



# Thermo-responsive hydrogels with tunable transition temperature crosslinked by multifunctional graphene oxide nanosheets



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## ABSTRACT

Hydrogels consisting of reactive monomers can respond to external stimuli, which is promising for many applications such as sensors, soft robotics, and actuators, etc. However, most of responsive hydrogels are hard to fabricate into smart devices due to their poor mechanical properties. In this paper, vinyl-modified graphene oxide (GO-VTES) nanosheets were facilely prepared through the coupling reaction between hydroxyl or carboxylic acid groups from graphene oxide (GO) and hydroxyl groups from hydrolyzed vinyltriethoxysilane (VTES). By using the multifunctional GO-VTES nanosheets as crosslinkers, *N*-isopropylacrylamide (NIPAM) and acrylamide (AAm) were copolymerized to generate a series of tough and thermo-responsive composite hydrogels. The structures and morphologies of GO-VTES were investigated by FTIR, Raman, XPS, XRD, AFM and TEM. The obtained thermo-responsive composite hydrogels exhibit enhanced mechanical properties, which can be tuned by varying the content of GO-VTES and AAm. Moreover, these hydrogels were thermo-responsive with the LCST tunable by manipulating the contents of GO-VTES and/or AAm in the hydrogels. This strategy to prepare responsive composite hydrogels with enhanced mechanical properties has attractive applications for fabricating smart soft actuators.

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## 1. Introduction

Responsive hydrogels have attracted great research interests [1–3] for potential applications in sensors [4], drug release [5], artificial muscles [6], and soft robotics [7], etc. Numerous responsive hydrogels have been prepared by incorporating functional moieties or monomers in the polymer network, which renders responsiveness upon changes in pH [8], ion strength [9], temperature [10], light [11], or electric field [12], etc. A major challenge for conventional responsive hydrogels is the poor mechanical properties, primarily due to the lack of energy dissipating mechanism. Therefore, great efforts have been endowed to develop responsive hydrogels with improved strength and toughness. Among the reinforcing strategies, nanocomposite hydrogels by incorporating functional inorganic nano-objects as additives have attracted more and more attentions due to their facile preparation and outstanding

comprehensive mechanical properties [13,14].

Poly (*N*-isopropylacrylamide) (PNIPAM) has been one of the most attractive thermo-responsive polymers with a lower critical solution temperature (LCST) at around 32 °C. By combining PNIPAM with other polymers, it is convenient to tune the LCST over a broad range, which is important for diverse applications such as drug delivery [15], injectable hydrogels [16], tissue engineering [17], sensors [18], or soft actuators [19], etc. However, conventional PNIPAM hydrogels have been notorious for the poor mechanical properties, hindering their applications for the past decades. Several thermo-responsive hydrogels containing PNIPAM have been recently toughened by incorporating clay nanosheets [19], graphene oxide [20], or microgels [21]. Therein, the so-called nanostructured reinforcing agents can serve as energy dissipation centers to toughen the hydrogels. The obtained tough and responsive hydrogels have been employed to fabricate bilayer actuators that are motivated by changing temperatures.

Graphene and graphene oxide (GO) have been used to reinforce and functionalize polymer hydrogels due to their high specific surface area, thermal effect and abundant surface functional groups

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[22]. As the GO nanosheets are blended with monomers, hydrogen bonding can form between monomers or hydrophilic polymer chains and GO, leading to improvements in strength and toughness of the hydrogels [23,24]. Ye et al. explored *in situ* polymerization and cross-linking of acrylic acid (AA) in GO suspension to prepare PAA/GO composite hydrogels with a tensile strength of 27 kPa and a strain at break of 280% [25]. Similar strategies have been utilized to prepare PNIPAM/GO hydrogels, with the GO subsequently reduced by using hydrazine monohydrate. Then the bilayer-type actuators comprised of a PNIPAM/rGO active layer and a poly (acrylamide) (PAAm) passive layer were fabricated [26]. Upon visible-light exposure, the particular photo energy to thermal energy conversion property of graphene drives the shrinking of the thermo-responsive PNIPAM hydrogel, resulting in a photo-actuator with full bending motions. However, the physical interactions between polymer chains and GO sheets are generally weak, further reinforcements of hydrogels are needed for applications in robust devices. Tong et al. used hectorite nanosheets to further reinforce the PNIPAM/GO hydrogels, generating composite hydrogels showing the tensile strength (220 kPa) and elongation at break (780%) several times higher than those of PNIPAM/GO hydrogels [27]. Covalent bonding of polymer chains to GO nanosheets was efficient in improving the resilience and strength of the hydrogels. Wang et al. irradiated GO by gamma ray in the presence of oxygen, generating peroxides on GO nanosheets that acted as initiators for subsequent polymerization and cross-linking of AAm. The obtained PAAm/GO composite hydrogels showed high tensile strength (0.2–1.2 MPa) and elongation (2000–5300%) [28].

