A high-yield ionic liquid-promoted synthesis of boron nitride nanosheets by direct exfoliation

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1. Materials.

h-BN (UHP-1K, SHOWA DENKO K. K., Japan, BN purity: 99.9%, mean lateral size of platelet: ~4 μ m (estimated by scanning electron microscopy)) was dried under vacuum at 80 °C for 12 h before use. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) (\geq 98%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) (\geq 98%), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][TfO]) (\geq 98%), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([emim][TfO]) (\geq 98%), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][TfO]) (\geq 98%), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) (\geq 98%) were purchased from Sigma-Aldrich Corporation (USA). 1-Butyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) (\geq 99.9%) were obtained from Kanto Chemical Co., Inc. (Japan). 1Butylpyridinium bis(trifluoromethylsulfonyl)imide ([BPy][Tf₂N]) (99%), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) (99%) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF₆]) (99%) were purchased from IoLiTec Ionic Liquids Technologies GmbH (Germany).

2. Characterization.

High-resolution transmission electron microscopy (HRTEM) images were obtained with an FEI Titan 80-300 instrument operating at 200 kV. HRTEM samples were prepared by dispersing the boron nitride nanosheet (BNNS)/IL complexes (BNNS/ILs) in IPA under bath sonication for 3 min and dropping the resulting mixtures onto microgrids. X-ray photoelectron spectroscopy (XPS) data were collected using an ULVAC PHI Quantera SXM spectrometer with a monochromated Al–K α (1486.6 eV). Experimental energy shifts were corrected relative to the C1s band at 284.6 eV (C–C bond). XPS spectra were collected for an acetone-washed and vacuum-dried BNNS/IL powder and pristine h-BN. Thermogravimetric analysis (TGA) measurements were performed using a Rigaku-Thermo plus TG8120 instrument. Samples were held at 100 °C for 30 min under a N₂ flow of 500 mL min⁻¹ and heated to 800 °C at 10 °C min⁻¹. UV–vis absorption spectra were measured using a spectrophotometer (Shimadzu UV–vis–NIR UV-3600). X-ray powder diffraction (XRD) patterns were recorded at a scan rate of 50°/min with the Cu–K α (1.542 Å) line using a Rigaku Ultima IV multipurpose XRD system. Powder samples were loaded onto XRD glass plates.

3. Typical procedure for the preparation of BNNS dispersions in IL and BNNS-adsorbed IL (BNNS/IL).

30 mL of IL was added into a flask containing dried h-BN (150 mg), and the mixture was subjected to bath sonication using an ultrasonic cleaner (Branson B-220) for 8 h. The resulting dispersion was centrifuged at 3,000 rpm (1,220 g) for 20 min and the supernatant containing BNNSs in IL was collected. To quantify the amount of BNNS/ILs, the supernatant was subjected to vacuum filtration through a preweighted 0.1 µm Teflon® membrane filter, washed with acetone, and dried under vacuum at 80 °C for 12 h. The BNNS/IL complexes were characterized by TGA and the amount of BNNS in the BNNS/ILs was subsequently calculated using the resulting weight loss corresponding to IL. Finally, the concentration of IL-dispersed BNNS (mg/mL) was deduced from the calculated weight of BNNSs. The yields after one sonication/centrifugation cycle were calculated using $y = 100 \times M_{BNNS}/M_{h-BN}$, where M_{BNNS} is the weight of BNNS estimated from the weight of the obtained BNNS/IL after one cycle and the FR value, and M_{h-BN} is the weight of the h-BN.

4. Supplementary figures and a supplementary table



Fig. S1. Chemical structures of ionic liquids used for exfoliation of h-BNs. [emim][PF₆] was not used in this study because it is a solid at room temperature (melting point of [emim][PF₆]: 62 °C).



