

**Supplementary Material for**

**Understanding of effects of carboxylated groups of functionalized graphene  
oxide on the curing behavior and intermolecular interactions of benzoxazine  
nanocomposites**

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**Experimental section**

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### **E.S.1 Synthesis and purification of benzoxazine**

Benzoxazine monomers (bis (3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane, BOZ) were typically synthesized by using bisphenol A, paraformaldehyde and aniline as starting materials by employing solution methods. The mole ratio of bisphenol A (analytical grade, Dibo Chemical Reagents Corp., Russia), aniline (analytical grade, Dibo Chemica Reagents Corp., Russia), and paraformaldehyde (analytical grade, Fydsa Chemical Reagents Corp., Spain) was predetermined theoretically to be 1: 2: 4.2. Paraformaldehyde was dissolved in distilled water, and sodium hydroxide aqueous solution (Kelong Chemical Reagents Corp., Chengdu, China) was added to adjust the pH value to 8-9. Bisphenol A and toluene were added to the solvent in sequence, and aniline was dropped into the mixture at 50 °C for 1 h. Then the mixture was reflux at 80 °C for 4 h to obtain the precursor solution which was a mixture of the monomer, dimers and other oligomers. The white crystal was appeared when the obtained solution was stored overnight. The precipitate was collected and washed thoroughly with ethanol. It was purified by re-dissolving in the mixture of acetone and toluene (75: 25 v/v) and filtered to remove the insoluble part, and then stored for 2-3 days to produce the recrystallized benzoxazine monomer. After evaporating the solvent, the product was dried in a vacuum oven at 50 °C for 3 h. A very fine white powder was obtained. Caution was taken to store the synthesized and purified products in a dry and cold environment (ca.-4 °C).

### **E.S.2 Synthesis of graphene oxide (GO)**

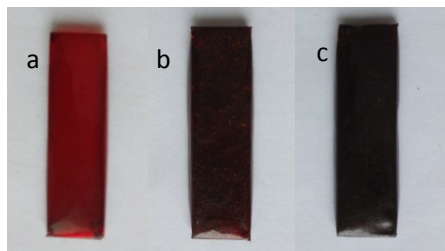
Graphene oxide was synthesized from nature graphite flake by a modified Hummers method. The size of natural graphite is 23  $\mu\text{m}$  used in this study, which is smaller than that we reported before (48  $\mu\text{m}$ ). 2g natural flake graphite (23  $\mu\text{m}$ , Guyu graphite Co., Qingdao, China) and 1g sodium nitrate ( $\text{NaNO}_3$ , analytical grade, Shanghai Chemical Reagents Corp., China), were dissolved in 46 mL sulphuric acid ( $\text{H}_2\text{SO}_4$ , analytical grade, Shanghai Chemical Reagents Corp., China), and the solution was stirred well under ice bath at 0  $^\circ\text{C}$ . Then 6 g potassium permanganate ( $\text{KMnO}_4$ , analytical grade, Shanghai Chemical Reagents Corp., China) was added to the solution as slowly as possible in order to control the reaction temperature below 20  $^\circ\text{C}$ . After adding the potassium permanganate, the mixture was stirred at 35  $^\circ\text{C}$  for 30 minutes. The suspension was diluted with 92 mL deionized water at 98  $^\circ\text{C}$  for 15 minutes, and further with 190 mL deionized water. Hydrogen peroxide solution was added to the mixture slowly until the color turned into luminous yellow. The precipitate was washed with hydrochloric acid until the filtered liquor has no sulfate ion which can be detected by  $\text{BaCl}_2$  solution, and then with deionized water to adjust the pH value to 7. Finally, the product was heated in vacuum oven at 50  $^\circ\text{C}$  for 24 hours to obtain the graphene oxide sample.

### **E.S.3 Characterization**

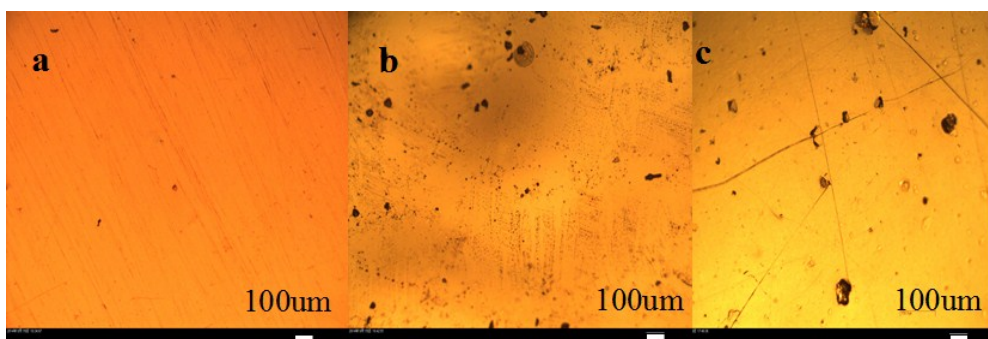
#### **Optical microscope (OM)**

The surface morphologies of the cured samples were obtained using a Leica DM2500 P polarized optical microscope (OM) at room temperature.

