



# Highly anisotropic graphene/boron nitride hybrid aerogels with long-range ordered architecture and moderate density for highly thermally conductive composites



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## ABSTRACT

Although graphene aerogels have great potentials in preparing heat dissipation composites on the basis of their continuous thermally conducting networks, their low density and isotropic architecture hinder further improvement of the thermal conductivity of their composites. Herein, highly anisotropic graphene/boron nitride (BN) hybrid aerogels with a long-range ordered architecture and moderate density are prepared for the first time by hydrothermally treating the suspension of graphene oxide sheets and BN nanoplatelets, air-drying the resultant hydrogels, and thermally annealing the highly anisotropic aerogels at 2000 °C. During the hydrothermal treatment, the chemically reduced graphene oxide (RGO) sheets are self-assembled into the highly anisotropic and long-range ordered network, while the BN nanoplatelets are distributed between the aligned RGO sheets to prevent the excessive volume shrinkage of the aerogel and retain its anisotropic porous structure with high porosity during the air-drying. Furthermore, the RGO/BN hybrid aerogel is thermally annealed at 2000 °C to fully remove the residual oxygen-containing groups and heal the defects on its RGO component. The thermally annealed hybrid aerogel is highly efficient in enhancing the thermal conductivity of epoxy resin, and the resultant composite exhibits an ultrahigh through-plane thermal conductivity of 11.01 W/(mK) with an excellent thermal conductivity enhancement of 277%.

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## 1. Introduction

With the rapid development of electronic devices, the management of heat dissipation has become a great challenge. Thermally conductive composites with satisfactory mechanical performances have attracted much attention not only because of their high efficiency in heat dissipation of electronics [1], but also due to their lightweight, anticorrosion and easy processing features. Currently, thermally conductive polymer composites are mainly prepared by blending of polymers with conductive fillers,

including metal particles of Ag and Cu, carbon materials of carbon nanotubes and graphene, and ceramics of hexagonal boron nitride (BN) and silicon carbide [2–7]. Among these fillers, graphene is highly promising due to its excellent intrinsic thermal conductivity and mechanical properties [8,9]. However, its polymer composites usually exhibit moderate thermal conductivities, far from the theoretical prediction, which may result from the random distribution of graphene sheets and the contact or interfacial thermal resistances between graphene sheets and at graphene/polymer interfaces [10]. It has been proved to be effective in improving the thermal conductivity by aligning conductive fillers or forming dense conducting networks [11–14]. In contrast to the randomly distributed fillers, highly aligned graphene sheets could fully utilize their high in-plane thermal conductance and form a high-quality thermal conduction network, improving further the through-plane thermal conductivity of their polymer composites [1].

Actually, a highly oriented three-dimensional (3D) graphene

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network would be an ideal thermally conducting network for fabricating thermally conductive polymer composites. Anisotropic 3D graphene aerogels or foams could be readily prepared by directional-freezing of graphene oxide (GO) suspension or reduced graphene oxide (RGO) hydrogels [15,16], where the unidirectional grown ice crystals lead to the alignment of the GO or RGO sheets. Self-assembly of GO liquid crystals is another approach to fabricate anisotropic graphene foams with long-range ordered microstructure by hydrothermal reduction [17]. It is noted that the resulting graphene aerogels and foams processed by freeze-drying usually have low densities of less than  $30 \text{ mg/cm}^3$ , which are not the best networks for high thermal conductivities that are positively correlated to the loading of conductive fillers. Usually, high-density graphene aerogels could be fabricated by using high concentration of graphene suspensions, controlling the compaction, and air-drying [18–20]. Although drying of graphene hydrogels at ambient conditions is more convenient and time-saving among these methods, the serious shrinkage of the resultant aerogels, due to their capillary force-driven structural collapse, results in solid monoliths with much high densities ( $>1 \text{ g/cm}^3$ ) and low porosities, which are difficult to be impregnated by polymers or monomers. Recently, Yang et al. fabricated isotropic graphene aerogels with moderate densities by self-assembly of aqueous mixtures of graphene oxide and high-quality graphene nanoplatelets followed by air drying [21]. The purpose of the current work is to construct highly aligned conducting 3D networks with moderate density and high porosity for thermally conductive polymer composites with excellent through-plane thermal conductivities.

Herein, highly anisotropic graphene/BN hybrid aerogels with moderate density and high porosity are prepared by hydrothermally treating the suspension of GO sheets and BN nanoplatelets to form RGO/BN hybrid hydrogels followed by air-drying. It is the first time that BN nanoplatelets are co-assembled with GO liquid crystals for the long-range ordered porous architectures. The presence of the highly conductive BN nanoplatelets efficiently prevents the volume shrinkage of the RGO/BN hydrogels at ambient conditions and benefits maintaining the long-range ordered porous architecture [22]. Besides, the density of the RGO/BN aerogels could be readily tuned by varying the initial mass ratio of GO/BN components. To fully remove the residual oxygen-containing groups and heal the defects on the RGO component, the RGO/BN aerogel is thermally annealed at  $2000 \text{ }^\circ\text{C}$  for 2 h in a flow of argon to generate graphene/BN aerogel (GBA-2000). After infiltrating with epoxy monomer and subsequent curing, the resulting epoxy/GBA-2000 composite with 4.2 wt% graphene and 39.8 wt% BN exhibits an ultrahigh through-plane thermal conductivity of  $\sim 11.01 \text{ W/(mK)}$ , which is  $\sim 72$  times higher than that of neat epoxy, indicating the high efficiency of the thermally annealed hybrid aerogels in improving the thermal conductivity of epoxy composites.

