Supporting Information

Bridge-type 1D/2D boron nitride enhances the thermal management capability of polymer composites

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Experimental Section

1. Chemicals

Boron nitride (BN) powder (10 μm diameter) was purchased from Dandong Rijin Co., Ltd. One-dimensional boron nitride materials (containing BNNFs\BNNTs) was sponsored by Zhejiang Boronmatrix New Material Technology Co., Ltd. PAN (M_w = 150,000 g/mol) were provided by Tianjin Heowns Co., Ltd. Hydrochloric acid and *N*, *N*-dimethylformamide (DMF, 99%) were obtained from Aladdin.

2. Preparation of BNNFs

BNNFs were synthesized by a typical boron oxide chemical vapor deposition (BOCVD) method. First, a mixed powder of boron powder and magnesium oxide (with molar ratio of 4:1) (250 mg) was loaded into a corundum combustion boat and placed in a tube furnace. Subsequently, the tube furnace temperature was raised to 1400 °C

under the protection of argon at 200 standard cubic centimeters per minute (sccm). The argon was then turned off and 200 standard cubic centimeters per minute (sccm) of NH_3 was introduced and maintained for 2 hours. Finally, NH_3 was turned off and cooled to room temperature at 200 sccm argon to obtain the BNNFs. Next, impurities were removed from the obtained BNNFs. Take 100 mg of the above unpurified one-dimensional structure boron nitrides in a glass bottle and add 20 ml of 17 wt% hydrochloric acid, and place the above glass bottle in a 60 ° C oven. After 24 h, the liquid and insoluble materials in the bottle were centrifuged at 9000 rpm, and the insoluble materials after centrifugation were oven dried to obtain one-dimensional nanostructured boron nitrides with the predominance of BNNFs.

3. Preparation of BNNSs

BNNSs were prepared by liquid phase stripping method. First, a certain amount of BN powder and 7.2 g DMF were mixed and stirred in a glass vial. Subsequently, the mixture solution was sonicated for 60 min (the output power is 20%) using an ultrasonic cell disintegrator (SCIENTZ). Finally, BN powder was exfoliated to obtain BNNSs. The obtained BNNSs do not need to be taken out or separated from the glass vial and can be directly used in the preparation of the precursor solution for subsequent electrospinning.

4. Preparation of BNNSs/PAN composites and BNNSs/BNNFs/PAN composites

The preparation of electrospun BNNSs/PAN and BNNSs/BNNFs/PAN composites is illustrated in Fig. S1. The electrospinning precursor solution was prepared with polyacrylonitrile as electrospinning assistant and DMF as solvent. The ratio of the electrospinning precursor solution was showed in Table S1. The electrospinning precursor solution was obtained by adding the BNNFs obtained after pretreatment into the above-mentioned glass vial containing BNNSs and DMF. And

then using an ultrasonic cell disintegrator to sonicate for 10 min (the output power is 20%). Next, 0.8 g of PAN was added to the above glass vial and stirred for 12 h to obtain the electrospinning precursor solution. The electrospinning equipment was purchased from TECH NOVA (China). During electrospinning, the spinning voltage was controlled at 12−15 kV, the operating distance between the spinneret and drum was 20 cm, injection rate was set at 0.02 mL/min for 4 h using a syringe, and the rotating speed of drum was collected at 50 rpm. The temperature was set at 25 ◦C, and the relative humidity were controlled from 30% to 50%. After then, the as-prepared composites were dried (60 ◦C for 12 h) and flatten (60 ◦C for 2 h). The BNNSs/PAN composites and BNNSs/BNNFs/PAN composites was named bs-x and bsf-x-y respectively, where x (wt%) was the BNNSs mass fraction and y (wt%) was the BNNFs mass fraction in composites, and specific numbering rules were shown in Table S1.

5. Characterization

The morphology of BNNSs, BNNFs, bs-x, and bsf-x was observed via field-emission SEM (FESEM, Hitachi 8100, Japan). The morphology of bs-x and bsf-x was obtained by TEM (Tecnai G2 F20 S-TWIN, FEI, USA). The change of BNNSs before and after exfoliation and the BNNFs before and after pretreatment was further characterized by XRD (Lab X, SHIMADZU, Japan), Raman (LabRAM HR Evolution), and FTIR (NICOLET iS10, Thermo Scientifc, U.S.A.). Thermogravimetric measurement (TGA) was carried out on NETZSCH STA 449 C instrument (Germany). The thermal conductivity (K) was measured and calculated by a laser flash thermal analyzer (NETZSCH LFA-447, Germany) and the following equation: $K = \alpha$ (thermal diffusivity) × Cp (specific heat capacity) × ρ (density). The practical heat dissipation effect of the as-prepared composites was simulated and evaluated via LED (5 W). The

LED surface temperature was recorded by an infrared thermograph (FOTRIC-345, China).

