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A novel reduced graphene oxide/epoxy sandwich structure composite film with thermo-, electro- and light-responsive shape memory effect

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Abstract: Development of multi-responsive shape recovery polymers and their composites is critical and has great potential. In this study, a novel reduced graphene oxide (RGO)/water-borne epoxy (WEP)/RGO sandwich structure composite film was fabricated and investigated. The results showed that the composite film exhibited excellent thermo-, electro- and light-responsive shape memory effect, which has potential applications for the sensors, switching devices, deployable structures, and medical apparatus.

Keywords: Shape memory materials; Polymeric composites; Functional; Epoxy; RGO paper

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1. Introduction:

Shape memory polymers (SMPs) is one of the emerging branches of active polymers that have the capacity of undergoing a predefined shape change from temporary shape to the initial shape when exposed to appropriate external stimuli, such as light, heat, water, pH, electric, and magnetic fields [1-3]. Over the past decades, SMPs have caught significant attention from both academia and industries due to their technological significance. Today, SMPs are widely applied in various areas, such applications can be found in smart textile, electronic package, actuator device, biomedicine and information carrier, and so on [4-6].

So far, the responsive mode of most SMPs is thermo-response type [7-10]. However, in some cases which are not suitable for direct heating, especially in some biomedical application. For example, it is not safe and rather difficult to implement during a thermo-responsive shape recovery process happen in a human body. It may cause damage to the human body. Therefore, it is necessary to develop SMP composites with the indirect thermo-response function, such as electro-, magnetic- and light-responsive [2, 7]. In the current study, we prepared and reported a novel RGO/water-borne epoxy (WEP)/RGO sandwich structure composite film, which exhibited multi-responsive shape memory functionality, containing thermo-, electro- and light-responsive shape memory performance simultaneously. The fabrication and performance of the composite film were synthetically investigated and discussed.

2. Materials and methods

2.1. Fabrication of GO paper

First, GO short fibers were synthesized by injecting GO spinning dopes (10 mg/ml) into a 5wt% $CaCl_2$ absolute ethyl alcohol coagulation bath with an excessive rotation speed of 80-100 r/min. Then, the as-spun GO fibers were collected by filtration and dried at 30 °C for 24 h. After re-dispersing of the dried fiber in deionized water with the assistance of an ultrasonic machine, a homogeneous flocculent GO dispersion was ready for the formation of GO paper by vacuum filtration, as shown in **Fig. 1 (a)**. This method provided a rapid and convenient way to prepare the GO paper. The thickness of the GO paper was adjustable by controlling the weight of the dried fibers, approximately 0.03 mm.

2.2. Fabrication of RGO/WEP/RGO sandwich structure composite film

WEP and curing agent (weight ratio of 4:1) [8, 9] were mixed to homogeneity via an intensive mixing in a flask at a speed of 200 r/min for 15 mins. The above mixture was then vacuum-dried in a Labconco Free Zone freeze-drier operated at 0.1 mbar and -20 °C after frozen in liquid nitrogen. Then, the dried WEP and curing agent mixture powder were achieved. Subsequently, the powder was uniformly spread on the GO paper and the other GO paper was covered on the top of the powder layer. Then the above material was compressed into a sandwich structure film at 120 °C under a pressure of 1 MPa for 2 h. Finally, the prepared GO/WEP/GO sandwich structure composite film was reduced by hydroiodate solution (37wt%) and then the composite film was successfully fabricated, as shown in **Fig. 1 (a)**. The thickness of the composite film was approximately 0.23 mm.

2.3 Experimental procedure

X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscope (AFM) were used to characterize the structural properties and surface morphologies of GO and RGO paper, respectively. The shape memory performance of the composite film was conveniently measured by thermal-mechanical cycle tests conducted on the TMA Q400 (TA Instruments). The samples were pulled with increasing stress from 0 to 0.75 MPa at 80 °C (> glass transition temperature (T_g, approximately 50 °C) [8, 9]). The samples were cooled down to 25 °C (<T_g) and held for 10 mins. Then, the load was released at 25 °C (the loading and unloading speed was 0.5 MPa/min). The samples were heated to 80 °C under no load and held for 10 mins, resulting in the recovery of the samples' strain. The heating and cooling speeds were 5 °C/min. The shape memory recovery ratios (R_r) of the composite films were calculated according to the following equation [11]: $R_r = (\theta_1 - \theta_2)/\theta_1 \times 100\%$, where θ_1 and θ_2 is the temporary and residual angle, respectively.

The electric responsive shape recovery process of the sample was investigated under different applied volts. Light responsive shape recovery experiments were conducted on a near-infrared (NIR) ray source control system, and the wavelength was approximately 808 nm.