## 2. Experimental

### 2.1. Materials

Commercially available hexagonal BN flakes with lateral size of  $\sim 10 \text{ }\mu\text{m}$  were purchased from Lida Chuangxing Co. Ltd. (China). Pristine graphite was supplied from Huatai Lubricant and Sealing Co. Ltd. (China). Polyvinyl pyrrolidone (PVP) and bisphenol-A liquid epoxy monomer were bought from Sigma-Aldrich (China) and Changshu Jiafa Chemical Co. (China), respectively. Reactive diluent of 1, 2-bis(2,3-epoxypropoxy)ethane and curing agent of methyl hexahydrophthalic anhydride were purchased from Adamas Reagent Co., Ltd. (China). The curing accelerator of 2, 4, 6-tris(dimethylaminomethyl)phenol was provided by Aladdin Industrial Inc. (China). Potassium permanganate (99.5%), sodium nitrate, sulfuric

acid (98%), hydrogen peroxide (30%), hydrochloric acid (37%), and potassium hydroxide (KOH) were purchased from Beijing Chemical Factory (China).

### 2.2. Fabrication of RGO/BN hybrid aerogels and their thermal annealing

Aqueous suspension of BN was prepared by ultrasonication-assisted exfoliation of BN flakes. A certain amount of BN and 0.1 g of PVP were mixed with 50 mL deionized water for 30 min under ultrasonication using a JY99-11DN ultrasonicator (China). GO was synthesized by a modified Hummers' method [23], and its aqueous suspension ( $10 \text{ mg/mL}$ ) was obtained by ultrasonication of GO with 50 mL of deionized water for 10 min. The BN suspension was added into the aqueous suspension of GO and the mixture was homogenized for 30 min using an IKA T18 homogenizer (Germany). After 0.741 g of KOH was added, the resultant mixture was transferred into an autoclave and heated at  $160 \text{ }^\circ\text{C}$  for 3 h to get a RGO/BN hybrid hydrogel, which was immersed in deionized water for 3 days to remove the residual KOH, and dried at ambient condition to form a RGO/BN hybrid aerogel (GBA). Different initial mass ratio of GO to BN (1/5, 1/10 and 1/15) were used and the resultant hybrid aerogels were designated as GBA5, GBA10 and GBA15, respectively. For comparison, the RGO/BN hybrid hydrogels were also freeze-dried at  $-50 \text{ }^\circ\text{C}$  for 3 days to obtain fGBA. The RGO/BN hydrogel was also fabricated in the absence of KOH and its dried counterpart under ambient condition was designated as random-GBA. A calcined GBA was prepared by thermally treating GBA at  $600 \text{ }^\circ\text{C}$  for 2 h in a muffle furnace in an air atmosphere. To fully reduce its RGO component and heal its defects, GBA5 was thermally annealed at 1000, 1500 and  $2000 \text{ }^\circ\text{C}$  in a flow of argon for 2 h and the annealed GBA5 was designated as GBA-1000, GBA-1500 and GBA-2000, respectively.

### 2.3. Fabrication of thermally conductive epoxy composites

Thermally conductive epoxy composites were prepared by impregnating the mixture of the epoxy resin, the reactive diluent, the curing agent and the accelerant into an aerogel under vacuum followed by curing at  $80 \text{ }^\circ\text{C}$  for 4 h and  $120 \text{ }^\circ\text{C}$  for 2 h in an oven. For comparison, GBA was ground to powders in an agate mortar and mixed with epoxy resin in a planetary centrifugal vacuum mixer, and the mixture was then poured into a mold, cured at  $80 \text{ }^\circ\text{C}$  for 4 h followed by  $120 \text{ }^\circ\text{C}$  for 2 h to obtain an epoxy/ground GBA composite. Similarly, epoxy/calcined GBA and epoxy/BN composites were also prepared under the same impregnation and curing conditions.

### 2.4. Characterization

The morphologies of the aerogels and their epoxy composites were characterized with a JEOL JSM-7800 F scanning electron microscope (SEM), and their energy-dispersive spectra (EDS) were obtained using its energy-dispersive spectra detector. Polarized-light optical microscope (POM) images were collected with a Nikon ECLIPSE Ci-POL. Raman spectra were measured by a Renishaw inVia Raman microscopy (Britain) at a laser excitation wavelength of 514 nm. The compositions of GO and its derivatives were characterized with a ThermoVG RSCAKAB  $250\times$  high-resolution X-ray photoelectron spectroscopy (XPS). X-ray diffraction patterns (XRD) were scanned by a Rigaku D/Max 2500 X-ray diffractometer with a  $\text{Cu K}\alpha$  radiation of  $0.154 \text{ nm}$  at a generator voltage of 40 kV. Thermal conductivity was calculated by  $K = \alpha \times C_p \times \rho$ , where  $C_p$  is the specific heat capacity,  $\alpha$  is the thermal diffusivity and  $\rho$  is the density of a composite. Through-

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