## **Supporting Information**

Rapid Room-Temperature Self-Healing Conductive Nanocomposites based on

**Naturally Dried Graphene Aerogels** 

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## **Experimental Procedures**

Materials: graphite powder (325 meshes, Qingdao Huarun graphite Co.LTD., Qingdao, China), ammonia solution (25% in water, A.R) and Hydrazine hydrate (Hydrazine, 64%) were used as received. 2-Methoxyethyl acrylate (MEA, 98%), N-isopropylacrylamide (NIPAM, 98.0%), N-(Methoxy methyl) methacrylamide (MMP, 85.0%) and N,N-Diethylacrylamide (DEAA, 98.0%) were purchased from TCI Development Co., Ltd. (Shanghai, China). Benzoyl peroxide (AR, > 99.0%) were purchased from Tianjin Damao Chemical Reagent Factory (China).

Synthesis of graphene oxide (GO): GO was prepared from natural graphite powder via a modified Hummers method. The detailed preparation process of GO and its characterization are consistent with our previous study.

Preparation of graphene aerogel (GA): A certain amount of ammonia solution was added into the stable GO dispersion obtained by ultrasonication of the GO suspension to adjust pH of the dispersion solution to 10. Then, a certain amount of hydrazine hydrate (hydrazine hydrate : GO = 3 : 1 (w/w)) was added into the previous dispersion solution under stirring. The mixture was sealed in a 25 ml hydrothermal reactor (KH-24) and then maintained at 150°C for 24 h to obtain a reduced graphene oxide hydrogel (RGH). The RGH was next completely frozen at -20°C for 5 h. With drying of the RGH under ambient temperature and pressure conditions for 36 h, the final graphene aerogel was obtained.

Preparation of self-healing polymer material poly(MEA-co-NIPAM) ( $M_xN_y$ ): Poly(MEA- co-NIPAM) was synthesized by the free-radical copolymerization of 2-methoxyethyl acrylate (MEA) and N-isopropylacrylamide (NIPAM). In a typical procedure, the monomers, MEA and NIPAM, and 1wt% (respect to the total weight of the total monomer) benzoyl peroxide were sequentially added into the a 20 ml glass vial and bubbled with nitrogen under stirring for 20 minutes at 35°C. Then the solution was transferred into a Teflon plate mold (10cm × 10cm, 2 mm thick) and maintained at 60°C for 24h to prepare the poly(MEA-co-NIPAM). The detailed synthesis procedures for poly(MEA-co-MMP) ( $M_xP_y$ ) and poly(MEA-co-DEAA) ( $M_xD_y$ ) were the same as that of poly(MEA-co-NIPAM). In this work, MN, MP and MD are shortening of  $M_xN_y$ ,  $M_xP_y$  and  $M_xD_y$ , respectively. X and Y refers to the molar ratio of the MEA and the other copolymer monomer (NIPAM, MMP or DEAA), respectively.

Preparation of  $GA/M_xN_Y$  nanocomposites: Firstly, a certain amount of  $M_xN_Y$  prepolymer was configured by the above-mentioned procedure. Then the prepared GA was immersed into the prepolymer solution under vacuum for 10 minutes to infiltrate the prepolymer solution into porous rGO networks. Subsequently, the wetted GA cylinder was taken out of the solution and kept in an oven at 60°C for 24 h to complete polymerization.

Characterizations: The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 instrument (Thermal Scientific, USA) in the range 500-4000 cm<sup>-1</sup>. The scanning electron microscope (SEM) measurements were performed on a JSM-7401F JEOL instrument at an

acceleration voltage of 15 KV. The differential scanning calorimetry (DSC) measurements were conducted on a Seiko instrument (DSC 6200) with a heating rate of 10°C/min. The thermogravimetric analysis (TGA) curves were carried out from 30 to 850°C using a TA Instruments Q50 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min in a highly purified N2 atmosphere. Conductivity measurements were performed with a Digital Four-probe Tester (ST2253, Suzhou Jingge Electronic Co., LTD, China) at room temperature. The sensitivity of resistance change tests were performed with a Digital Multimeter (Agilent Technologies, 34401A). The tensile measurements were performed on samples with parallelepiped (40 mm × 4 mm × 1mm) structures using an Autograph ASG-J electronic universal testing machine (Shimadzu Co., Japan) with the crosshead speed of 50 mm/min. The compressive stress-strain curves were measured by the same mechanical machine at a strain rate of 5 mm min<sup>-1</sup>. And all samples were prepared with a cylindrical shape with diameters of 15 mm diameter and gauge lengths of 20 mm.