3. Results and discussion

The surface morphology of RGO paper was observed via SEM measurement, as shown in **Fig. 1(a).** The image manifests the characterized sheet-like microstructure with relatively wrinkled surface. TEM image supports the assertion that the prepared GO was a few layer (see **Fig. 1(b)**). AFM image shows that the thickness of the GO layer was approximately 1.0 nm (see **Fig. 1(c)**). XPS patterns of GO and RGO in **Fig.1 (d)** and **(e)** indicated that GO was effectively reduced. With the excellent electrical and thermal conductivity, RGO paper could act as a functional layer in the multi-responsive shape memory material fabrication.

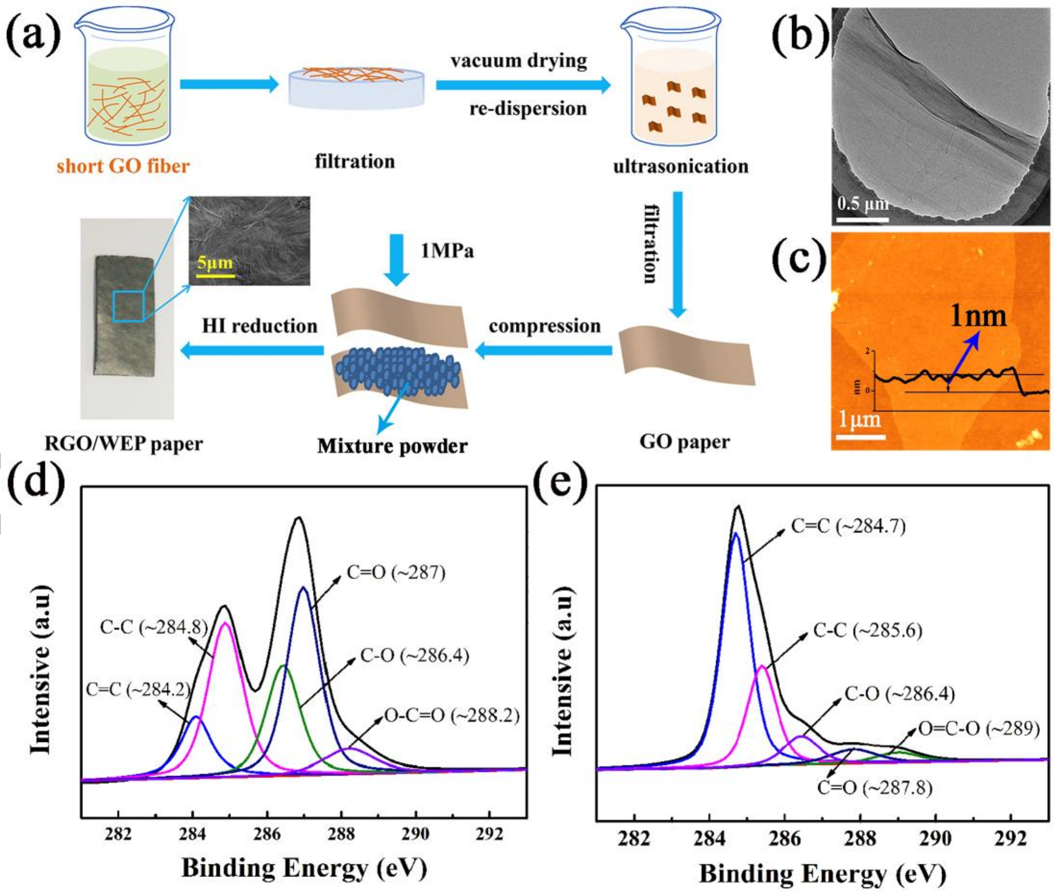

Fig.1. (a) Preparation procedures of RGO/WEP/RGO sandwich structure composite film; (b) TEM and (c) AFM of GO; (d) C1s XPS peaks of GO paper and (e) RGO paper.

The thermo-responsive shape memory process of the composite film was shown in **Fig. 2 (a)**. Firstly, a sample ($30 \times 6 \times 0.25$ mm^3) was rolled after heating above T_g of the sample. Then the rolled sample was dipped into chilled water to store the temporary shape. Finally, the rolled and fixed sample was put in a Petri dish filled with hot water (80 °C) and it could complete the thermo-responsive shape recovery process in only 3 s.

Fig. 2(b) shows a particularly proper form graphically described the shape memory effect of the samples from the thermal-mechanical cycle measurements under controlled stress, represented as 3D plots of temperature vs. strain and stress [12]. WEP chains set the permanent shape and cannot undergo conformational changes below T_g. Upon heating above T_g, WEP chains could be programmed with a temporary shape when an external load was applied (Deformation). When the sample was cooled below T_g, the kind of elevated temperature deformation could be fixed due to the frozen chain segments (Fixing). Upon subsequent reheating above T_g without applied stress, the stored strain energy could be released as WEP chain mobility was reactivated (Unloading and Recovery). The fixity ratio of the composite film was almost the same as the pristine WEP. However, the introduced RGO layers were not shape memory materials, it generated hindrance and thermal contact resistance in the shape memory recovery process [13], causing that the recovery ratio of the RGO/WEP/RGO sandwich structure composite lower than that of the pristine WEP.

