## **Electronic Supplementary Information (ESI)**

## Aminopropyltrimethoxysilane-Functionalized Boron Nitride Nanotube Based Epoxy Nanocomposites with Simultaneous High Thermal Conductivity and Excellent Electrical Insulation

Chi Zhang, Rongjin Huang,\* Yongguang Wang, Zhixiong Wu, Shibin Guo, Hua Zhang, Jian Li, Chuanjun Huang, Wei Wang, and Laifeng Li\*

**Preparation of BNNTs by BOCVD**: A vertical induction furnace was used. First, 1.5 g mixture of B and MgO powders with molar ratio of 1:1 was loaded into a BN crucible and placed at the bottom of the BN reaction chamber. The furnace was then heated to 1300 °C under a protecting Ar flow. At this temperature, B reacted with MgO to form  $B_2O_2$  and Mg vapors:  $2B(s) + 2MgO(s) \rightarrow B_2O_2(g) + 2Mg(g)$ . The vapors were argon-transported upwardly and a flow of NH<sub>3</sub> was then introduced to produce BNNTs:  $B_2O_2(g) + 2 NH_3(g) \rightarrow 2BN(s) + 2H_2O(g) + H_2(g)$ . After reacting for 2 h, about 300 mg white-colored products were collected and washed with HCl and deionized water.

**Preparation of APS-functionalized BNNTs:** First, the purified BNNTs were suspended in a 5 M NaOH solution under 1 h sonication, followed by a reflux at 120 °C for 24 h. After cooling, the BNNTs were filtered and washed with deionized water several times. The BNNTs were dried in a vacuum oven at 80 °C for 12 h and then cooled to room temperature. Next, an appropriate amount of APS was added to deionized water and stirred at 60 °C for 1 h. The aforementioned BNNTs were then added to the solution and refluxed at 80 °C for 12 h. After cooling, the product (BNNT-APS) was filtered, washed with deionized water, and then vacuum dried at 80 °C for 12 h.

**Preparation of the epoxy/BNNT-APS nanocomposites:** The prepared BNNT-APS was dispersed in an epoxy (DGEBF)/curing agent (DETD)/acetone solution (Scheme S1) by sonication for 30 min in an ice bath. After that, the mixture solution was stirred and degassed under vacuum at 60 °C for 30 min to remove the solvent (acetone). The epoxy/BNNT mixture was then injected into the preheated mold by RTM method. The mold was put into a vacuum oven to cure the composites, followed by a post-curing step at 80 °C for 24 h and 130 °C for 12 h.

**Characterizations:** TEM image of BNNTs dispersed in ethanol was obtained from a JEM-2100F instrument. The morphology of BNNTs and the epoxy/BNNT-APS nanocomposites were observed with a Hitachi S-4800 field-emission scanning electron microscope (SEM). X-ray diffraction (XRD; D8 focus), Raman spectroscopy (inVia-Reflex) and X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi) were used to characterize the BNNTs synthesized by BOCVD. Fourier transform infrared (FTIR) data was collected by an Excalibur 3100 instrument. Thermogravimetric analysis (TGA; Diamond TG/DTA) was used to study the weight loss of BNNTs. A temperature increase rate was set at 20 °C/min in the temperature range of 25-800 °C and all the processes were carried out under N<sub>2</sub> atmosphere. Dynamic mechanical analysis (DMA)

was performed on a DMA800 instrument at a frequency of 1 Hz. Thermal conductivity  $(\lambda)$  was measured using the steady state method (Scheme S2) over the temperature range from 77K to 298K and calculated by the following equation:  $\lambda = Q \frac{L}{\Delta T \times S}$ , where Q is the power supplied, L is the distance of the sample, S is the section area of the sample, and  $\Delta T$  is the measured temperature difference. Dielectric constant ( $\epsilon$ ) and dielectric loss (tan $\delta$ ) were measured by a TH26008A test fixture. Linear thermal expansion ( $\Delta L/L$ ) was measured through the strain gauge technique over the temperature range from 77K to 273K and the CTE was calculated as the slope of the  $\Delta L/L$  – Temperature curve.



Scheme S1 Chemical structures of (a) DGEBF and (b) DETD.



Scheme S2 Schematic of equipment for thermal conductivity measurement.



Fig. S1 Energy dispersive spectroscopy of BNNTs synthesized by BOCVD. The presence of C and Cu is attributed to the carbon-coated copper grid used in the sample preparation.



Fig. S2 X-ray photoelectron spectroscopy of BNNTs: (a) B 1s, (b) N 1s and (c) O 1s spectra.



Fig. S3 Dynamic mechanical analysis of the epoxy/BNNT-APS nanocomposites: (a)

storage moduli and (b) loss factor.