Supporting Information

Fabrication of Oriented hBN Scaffolds for Thermal Interface Materials

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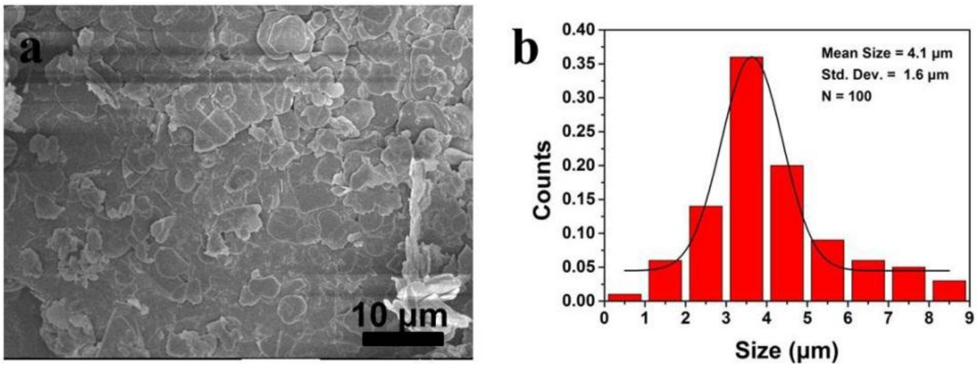

Figure S1. (a) SEM image and (b) lateral size distribution of hBN microplatelets.

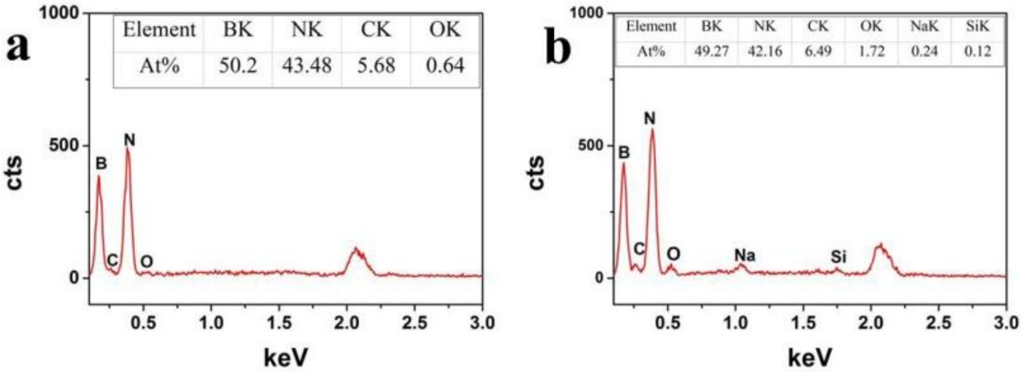

Figure S2. EDS results of (a) the pristine hBN and (b) the hBN Scaffold. The signals from Na_2SiO_3 can be detected in the scaffold.

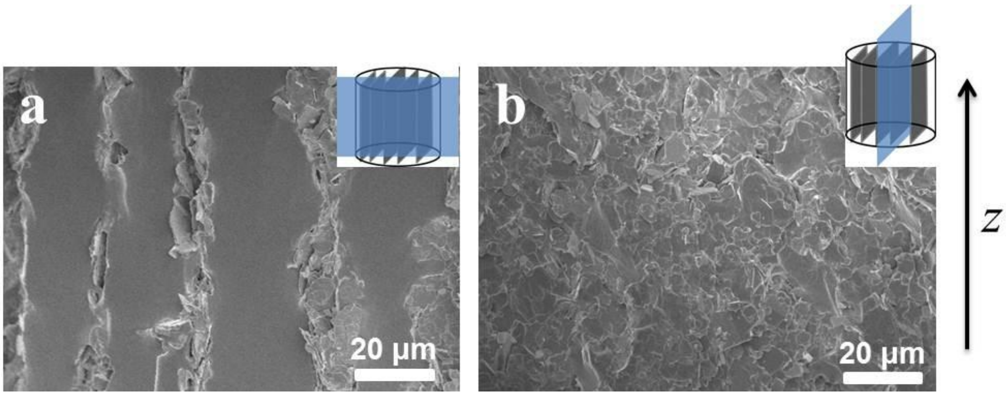

Figure S3. Cross section SEM images of Composite A2 along *z* direction.