As shown in **Fig. 2(c),** a '∩' like shape sample was cut to conduct the electro-responsive shape memory test of the composite film. The sample was heated above T_g, then it could be bent into '**U**' like shape, and the temporary shape would be fixed when the sample was cooled to 25 °C. The electro-responsive shape recovery process of the sample was observed and recorded at 8 volts direct current, as shown in **Fig. 2 (e)**. To further research the shape memory performance, the bent samples were subjected to applied 2-9 volts. From **Table 1** and **Fig. 2 (e)**, we can conclude that the fabricated composite film in this work exhibited superior electro-responsive shape memory behavior.

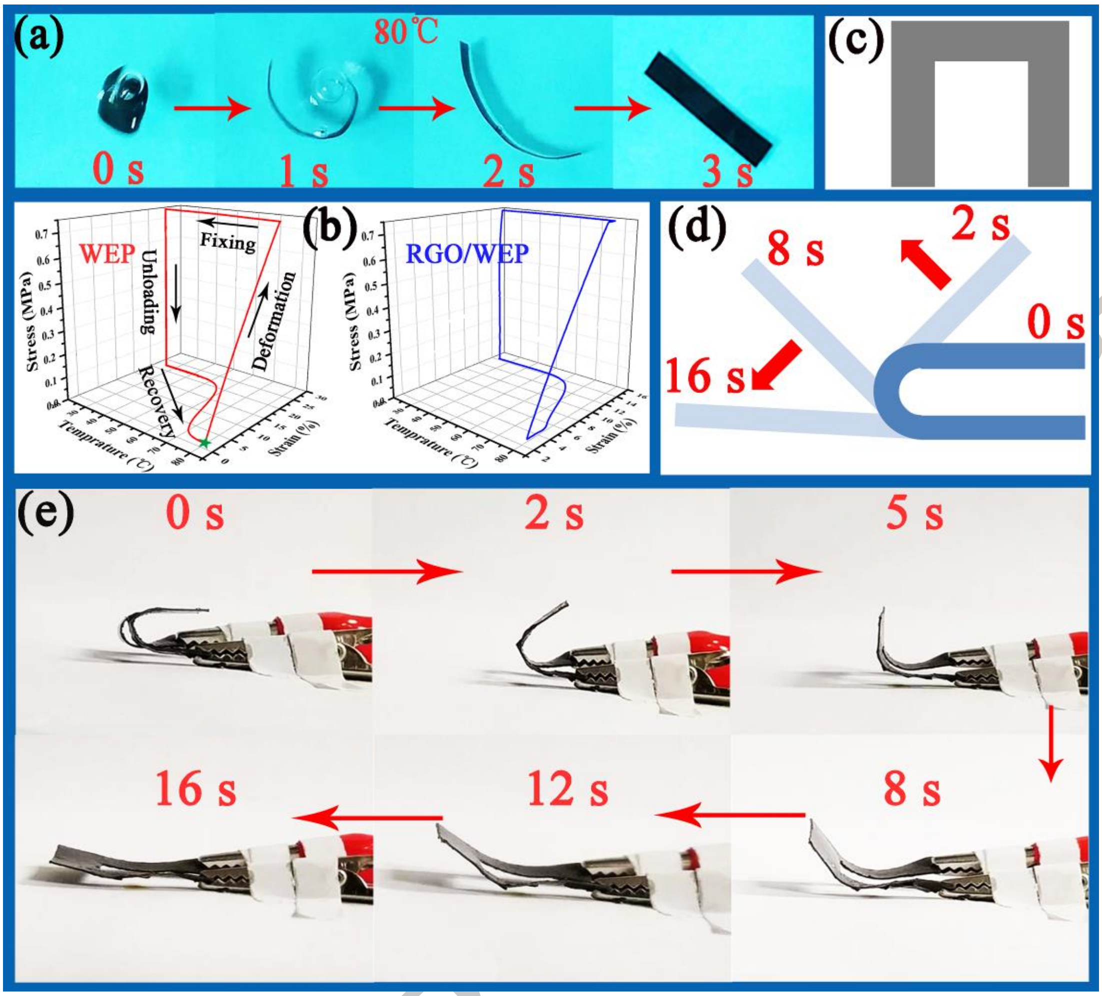

Fig.2. (a) Thermo-responsive shape memory effect of the composite film; (b) 3D plots of temperature vs. strain and stress of WEP and the composite films; Schematic diagram of (c) '∩' like shape sample and (d) Shape recovery process; (e) Electro-responsive shape memory effect of the composite film at 8 V applied voltage.