Self-healing experiments: The samples of  $GA/M_7N_3$  ( $\approx 0.5mm \times 35mm \times 2mm$ ) were cut into two parts and subsequently jointed back together by hand. Then the adjoined sample was placed in a sealed bag at room temperature for different times (0-2h). After a preset time, the mechanical measurements were carried out on the healed sample to obtain the tensile stressstrain curve. And the conductivity change of the sample was monitored in a Digital Multimeter to obtain the electrical conductivity self-healing efficiency. The mechanical self-healing experiments of plate copolymers (MN, MP, MD) were also carried out by the above-mentioned machine. The mechanical self-healing efficiency was calculated by the equation:  $Rs=(S_1/S_0)\times100\%$ ,  $Re=(E_1/E_0)\times100\%$  (the  $S_1$ ,  $S_0$ ,  $E_1$ ,  $E_0$  represent the self-healed tensile stress, original tensile stress, self-healed tensile elongation and original tensile elongation, respectively).



**Figure S1**. a) Digital images of GA with different experimental parameters: hydrothermal reduction time, pre-freeze time and pre-freeze temperature. The volume shrinkage of GA as a function of b) hydrothermal reduction time, c) pre-freeze time and d) pre-freeze temperature, respectively.



**Figure S2** . a). The volume shrinkage of GA as a function of the concentration of GO; b). The density of GA as a function of the concentration of GO; c). The conductivity of GA as a function of the concentration of GO.



**Figure S3**. a) Nitrogen adsorption-desorption isotherms and b) BJH pore size distribution curves of GA samples prepared with different concentration of GO solution.



**Figure S4.** a). The tensile stress-strain curves of  $M_xN_y$ ; b-d).The tensile stress-strain curves of the recovery of  $M_7N_3$ ,  $M_8N_2$  and  $M_9N_1$ , respectively.

**Table S1**. Stress and elongation at break and recovery percent of  $M_7N_3$ ,  $M_7P_3$ ,  $M_7D_3$  (virgin and healed polymers after for 2h at 25°C)

Entry		M <sub>7</sub> N <sub>3</sub>	M <sub>7</sub> P <sub>3</sub>	M <sub>7</sub> D <sub>3</sub>
Virgin Sample	Stress at break (MPa)	1.45	2.21	0.48
	Elongation at break (%)	697.2	275.6	1505.1
healed (dabbing 2 h at 25 °C)	Recovery of stress (%)	98	62	35
	Recovery of elongation(%)	97	84	27



Figure S5. The tensile stress-strain curves of the recovery of a)  $M_7P_3$  and b)  $M_7D_3$ .



**Figure S6**. a). The content of rGO in the GA/M<sub>7</sub>N<sub>3</sub> as a function of the concentration of GO; b). Thermogravimetric analysis curves of GA,  $M_7N_3$  copolymer and GA/M<sub>7</sub>N<sub>3</sub> nanocomposite. Here, it can be seen that GA has only 15 wt% mass loss until 850°C, whereas  $M_7N_3$  is completely decomposed. For GA/M<sub>7</sub>N<sub>3</sub> nanocomposite, the residue is approximately 0.8 wt%, which is assigned to graphene.



**Figure S7**. DSC isotherms of  $M_7N_3$  and  $GA/M_7N_3$  composite.



**Figure S8**. The cross-sectional SEM images of the  $GA/M_7N_3$  with different rGO content. a) 1.0 wt%, b) 0.8 wt%, c) 0.5 wt%.



**Figure S9**. a) The conductivity, b) the tensile stress-strain curves, and c) the compressive stress-strain curves of GA and  $GA/M_7N_3$  nanocomposites with different RGO contents.



**Figure S10**. Conductivity changes as a function of repeated healing time for  $GA/M_7N_3$  nanocomposite with 0.8 wt% graphene at the same location.

Movie S1: The highly elastic of GA with compressive test.

Movie S2: The electrical conductivity self-healing of  $GA/M_7N_3$  with LED test.