Table S1. Materials required for composites preparation and nomenclature rules.

sample name	Mass of DMF (g)	Mass of PAN (g)	Mass of BNNS (g)	Mass of BNNF (g)	Mass fraction of BNNS in composites	Mass fraction of BNNF in composites	Mass fraction of total BN in composites
bs-10	7.2	0.8	0.0889		10%		10%
bs-20	7.2	0.8	0.2000		20%		20%
bs-30	7.2	0.8	0.3429		30%		30%
bs-40	7.2	0.8	0.5333		40%		40%
bs-50	7.2	0.8	0.8000		50%		50%
bsf-10	7.2	0.8	0.0178	0.0178	8%	2%	10%
bsf-20	7.2	0.8	0.0200	0.0200	18%	2%	20%
bsf-30	7.2	0.8	0.0229	0.0229	28%	2%	30%
bsf-40	7.2	0.8	0.0267	0.0267	38%	2%	40%
bsf-50	7.2	0.8	0.0320	0.0320	48%	2%	50%
bsf-29-1	7.2	0.8	0.3314	0.0114	29%	1%	30%
bsf-27-3	7.2	0.8	0.3086	0.0343	27%	3%	30%
bsf-25-5	7.2	0.8	0.2857	0.0571	25%	5%	30%

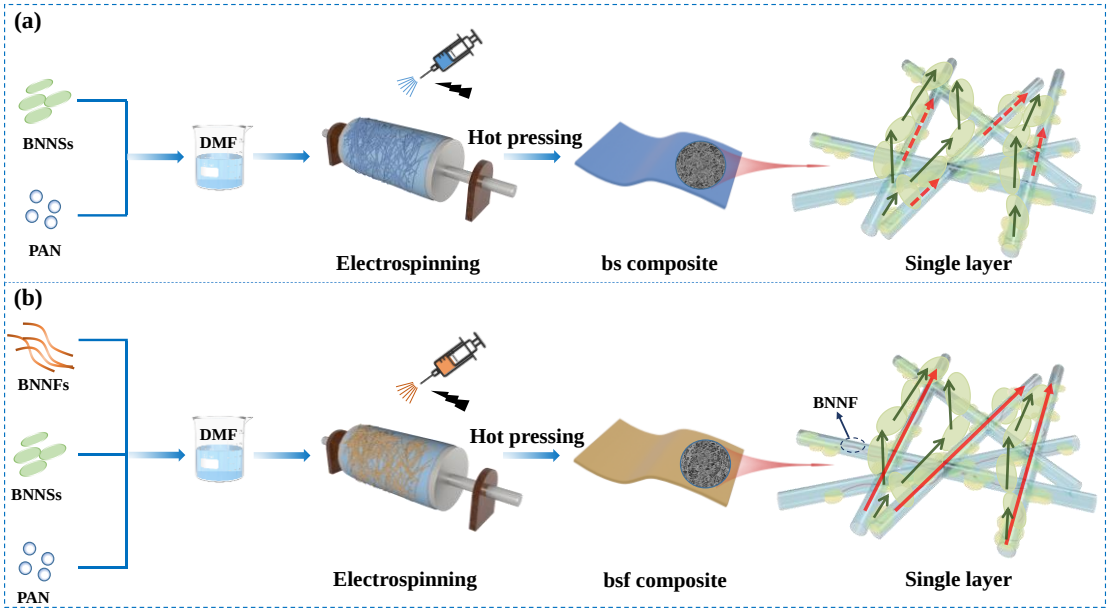

Fig. S1 Schematic illustrations of the fabrication routes of (a) bs composite and (b) bsf composite.