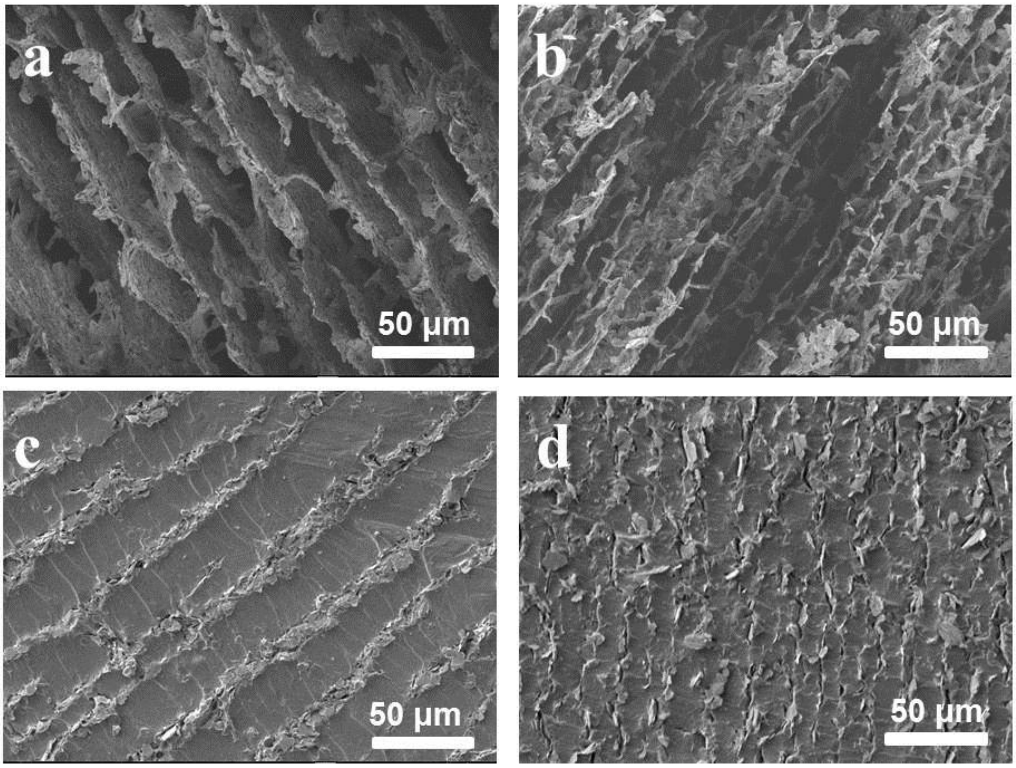

Figure S4. Cross section SEM images of (a) Scaffold a1, (b) Scaffold b1, (c) Composite A1 and (d) Composite B1.

