.50   | 25     | 1.1318    | 10       | 8          | 10.0    |

2.4. Measurement of mechanical properties
All of the mechanical properties of the hydrogels were tested on an ASG-I electronic universal testing machine (Shimadzu Co., Japan) at room temperature. Samples with size of Φ 3.3 mm×10 mm and Φ 6 mm×10 mm were used for tensile tests and compressive tests with a speed of 100 and 5 mm min⁻¹, respectively, and five specimens were tested for each measurement. The elastic modulus and toughness were achieved from the stress-strain curve.

2.5. Scanning electron microscopy (SEM)
The samples for SEM investigations were plunged into liquid nitrogen for about 20 min. The frozen samples were subsequently freeze-dried in a vacuum freeze dryer until all water was removed. The
morphologies of these fractured surfaces were observed with a JSM-7500F field emission scanning electron microscope with an accelerating voltage of 5 kV.

2.6. Swelling properties of hydrogels.
The confirmed weight of hydrogel was placed into a 20-mL bottle with H\textsubscript{2}O at different temperature. Over a specified period of time, the hydrogel was taken out, and the weight was determined after sweeping excess water on its surface. The swelling ratio (SR) of hydrogel was calculated as follows:

$$\text{SR} = \frac{(W_t-W_0)}{W_0} \times 100\%$$

where $W_t$ and $W_0$ are the weight of the swollen hydrogel and the initial weight, respectively. For each sample, the experiments were repeated three times, and the final results were calculated by averaging the replicates.

3. Results and discussion

Figure 1. (a) tensile strength and (b) compressive strength of GO-PVA/PNIPA hydrogels with different amounts of GO.

The result of Figure 1a shows that the GO-PVA/PNIPA hydrogels have a much better mechanical property than the pure PVA/PNIPA hydrogels. GO3-PVA2/PNIPA hydrogel displays the tensile strength of 151.9 KPa. In contrast, tensile strength of PVA2/PNIPA hydrogel is only 50.7 KPa. As shown in Figure 1b, the compressive stress–strain curves show that none of the hydrogels break even under a strain up to 90%. The hydrogels show the excellent compressive strength with increasing GO content from 1.5 MPa (PVA2/PNIPA hydrogel) to 4.1 MPa (GO3-PVA2/PNIPA).

Figure 2. SEM images of (a) PVA2/PNIPA hydrogel; (b) GO1-PVA2/PNIPA hydrogel; (c) GO2-PVA2/PNIPA hydrogel.

The SEM images in Figure 2 provide some possible explanations for the high tensile strength of GO-PVA/PNIPA hydrogels. All the hydrogels are interconnected by porous structure from different pore sizes. The uniform and small size pores distribution plays an important role in the mechanical
properties of hydrogel. The pore size of GO1-PVA2/PNIPA hydrogel (Figure 2b) is smaller than that of PVA2/PNIPA hydrogel (Figure 2a), indicating the former has a denser structure. In Figure 2c, with the increasing content of GO, pore sizes changed from 1–2 μm to nanometer scales. Therefore, we deduce that the present porous morphology with interconnected pore sizes at micro- and nanometer scales contributes significantly to the high mechanical strength of these hydrogels.

Figure 3. DSC thermograms of GO-PVA/PNIPA hydrogels.

Temperature behavior of resulting hydrogels is determined by DSC with the VPTT reported as the peak temperature. From Figure 3, the PVA/PNIPA hydrogel reveals a VPTT around 34.9 °C. Moreover, with the addition of GO, the VPTT of the GO-PVA/PNIPA hydrogel decrease to 34.0 °C. The results indicate that the incorporation of the GO has a big effect on the VPTT of the hydrogels. The phenomenon is attributed to the high value of thermal conductivity of graphene which has been reported to be up to 5300 W m⁻¹ K⁻¹ at room temperature. In that case, GO-PVA/PNIPA hydrogel has superb temperature responsive property due to faster heat conduction of GO.

Figure 4. Swelling ratios of GO-PVA/PNIPA hydrogels as a function of temperature.

From Figure 4, with the introduction of GO, the increasing response rate and the decreasing VPTT (approximately 1 °C) are consistent with DSC result. The possible reason is that the incorporated GO produces a denser hydrogel network than the PVA/PNIPA hydrogel, and thus less amounts of water is precipitated. In that case, these GO-PVA/PNIPA hydrogels have low swelling ratios and rapid volume
changes in response to temperature and the response rate of GO-PVA/PNIPA hydrogels increases with the addition of GO.

4. Conclusion
In this study, we have investigated a novel GO-PVA/PNIPA hydrogel, which exhibits not only excellent mechanical property but also a good temperature sensitivity. The PVA/PNIPA hydrogel exhibit a volume phase transition temperature at around 34.9 °C, which is decreased by 1 °C due to the incorporation of the GO. The above-mentioned advantages make the as-prepared GO-PVA/PNIPA hydrogel suitable for many applications in various fields.

Acknowledgments
This work was supported by the Natural Science Foundation of China (21174017)

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