In this work, in order to form covalent bonds between GO and polymer network, we propose a new and facile method to functionalize GO with vinyl groups by grafting vinyltriethoxysilane (VTES) onto the 2D materials. The functionalized GO nanosheets (GO-VTES) were used as macro-crosslinkers for the synthesis of hydrogels through free radical polymerization of thermo-responsive monomer (NIPAM) and hydrophilic comonomer (AAm) (see Scheme 1). The obtained P(NIPAM-AAm)/GO hydrogels showed excellent mechanical properties. Moreover, the hydrogels are responsive to temperature changes, with the LCST systematically manipulated by adjusting the molar ratio between NIPAM and AAm. The structures, mechanical properties and thermo-responsiveness of the composite hydrogels have been investigated in detail.

## 2. Experimental

### 2.1. Materials

Sodium nitrate ( $\text{NaNO}_3$ , AR), sulfuric acid ( $\text{H}_2\text{SO}_4$ , GR, 98%), potassium permanganate ( $\text{KMnO}_4$ , AR), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , GR, 30%), hydrochloric acid (HCl, AR) and vinyltriethoxysilane (VTES, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphite, acrylamide (AAm, AR, 99%), *N*-isopropylacrylamide (NIPAM, 98%), potassium persulfate (KPS, AR, 99.5%) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99%) were bought from Aladdin Chemistry Co., Ltd.

### 2.2. Synthesis of graphene oxide

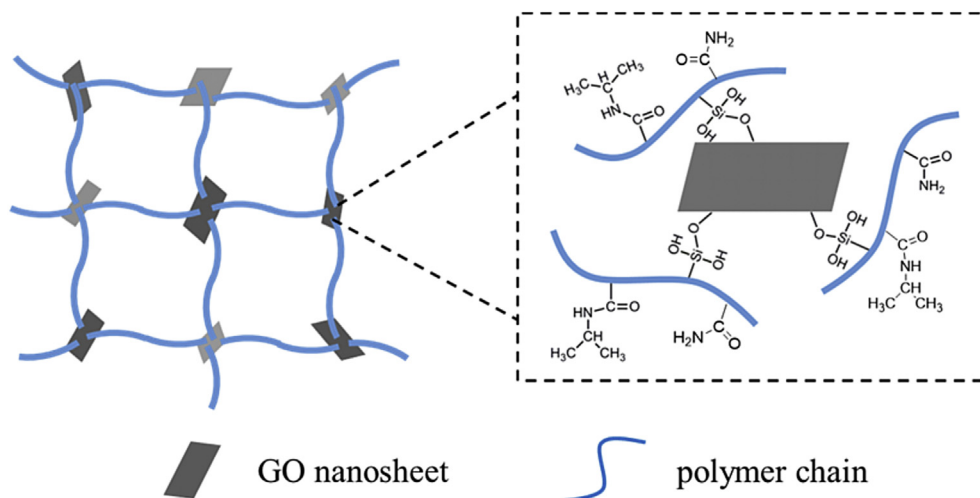
The graphite was oxidized to graphene oxide by using a modified Hummers' method [29]. In a typical synthesis, 1.2 g of  $\text{NaNO}_3$ , 1.0 g of graphite and 46 mL of concentrated  $\text{H}_2\text{SO}_4$  were charged into a 250 mL flask and stirred for 10 min. Then, 6.0 g of  $\text{KMnO}_4$  was added slowly, and the mixture was heated to 35 °C for 6 h. Subsequently, the mixture was heated to 80 °C with stirring, and then 80 mL of deionized water was added dropwise. After a continuous stirring for 30 min, 200 mL of deionized water and 6 mL of  $\text{H}_2\text{O}_2$  solution (30%) were added in order. The resulting product was washed with a large amount of deionized water, followed by centrifugation in order to obtain a stable graphene oxide suspension. Then, the suspension was freeze-dried for use.

### 2.3. Synthesis of GO-VTES

In a typical synthesis, 10 mL of GO suspension in deionized water (2 mg/mL) was prepared by sonication for 70 min, before the addition of 0.1 mL of VTES and 0.05 mL of HCl solution (37%) for a reaction at 75 °C for 2 h [30]. The resulting GO-VTES suspension was used for the preparation of hydrogels.

### 2.4. Synthesis of hydrogels

To prepare hydrogels, the monomers (NIPAM and AAm) and the initiator KPS were mixed with the as-prepared GO-VTES suspension, followed by stirring for 2 h. The activator TEMED was then added under stirring. Subsequently, the solution was quickly injected into a mould comprised of two glass substrates spaced



Scheme 1. Network structure of the GO composited hydrogels.

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