(Note: the arrows in a single direction (upward) indicate the direction of heat flow within the fibers)

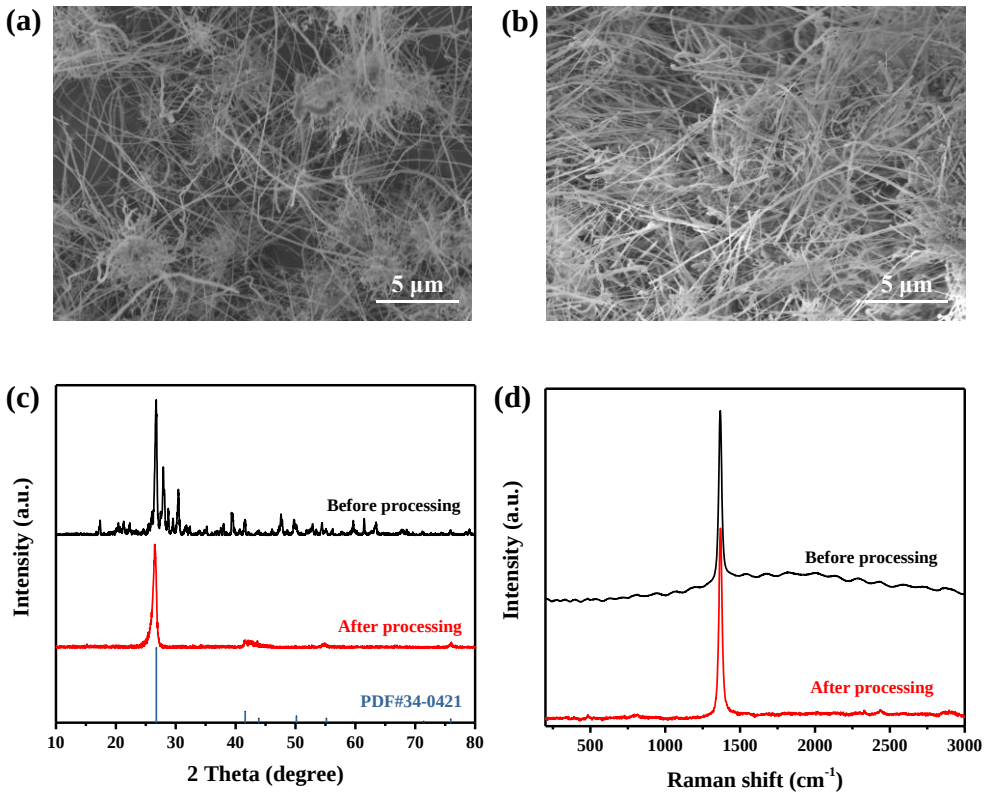

Fig. S2 SEM images of (a) original BNNFs and (b) BNNFs after pretreatment; (c) XRD pattern of

the BNNFs before and after pretreatment and the h-BN standard powder diffraction card; (d) Raman pattern of the BNNFs before and after pretreatment.

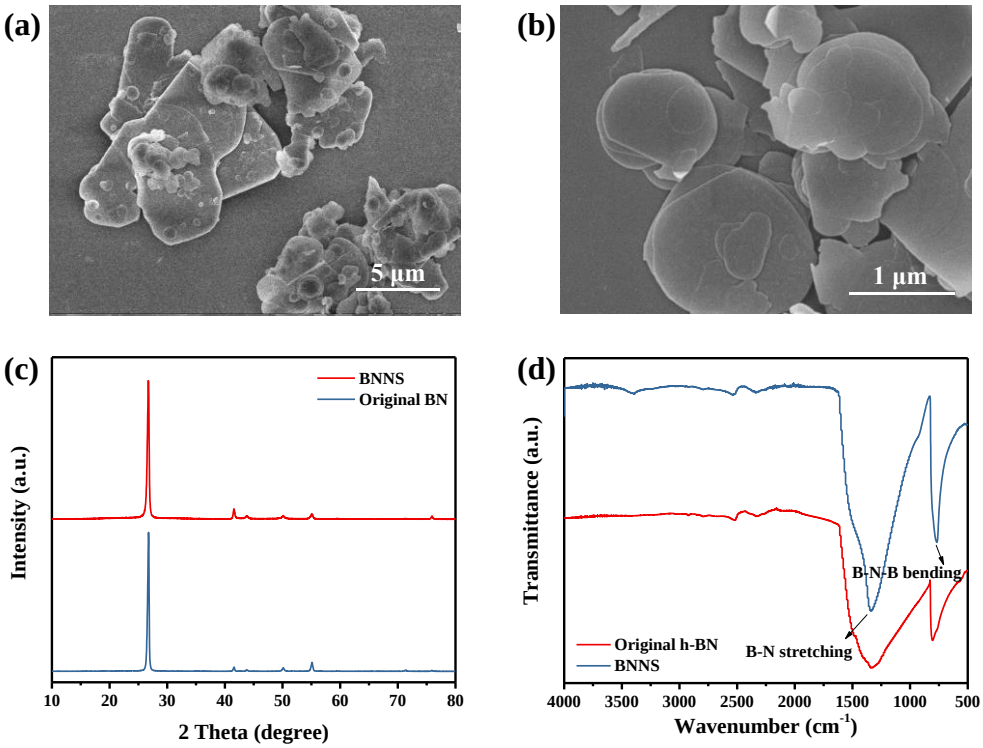

Fig. S3 SEM images of (a) the pristine BN and (b) the exfoliated BNNSs; (c) XRD pattern of the pristine BN and the exfoliated BNNSs; (d) FTIR pattern of the pristine BN and the exfoliated BNNSs.