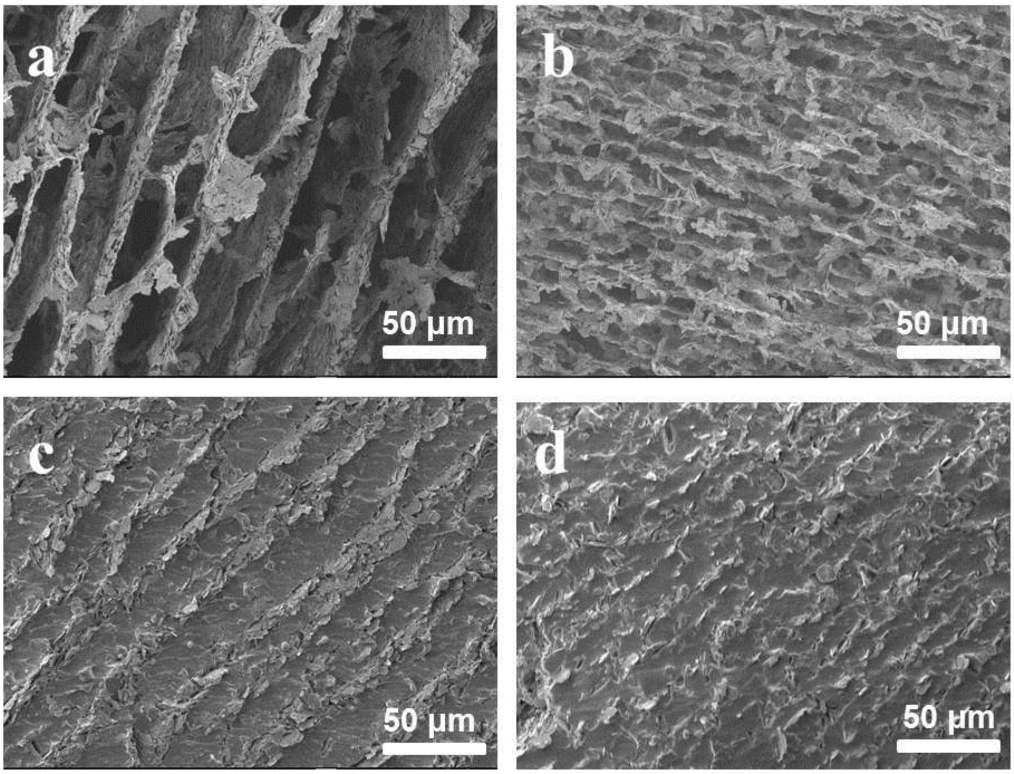

Figure S5. Cross section SEM images of (a) Scaffold a3, (b) Scaffold b3, (c) Composite A3 and (d) Composite B3.

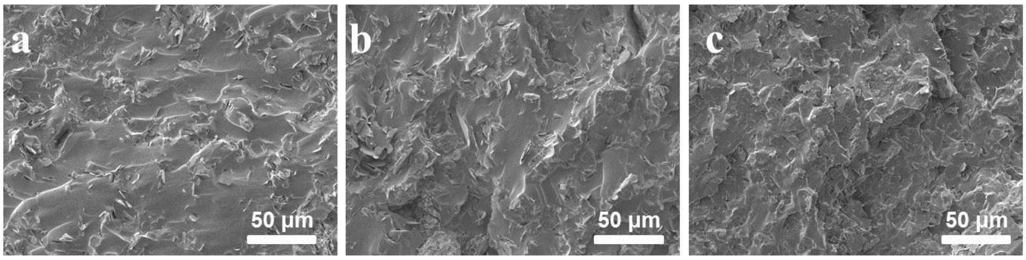

Figure S6. Cross section SEM images of (a) Composite C1, (b) Composite C2 and (c) Composite C3, in which the *z* direction was out of the page.

Calculation of content of hBN filler in hBN/PDMS composites.

The density of PDMS donated as ρ_{PDMS} was 1.06 g cm^{-3}, and the real density of the hBN scaffold donated as ρ_{hBN} was 2.37 g cm^{-3}, the volume fraction (V) of hBN in the composite was calculated by the equation:

$$\rho_{hBN} \times V + \rho_{PDMS} \times (1 - V) = \rho_{composite} \quad (1)$$

The weight fraction (M) was calculated by the equation:

$$M = \rho_{hBN} \times V / \rho_{composite} \quad (2)$$

The detected density of composite A and the calculated volume fraction and weight fraction were listed in Table S1.

Table S1. The detected density, the calculated volume fraction and weight fraction of Composite A.