**Figure S.1**



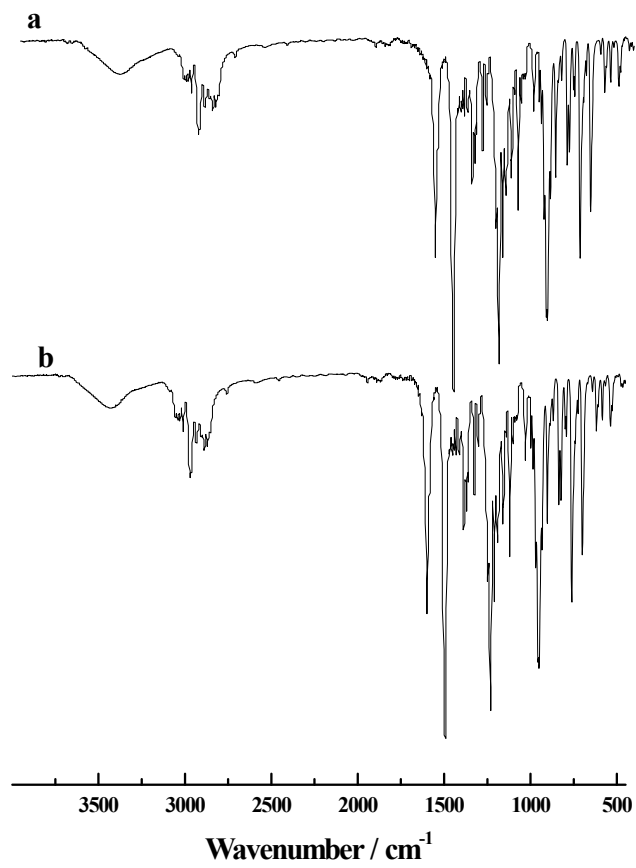
(A)



(B)

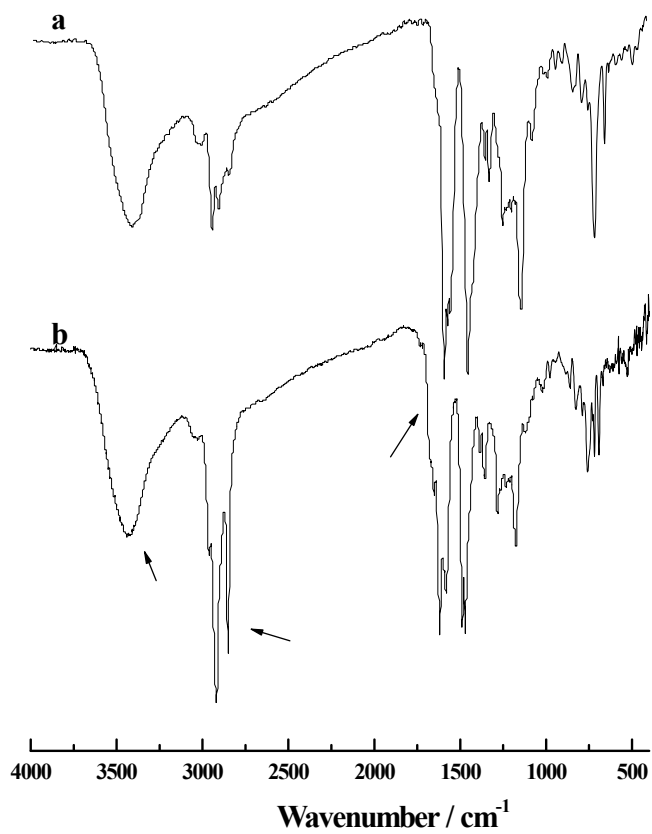
**Figure S.1 (A) the digital photos of cured samples of BOZ (a), GO/BOZ-1 (b) and GO-COOH/BOZ-1 (c); (B) the polarized OM images of BOZ (a), GO/BOZ-1 (b) and GO-COOH/BOZ-1 (c).**

**Figure S.2**



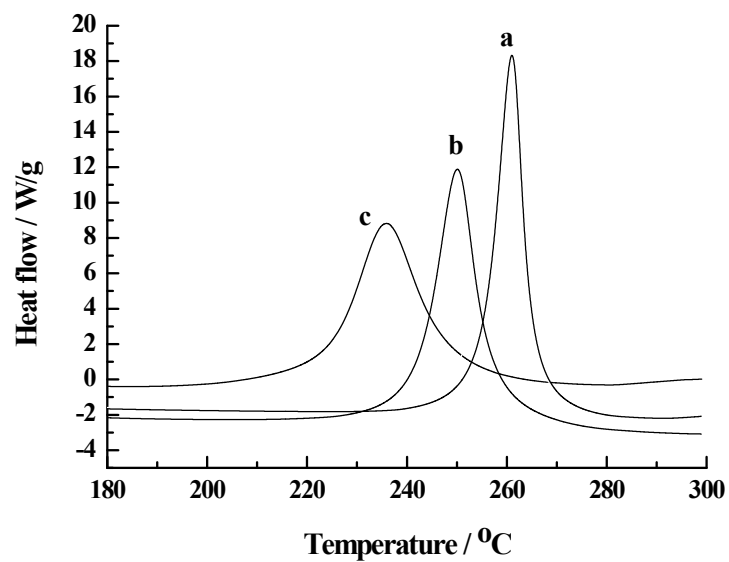
**Figure S.2 FTIR spectra of uncured G/BOZ-1 (a) and GO/BOZ-1 (b).**

**Figure S.3**



**Figure S.3 FTIR spectra of cured G/BOZ-1 (a) and GO/BOZ-1 (b).**

**Figure S.4**



**Figure S.4** The curing behaviors of BOZ (a), GO/BOZ-1 (b) and GO/BOZ-3 (c) observed by DSC.