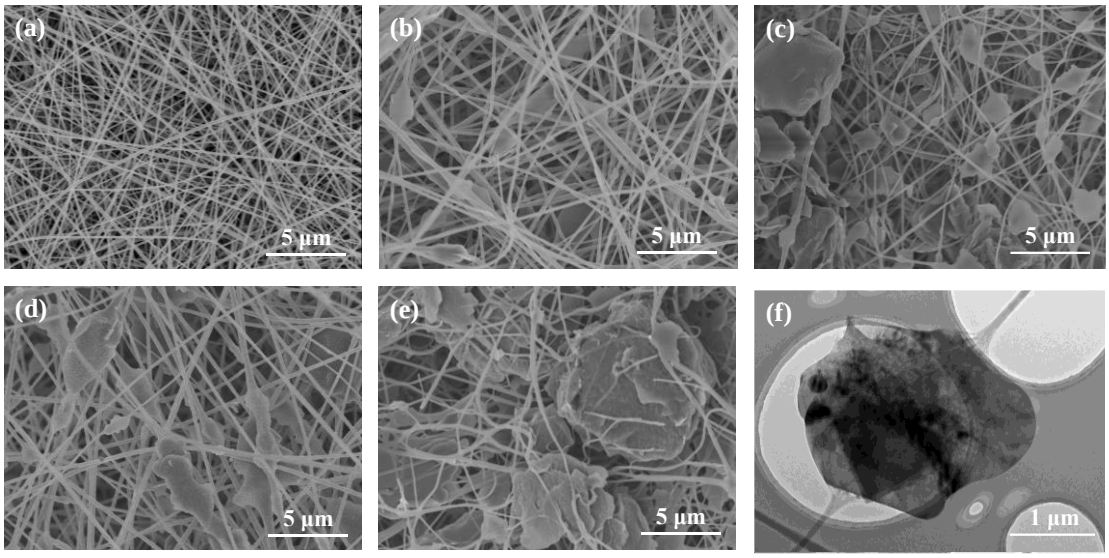

Fig. S4 SEM images of (a) PAN fibers; SEM images of the bs composites of (b) bs-20 and (c) bs-50; SEM images of the bsf composites of (d) bsf-20 and (e) bsf-50; TEM images of (f) the isolated BNNSs in the bsf composite fibers.

Table S2 Custom calculation formulas

Sequence number	Calculation formula	Related note
(1)	$\alpha_1 = \frac{\lambda_{bs\ composites} - \lambda_{PAN}}{\lambda_{PAN}}$	$\lambda_{bs}, \lambda_{PAN}$ ——The thermal conductivity of the bs composites and pure PAN
(2)	$\beta_1 = \frac{\alpha_1}{x}$	x — — The mass fractions of BNNSs

(3)	$\alpha_2 = \frac{\lambda_{bsf\ composites} - \lambda_{bs\ composites-30}}{\lambda_{bs\ composites-30}}$	λ_{bsf}, $\lambda_{bs\text{-}30}$ —— The thermal conductivity of the bsf composites with different proportions of hybrid fillers under the total filler amount of 30 wt% and the bs composites with the BNNSs content at 30 wt%
(4)	$\beta_2 = \frac{\alpha_2}{y}$	y — — The mass fractions of BNNFs.
(5)	$\alpha_3 = \frac{\lambda_{bsf\ composites-2} - \lambda_{PAN}}{\lambda_{PAN}}$	$\lambda_{bsf\ \ composites\text{-}2}$, λ_{PAN} — — The thermal conductivity of the bsf composites with different total BN filler contents (keeping the BNNF content at 2 wt%) and pure PAN
(6)	$\beta_3 = \frac{\alpha_3}{z}$	z ——The mass fractions of BN
(7)	$\alpha_4 = \frac{\lambda_{bsf composites-2} - \lambda_{bs\ composites}}{\lambda_{bs\ composites}}$	$\lambda_{bsf\text{-}2}$, $\lambda_{b\ s}$ —— The thermal conductivity of the bsf composites with different total BN filler contents (keeping the BNNF content at 2 wt%) and the bs composites.
(8)	$\beta_4 = \frac{\alpha_4}{z}$	z ——The mass fractions of BN.