	Composite A1	Composite A2	Composite A3
ρ (g cm^{-3})	1.15	1.18	1.21
V (vol%)	7.58	9.84	12.1
M (wt%)	15.6	19.8	23.7

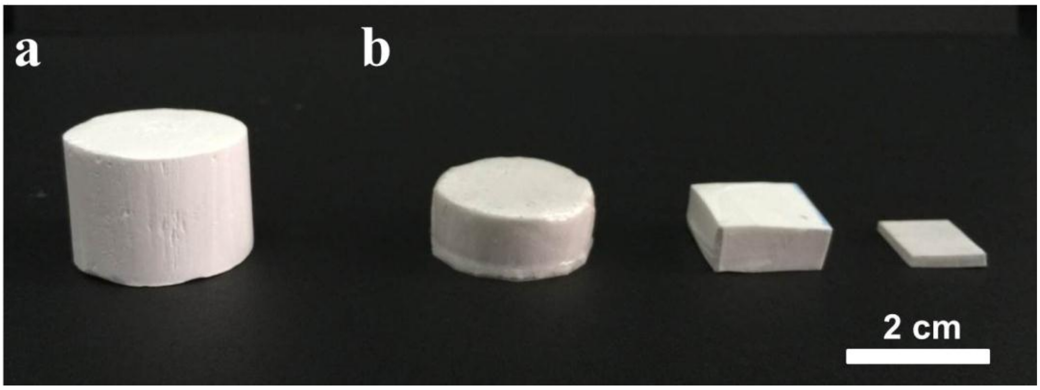

Figure S7. Photos of (a) Scaffold a2 and (b) Composite A2 with different shapes and thicknesses.

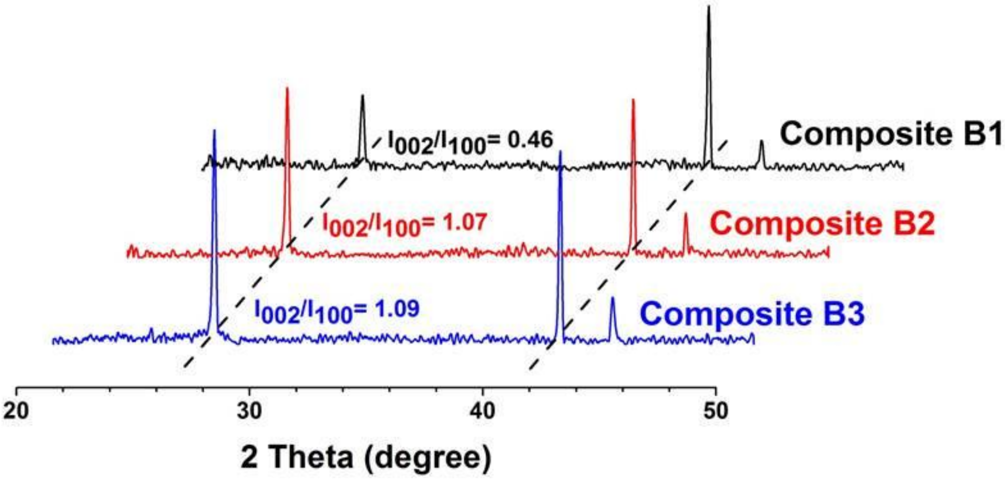

Figure S8. XRD patterns of Composite B.