Fig. S2. Photographs of supernatants after centrifugation (3,000 rpm, 20 min) of BNNS/IL dispersions. (a) BNNS/[bmim][BF₄], (b) BNNS/[emim][Tf₂N], (c) BNNS/[emim][TfO], and (d) BNNS/[bmim][TfO]. ILs involving sulfonate-bearing [Tf₂N] or [TfO] anions (b, c, and d) turned light orange in BNNS/IL dispersions, while BNNS/[bmim][BF₄] (a) showed white color. The filtrate, which was collected after filtration (0.1 µm filter) of BNNS/[emim][Tf₂N], BNNS/[emim][TfO], or BNNS/[bmim][TfO] supernatants, also showed the same orange color. These color changes after bath sonication are very similar to the previous study preparing BNNSs in methanesulfonic acid including sulfonate-based anions under bath sonication.¹ In addition, it has been reported that ILs themselves darkened from colorless to amber due to some decomposition during sonication at 85 °C.² As shown in Fig. S3, ILs including sulfonate-bearing anions ([bmim][Tf₂N], and [emim][Tf₂N]) without BNNSs became very light vellow after 8h sonication at room temperature, although ILs including [PF₆] remained colorless after the sonication (Fig. S3). TGA curves (Fig. S4) and UV-vis spectra (Fig. S5) showed no significant differences before and after sonication of [bmim][Tf₂N]. Therefore, these color changes are considered to originate from some decomposition of very small amounts of ILs involving sulfonate-bearing anions under sonication, and once ILs attached onto BNNS surfaces via cation-mediated interactions, some of their sulfonate-based anions might be more unstable and the decomposition may be accelerated. However, there was no significant difference in TGA curves between pristine [bmim][Tf₂N] and [bmim][Tf₂N] filtrate collected from the BNNS/[bmim][Tf_2N] supernatant (Fig. S4). Therefore, the decomposition of the sulfonate-based ILs in [bmim][Tf₂N] filtrate, which leads to the light vellow color, is considered to be very small. Moreover, XRD patterns of BNNS/[bmim][Tf₂N] complexes (Fig. S6) did not show any possible decomposition products of h-BNs such as boron at $2\theta = \sim 17-19^\circ$, which is formed by etching of h-BNs and may show vellow color.³



Fig. S3. Photographs of pristine [bmim][Tf₂N], [bmim][Tf₂N] after 8h bath sonication, pristine [emim][Tf₂N], [emim][Tf₂N] after 8h bath sonication, pristine [bmim][PF₆], and [bmim][PF₆] after 8h bath sonication. Sulfonate-bearing ILs ([bmim][Tf₂N] and [emim][Tf₂N]) became very light yellow after 8h bath sonication at room temperature, although [bmim][PF₆] remained colorless during 8h sonication at room temperature.



Fig. S4. TGA diagrams of [bmim][Tf₂N] (dashed line), [bmim][Tf₂N] after 8 h bath sonication (solid line), and [bmim][Tf₂N] filtrate collected from the BNNS/[bmim][Tf₂N] supernatant (red line). Heating rate = 10 °C min⁻¹, N₂ atmosphere.



Fig. S5. UV–vis spectra of (a) pristine [bmim][Tf₂N], and (b) [bmim][Tf₂N] after 8 h bath sonication, and (c) light orange BNNS/[bmim][Tf₂N] supernatant diluted four times using pure [bmim][Tf₂N] (pristine [bmim][Tf₂N] was used as a reference sample for the measurements of BNNS/[bmim][Tf₂N] supernatant).



Fig. S6. XRD diffractograms of pristine h-BN, and BNNS/[bmim][Tf₂N] after acetone wash and drying. XRD patterns of the obtained BNNS/[bmim][Tf₂N] powders showed a clear BN (002) peak at a 2 θ value of ~26.6°. The (002) peak intensity was weaker than that of pristine h-BNs. Peak intensity can be affected by various factors but all XRD samples were prepared and measured identically, in the same shape and volume. In addition, the XRD pattern did not show any possible decomposition products such as boron which is formed by etching of h-BNs and is known to be observed at $2\theta = \sim 17-19^{\circ}$.²

	С	В	N	0	S	F	Na	AI	Si
BNNS/[bmim][Tf ₂ N] ^a	17.7	30.1	32.3	6.8	2.1	5.6	1.5	0.7	2.9 ^c
BNNS/[bmim][Tf₂N] after TGA ^ª	12.1	39.0	40.6	4.5	0.2	0.7	0.8	0.3	1.8°
h-BN ^{a,b}	8.6 [°]	42.5	44.5	2.9 ^{<i>c</i>}	0.0	0.0	0.0	0.0	1.6°

Table S1. Surface elemental compositions (atomic %) of BNNS/[bmim][Tf₂N] complex, BNNS/[bmim][Tf₂N] complex after the TGA measurement, and h-BN measured by XPS survey scans.

