Supplementary Information

Highly thermally conductive and electrically insulating polymer nanocomposites with boron nitride nanosheet/ionic liquid complexes

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Contents:

1. Preparation of BNNS/IL/PC composite films (BNNS content, 50 wt%)

First, 157.1 mg of BNNS/1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) complex, containing 150 mg of BNNS and 7.1 mg of [bmim][PF_6], was added to 1.0 g of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). After the mixture was bath-sonicated for 20 min, it was mixed with PC/HFIP (142.9 mg/2.0 g) solution under bath-sonication for 30 min. The resulting BNNS/[bmim][PF_6]/PC/HFIP solution was spread on a glass plate. Then HFIP was naturally volatilized for at least 24 h. BNNS/[bmim][PF_6]/PC (BNNS content, 50 wt% ≈ 35 vol%) composite films with approx. 0.3 mm thickness were obtained after further drying at 50 °C for 12 h under vacuum to remove the residual HFIP.

2. Preparation of h-BN/PMMA composite films (h-BN content, 2 wt%)

After 60.0 mg of h-BN (UHP-1K) was added to 2.0 g of acetone, it was bath-sonicated for 20 min. The h-BN/acetone mixture was mixed with a PMMA/acetone (3.0 g/8.0 g) solution under bath-sonication for 30 min. The resulting h-BN/PMMA/acetone solution was spread on a glass plate. Acetone was naturally volatilized for at least 24 h. h-BN/PMMA (h-BN content, 2 wt% ≈ 1.1 vol%) composite films with approx. 0.3 mm thickness were obtained after further drying at 50 °C for 12 h under vacuum to remove residual acetone.

3. Supplementary tables and figures

Table S1 Thermal conductivities of the BNNS/IL/PMMA composites in this study, and previously reported BNNS/polymer composites.[S1–S15]

BNNS/polymer composites	Polymer type	BNNS content	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)		Year [reference]
			Through-plane	In-plane	
BNNS/IL/PMMA	Thermoplastic	50 wt% (≈ 34 vol%)	5.4	7.3	This work
BNNS/PMMA		14 wt%	1.2	–	2017 [S1]
BNNS/PMMA		23 wt%	2.6	–	2012 [S2]
BNNS/polyrhodanine/styrene-butadiene rubber		27.5 vol%	0.75	1.5	2017 [S3]
BNNS/polyamide-6		40 wt%	2.5	–	2017 [S4]
BNNS/poly(vinyl alcohol)		50 wt%	~0.85	~7	2016 [S5]
microplasma-treated BNNS/poly(vinyl alcohol)		50 wt%	~2.1	13	
BNNS/polyamide-66		50 vol%	~1.2	–	2013 [S6]
BNNS/poly(vinyl alcohol)		50 vol%	–	13	2012 [S7]
BNNS/polystyrene		67 vol%	1.1	–	2015 [S8]
BNNS/HSO_3Cl/PMMA		80 wt%	10.2	14.7	2016 [S9]
BNNS/poly(vinyl alcohol)		94 wt%	–	6.9	2015 [S10]
BNNS/Ag nanoparticle/liquid crystalline epoxy	Thermoset	25.1 vol%	–	12.6	2016 [S11]
BNNS/epoxy		40 wt%	6.0	–	2014 [S12]
BNNS/epoxy		50 vol%	9.8	–	2015 [S13]
BNNS/epoxy		50 vol%	–	30	2012 [S7]
BNNS/graphene oxide/polyimide		50 wt%	2.1	–	2014 [S14]
BNNS/epoxy		61 wt% (= 42.8 vol%)	3.6	–	2014 [S15]

Table S2 Surface elemental compositions (atomic %) of BNNS/[bmim][PF_6] complex, and h-BN measured using X-ray photoelectron spectroscopy (XPS) survey scans.

	C	B	N	O	P	F	Si	S
BNNS/[bmim][PF_6] complex 2a[a]	12.6	38.5	40.3	3.39	0.31	2.63	2.32	0.0
h-BN[a,b]	8.60[c]	42.5	44.5	2.90[c]	0.0	0.0	1.60[c]	0.0

[a] Dried under vacuum at 80 °C for 12 h before XPS measurements. [b] Grade: UHP-1K, Showa Denko K. K., Japan, BN purity: 99.9%. [c] Surface contamination and adsorption of organic substances usually observed on BN surfaces. XPS sample surfaces are easily contaminated by impurities such as carbon and oxygen atoms from the atmosphere.[S9,S16]