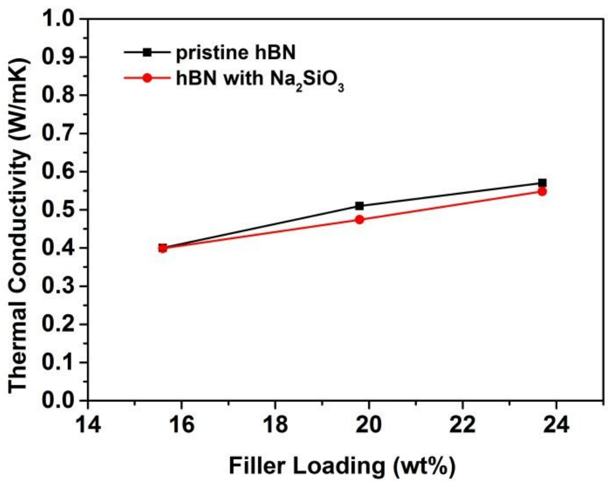

Figure S9. The thermal conductivity of Composite C containing pristine hBN and hBN-Na_2SiO_3, respectivley.

Effective Medium Approximation for the prediction of thermal conductivity of composites.

1. Basic framework

Referring to the effective medium approximation (EMA) theory, the effective out-of-plane thermal conductivity of the composites can be calculated by:

$$k_{33}^{*} = k_m \frac{1+f[\beta_{11}(1-L_{11})(1-<\cos^2\theta>)+\beta_{33}(1-L_{33})<\cos^2\theta>]}{1-f[\beta_{11}L_{11}(1-<\cos^2\theta>)+\beta_{33}L_{33}<\cos^2\theta>]} \tag{3}$$

With

$$\beta_{ii} = \frac{k_{ii}^{c}-k_m}{k_m+L_{ii}(k_{ii}^{c}-k_m)} \tag{4}$$

$$< \cos^2\theta >= \frac{\int \rho(\theta)\cos^2\theta \sin\theta d\theta}{\int \rho(\theta)\sin\theta d\theta} \quad (5)$$

Where 11 and 33 represent in-plane and out-of-plane directions, respectively; θ is the angle between the composite axis X_3 and the local particle symmetric axis $X_3^{'}$; $\rho(\theta)$ is a distribution function describing the orientation of the particles; f is the volume fraction of the particles; k_{ii}^{c} is the equipment thermal conductivity along the ii symmetric axis of the unit cell of the composites:

$$k_{ii}^{c} = {k_p}\Big/\left(1 + \frac{\gamma L_{ii} k_p}{k_m}\right) \quad (6)$$

Where k_p and k_m are the thermal conductivities of the particles and matrix, respectively; L_{ii} is the geometrical factor dependent on the shape of particle, which is platelet here:

$$L_{11} = \frac{p^2}{2(p^2-1)} + \frac{p}{2(1-p^2)^{3/2}}\cos^{-1}p \quad (7)$$

$$L_{33} = 1 - 2L_{11} \quad (8)$$

$$p=a_3/a_1 \quad (9)$$

where p is the aspect ratio of particles, a_3 and a_1 are the thickness and diameter of the particles, respectively. For platelets, $p < 1$.

$$\gamma = (1 + 2p)R_b k_m/t \quad (10)$$

where R_b is thermal boundary resistance between the particles and matrix.

2. Extraction of R_b for Composite C

For Composite C of which the microplatelets were randomly oriented, $< \cos^2\theta >= 1/3$, Equation (S3) could be reduced to:

$$k_{33}^{*} = k_m \frac{3+f[2\beta_{11}(1-L_{11})+\beta_{33}(1-L_{33})]}{3-f[2\beta_{11}L_{11}+\beta_{33}L_{33}]} \quad (11)$$

k_p, k_m, a_3 and a_1 are known parameters. In this research: $k_p = 600\ \mathrm{W/mK}$, $k_m = 0.15\ \mathrm{W/mK}$, $a_3 = 100\ \mathrm{nm}$, $a_1 = 4\ \mu\mathrm{m}$.

Therefore, R_b is the only unknown parameter in the calculation of k_{33}^{*}. R_b can be extracted by fitting the experimental data to the predicting results. The fitting result was shown in Figure S9, and R_b is approximately $420 \times 10^{-9}\ \mathrm{m^2K/W}$.