^aDried under vacuum at 80 °C for 12 h before XPS measurements

^bGrade: UHP-1K, SHOWA DENKO K. K., Japan, BN purity: 99.9%

^cSurface contamination and/or 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.^{4,5}

As shown in Table S1, the XPS survey scan of the BNNS/[bmim][Tf₂N] after the TGA measurement revealed that the S and F elements of [bmim][Tf₂N] almost disappeared, although very small amounts of residual S and F atoms were still observed because of high sensitivity of the XPS analysis.



Fig. S7. Photographs of BNNS/[bmim][Tf₂N] complex (a) before and (b) after TGA measurement (heating rate = $10 \text{ }^{\circ}\text{C} \text{ min}^{-1}$, N₂ atmosphere).



Fig. S8. Thickness histograms of BNNSs obtained after TGA measurement of BNNS/[bmim][Tf₂N] complexes (20 flakes were measured by HRTEM). Average number of layers is ~5.9.



Fig. S9. TGA diagrams of (a) BNNS/[emim][Tf₂N] complex, (b) BNNS/[bmim][PF₆] complex, (c) h-BN, (d) [emim][Tf₂N], and (e) [bmim][PF₆]. Heating rate = 10 °C min⁻¹, N₂ atmosphere. The adsorbed ILs started decomposing at a slightly lower temperature than its free counterpart, while IL filtrate without BNNSs showed the same decomposition temperature as pure IL (Fig. S4). Therefore, this lower decomposition temperature may result from potential interactions between [bmim] cations and BNNS surfaces, which may reduce electrostatic interactions within the IL, leading to lower-temperature decomposition of [Tf₂N] anions. On the other hand, a small weight loss observed at a higher temperature (around 600 °C) is considered to be due to decomposition of [bmim] cations adsorbed on BNNS surfaces.



Fig. S10. (a) Thickness and (b) length histograms of BNNS/[bmim][PF₆] by HRTEM (40 flakes were measured).



Fig. S11. (a), (b) HRTEM images of BNNS/[bmim][PF₆] complexes and enlarged image for the curled edges. (c) Electron diffraction pattern of the area marked by the dotted white circle in (a). (d) Electron diffraction pattern of the area marked by the dotted white circle in (b).



Fig. S12. (a) Thickness and (b) length histograms of BNNS/[bmim][PF₆] complexes collected by additional extraction cycle (20 flakes were measured for the thickness and 27 flakes were measured for the length by HRTEM).



Fig. S13. An example of preparation of gram-scale BNNS/[bmim][PF₆]. ~1.0 g of BNNSs uniformly dispersed in 500 mL of [bmim][PF₆] in the supernatant after centrifugation (3000 rpm, 20 min).



Fig. S14. Photographs of BNNS/IL dispersions in dimethylformamide (DMF) taken after allowing each initial dispersion to stand for 1h. (a) BNNS/[bmim][Tf₂N] in DMF (BNNS concentration: ~0.5 mg mL⁻¹), (b) BNNS/[bmim][PF₆] in DMF (BNNS concentration in the supernatant: ~0.2 mg mL⁻¹). Each initial dispersion was prepared after 10 minutes' bath sonication, and the initial BNNS concentration in DMF was adjusted to 0.5 mg mL⁻¹. BNNS/[bmim][Tf₂N] gave stable BNNS dispersion in DMF, although most of the BNNS/[bmim][PF₆] were precipitated after standing for 1h. This result is probably due to the difference in their surface energy. The surface tension value of [bmim][Tf₂N] (~33 mN m⁻¹ (mJ m⁻²)) adsorbed on the BNNS surface is similar to that of DMF (~36 mJ m⁻²)⁶, while the surface tension value of [bmim][PF₆] (~49 mJ m⁻²) is much larger than that of DMF.



Fig. S15. Photographs of BNNS/[bmim][PF₆] dispersions in *N*-methyl-2-pyrrolidone (NMP) taken after allowing each initial dispersion (after 10 min sonication) to stand for 1h. (a) BNNS concentration in NMP: ~0.5 mg mL⁻¹, (b) BNNS concentration in NMP: ~1.0 mg mL⁻¹. BNNS/[bmim][PF₆] gave homogenous BNNS dispersions in NMP after a brief bath sonication. This is probably because the surface tension of NMP (~40 mJ m⁻²)⁷ approximate that of [bmim][PF₆].

2. References

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