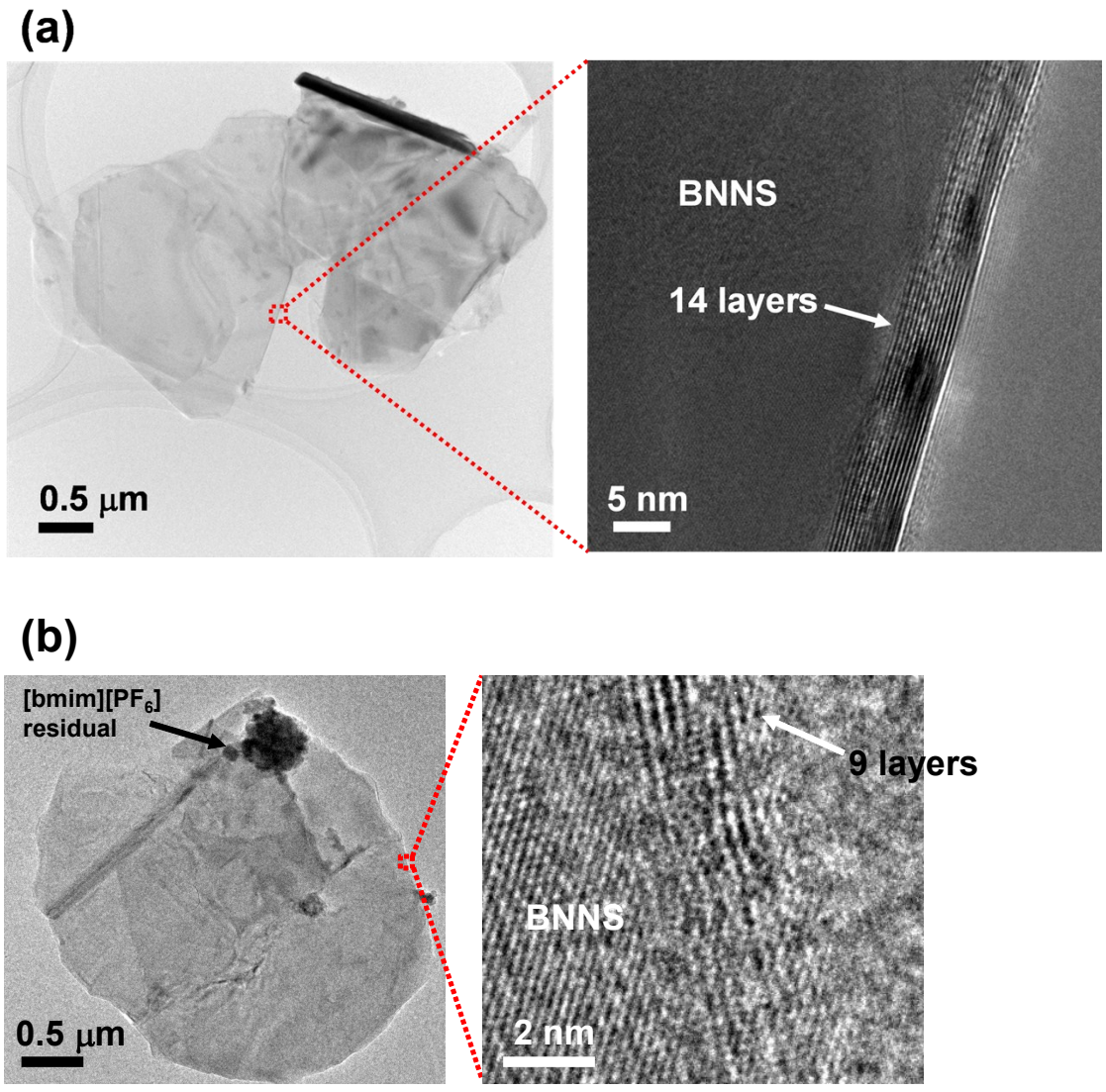

Fig. S1 (a) High-resolution transmission electron microscopy (HRTEM) images of BNNS/[bmim][Tf_2N] complexes. (b) HRTEM images of BNNS/[bmim][PF_6] complexes.