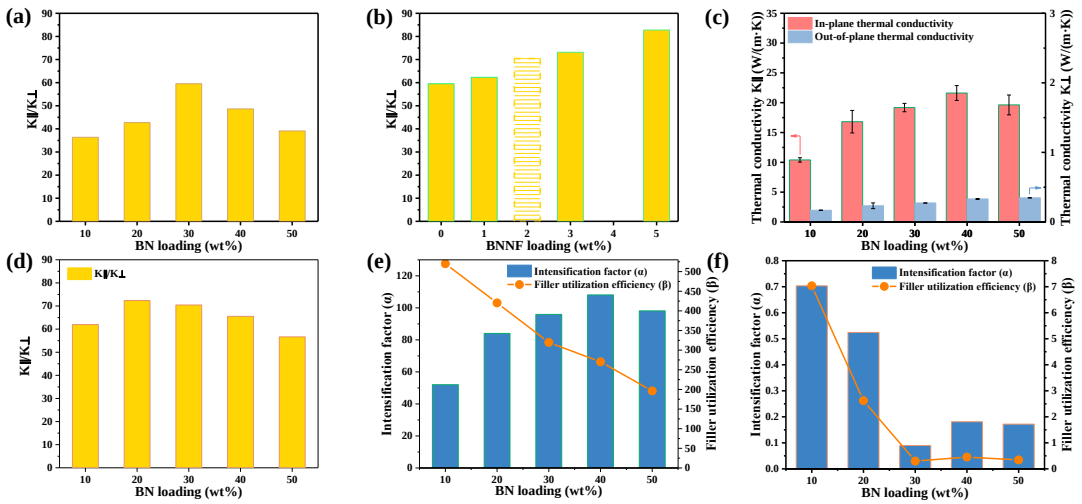

Fig. S5 Anisotropies in thermal conductivities of (a) the bs composite, and (b) the bsf composite with a total filler content of 30 wt%; Thermal properties of the bsf composite with increasing levels of BN content (keeping the BNNF content at 2 wt%) of (c) thermal conductivity, (d) anisotropies in thermal conductivities, (e) the in-plane thermal conductivity improvement factor (α3) and BN utilization efficiency (β3), (f) The in-plane thermal conductivity improvement factor (α4) and BN utilization efficiency (β4) relative to the bs composite after the introduction of 2 wt% BNNF.

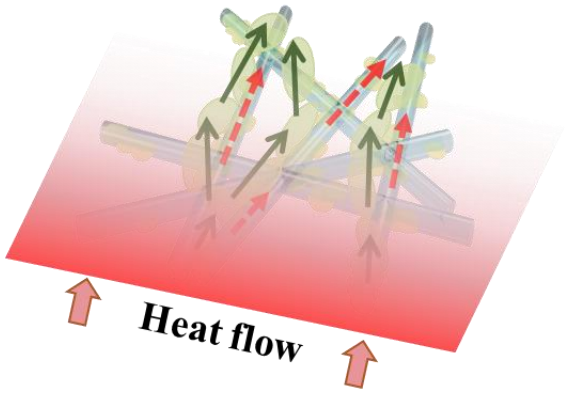

Fig. S6 Schematic diagrams of the thermal conductivity mechanism of the bs composite.

Table S3 Theoretical models.

Name	Basic hypothesis	Calculation formula
Series	heat transfer takes place in the matrix and filler in turn	$\frac{1}{\lambda}=\frac{V_2}{\lambda_2}+\frac{V_1}{\lambda_1}$
Parallel	heat is transferred through two independent channels of filler and matrix in the same time	$\lambda = V_2\lambda_2 + V_1\lambda_1$
Maxwell Eucken HS$^+$	the matrix particles are randomly embedded in the filler without interaction	$\lambda = \lambda_2 \frac{2\lambda_2 + \lambda_1 + 2(\lambda_1 - \lambda_2)V_1}{2\lambda_2 + \lambda_1 - (\lambda_1 - \lambda_2)V_1}$
Maxwell Eucken HS$^-$	the filler particles are randomly embedded in the matrix without interaction	$\lambda = \lambda_1 \frac{2\lambda_1 + \lambda_2 - 2(\lambda_1 - \lambda_2)V_2}{2\lambda_1 + \lambda_2 + (\lambda_1 - \lambda_2)V_2}$

Note:

λ, λ_1, λ_2——The thermal conductivity of composite, matrix and filler

V_1, V_2——The volume fraction of matrix and filler