Table 1. The electro-responsive shape recovery data of composite films.

Applied voltage (V)	2	3	4	5	6	7	8	9
Recovery time (s)	-	105	87	65	41	25	16	10
R_r (%)	-	55	70	80	90	>90	>90	>90

Light is an attracted and significant stimulus due to the fact that it can temporally and spatially control the shape recovery process in a non-contact way [14]. With the outstanding photo-thermal conversion performance of the RGO paper, the RGO/WEP/RGO sandwich structure composite film showed excellent NIR light-induced (808 nm) shape memory effect. **Fig.3** presents the NIR light-responsive shape memory effect of the composite films (30 × 4 × 0.25 mm^3) in different power density of NIR light irradiation. Such unique light-sensitive switch possessed a large number of distinctive advantages, such as remote and accuracy control, high-level integrity, and safety for living body, which would enlarge the application range of SMPs.

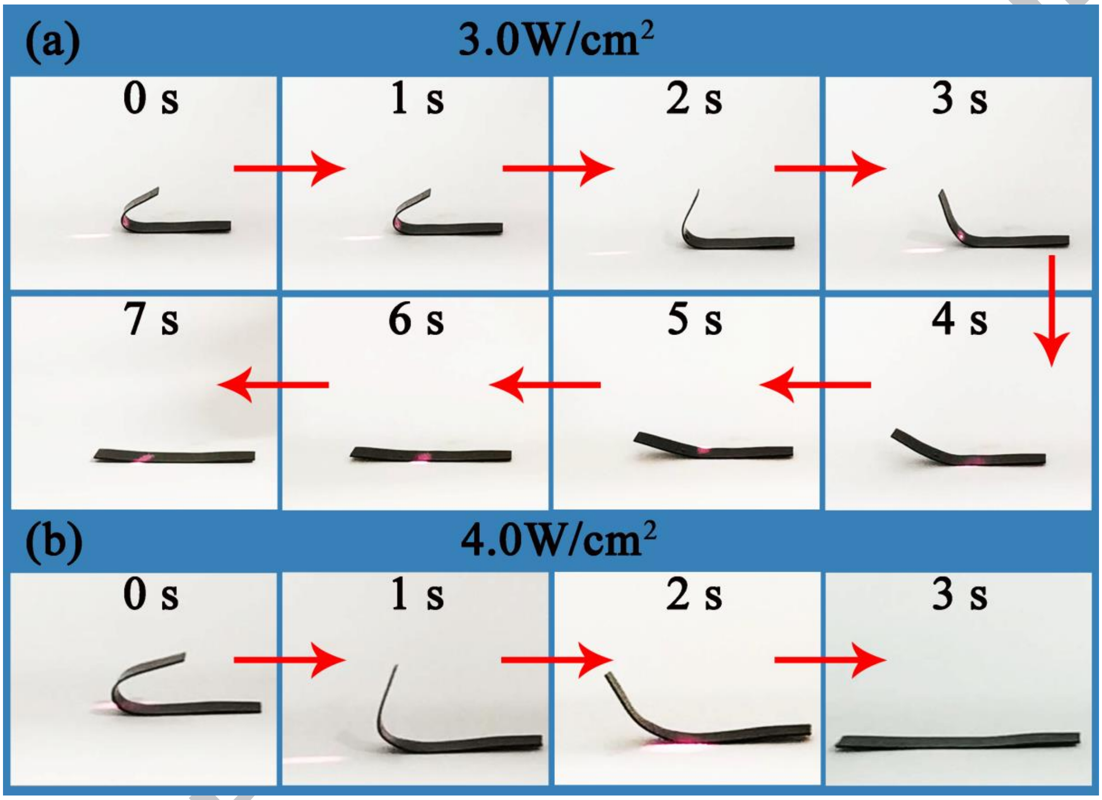

Fig.3. Light-responsive shape memory effect of RGO/WEP/RGO sandwich structure composite films in different power density of NIR light irradiation.

4. Conclusion

In the present work, a novel multi-responsive RGO/WEP/RGO sandwich structure composite film was successfully fabricated. Besides thermo-responsive shape memory effect, the composite film also exhibited electro- and light-responsive shape memory behavior. Under the applied voltage of 8.0 V and NIR light irradiation with 3.0 W/cm^2, the composite film completed the shape memory process in 16 s and 7 s, respectively. The diverse driven manners of the composite film endow the potential material use and meet more complex and broader requirements for the future application.

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Highlights

► A novel reduced graphene oxide (RGO)/epoxy/RGO sandwich structure composite film was fabricated.

► RGO paper was introduced to the composite film as a functional layer.

► The composite film showed excellent thermo-, electro- and light-responsive shape memory effect.

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