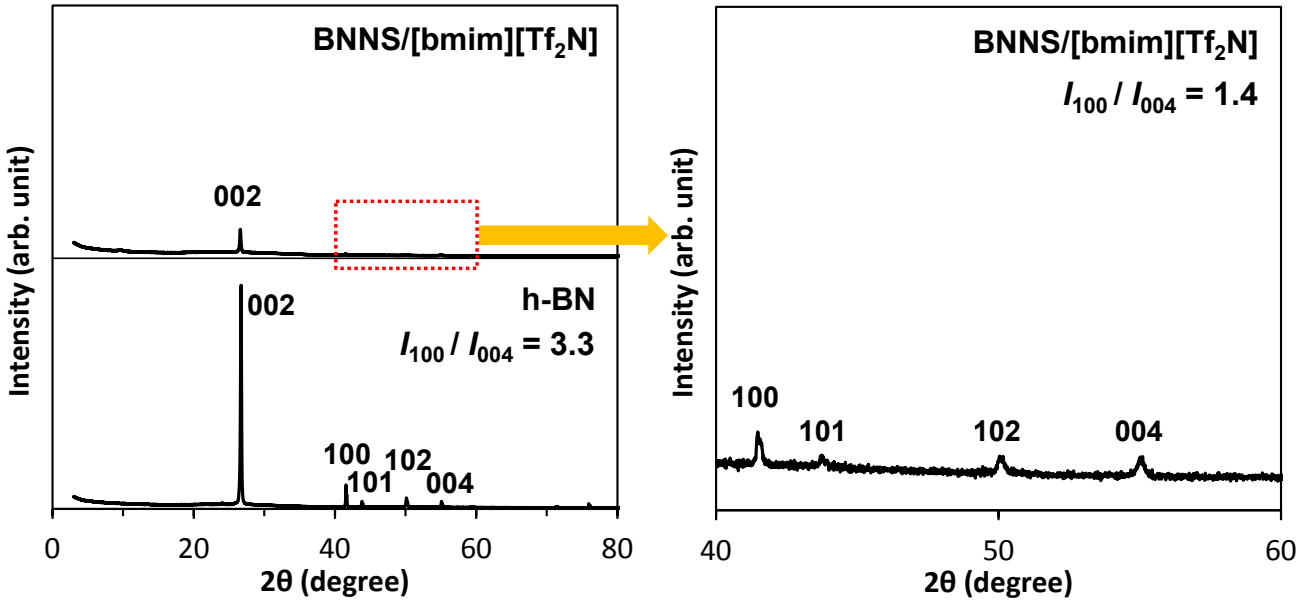

Fig. S2 X-ray powder diffraction (XRD) spectra of BNNS/[bmim][Tf_2N] complex and pristine h-BN. Various factors can affect the peak intensity, however each XRD powder sample was measured in the same shape and volume.

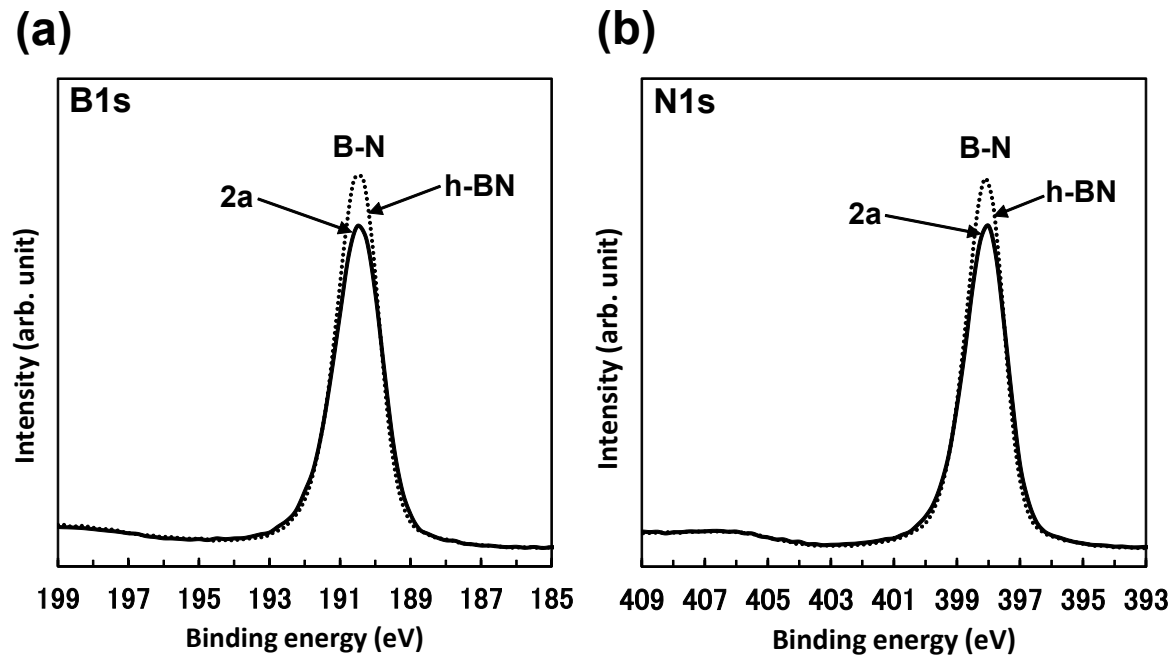

Fig. S3 (a) B 1s and (b) N 1s XPS spectra of BNNS/[bmim][PF_6] complex **2a**, and h-BN.