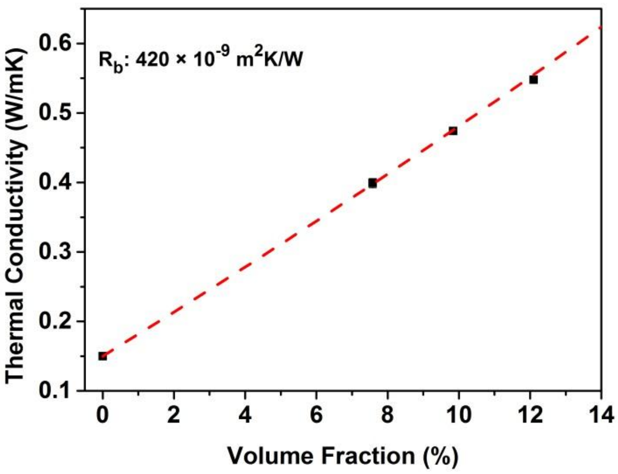

Figure S10. Data fitting to extract R_b of Composite C.

3. Extraction of R_b for Composite B

For Composite B of which most of the microplatelets were vertically oriented, $< \cos^2\theta > \geq 0$, Equation (S3) could be reduced to:

$$k_{33}^* = k_m \frac{1+f\beta_{11}(1-L_{11})}{1-f\beta_{11}L_{11}} \tag{12}$$

The fitting result was shown in Figure S10, and R_b is approximately 60 × 10^{-9} m^2K/W.

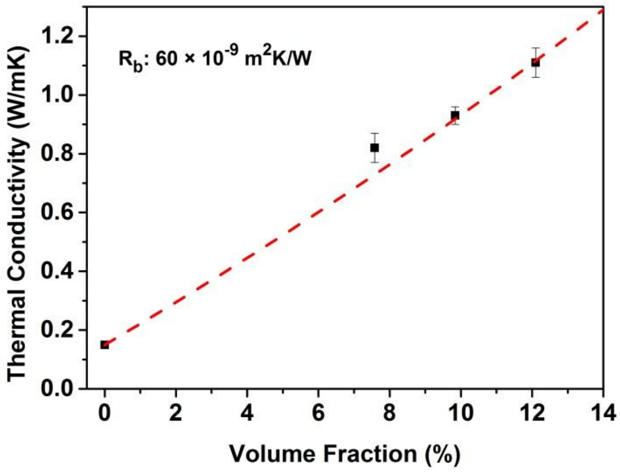

Figure S11. Data fitting to extract R_b of Composite B.

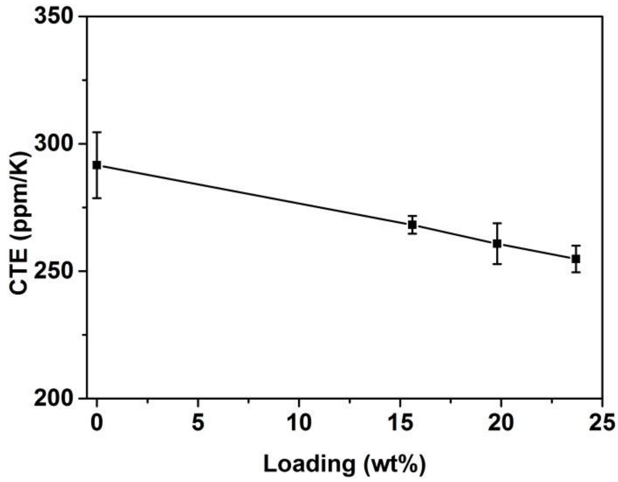

Figure S12. CTEs of Composite A perpendicular to z direction.

Table S2. Young's Modulus of PDMS and Composite A.

	PDMS	Composite A1	Composite A2	Composite A3
Young' Modulus (MPa)	1.8 ± 0.1	16.8 ± 0.1	24.6 ± 1.0	29.7 ± 2.8