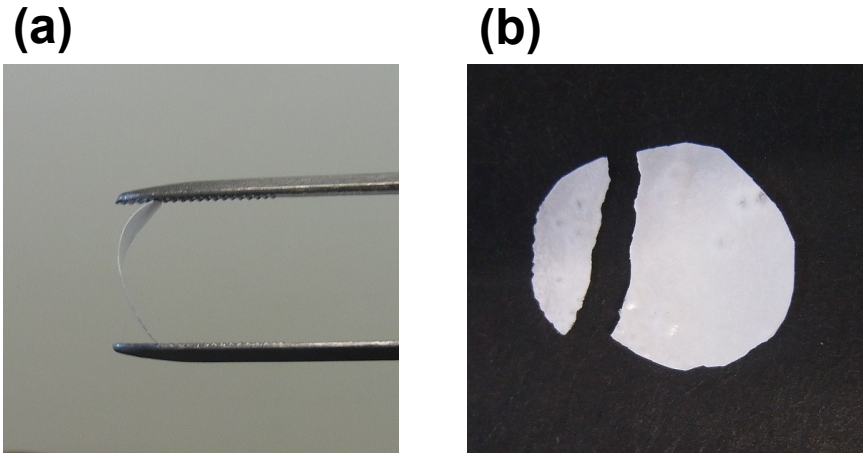

Fig. S4 Photographs of films to show their flexibility. (a) BNNS/[bmim][PF_6]/PMMA composite film containing 24.5 wt% of BNNS. (b) h-BN/PMMA (24.5 wt%/75.5 wt%) composite film broken by bending. The BNNS/[bmim][PF_6]/PMMA composite film showed good flexibility and it was not broken and not cracked after bending. Meanwhile, the h-BN/PMMA composite film is much more brittle and has rough surface appearance. The h-BN/PMMA composite film was easily broken by bending.

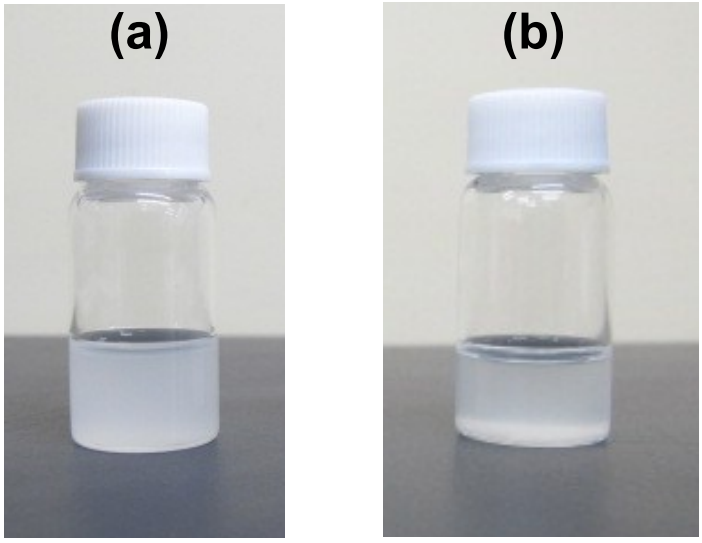

Fig. S5 Photographs of (a) BNNS/[bmim][PF_6] dispersion in *N*-methyl-2-pyrrolidone (NMP) and (b) BNNS/[bmim][PF_6] dispersions in dimethylformamide (DMF). Each photograph was taken after letting each initial BNNS dispersion stand for 1 h. The initial dispersion was prepared after 10 min bath-sonication of a mixture of BNNS/[bmim][PF_6] complex **2b** and solvent (initial BNNS concentration in

NMP or DMF was adjusted to 0.5 mg mL^{-1}). BNNS/[bmim][PF_6] gave stable BNNS dispersion in NMP (BNNS concentration, ~0.5 mg mL^{-1}), although most of the BNNS/[bmim][PF_6] complex had precipitated in DMF after standing for 1 h.

4. References

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