Liquid phase exfoliation and crumpling of inorganic nanosheets

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SUPPLEMENTARY INFORMATION



Section S1: Measurement of extinction coefficients

Figure S1. Absorbance spectrum of PVP-stabilized (a) BNNSs, (c) MoS_2 , (e) WS_2 dispersions and the Lambert-Beer plots of PVP-stabilized (b) BNNSs, (d) MoS_2 , and (f) WS_2 dispersions are used to determine the extinction coefficients in water. The extinction coefficient of PVP-stabilized BNNSs dispersion is $1.1 \times 10^3 \text{ mL mg}^{-1} \text{ m}^{-1}$ at 350 nm; for MoS_2 , the value is $5.2 \times 10^2 \text{ mL mg}^{-1} \text{ m}^{-1}$ at 674 nm; for WS_2 , the value is $4.2 \times 10^2 \text{ mL mg}^{-1} \text{ m}^{-1}$ at 630 nm.

Section S2: Transmission Electron Microscopy (TEM) images of nanosheets



Figure S2. Additional TEM images of dispersed nanosheets. (a, b) BNNSs, (c,d) MoS2 nanosheets, (e, f) WS2 nanosheets. (This figure supports Figure 5 in the main manuscript)

Section S3: Size characterization by Dynamic Light Scattering (DLS)

The effect of sonication time and source material (parent material with different flake size) on the nanosheets size (hydrodynamic radius) of BNNSs in the dispersion was investigated by dynamic light scattering (DLS) measurements. We utilized two different source materials and investigated the size characterization. The different source materials are described in the experimental section; the parent hBN-I (\sim 1 µm) has smaller flake size than parent hBN-II (\sim 3 µm). Size characterization was also performed on the dispersion after different sonication times. Centrifugation was performed after 1 hour sonication and the supernatant was collected. Then the dispersion was further sonicated for an additional 1.5 hours. Sonication is used to exfoliate the nanosheets and reduce the number of layers; however, prior studies have shown sonication simultaneously reduces the lateral area of dispersed graphene, so a similar effect is expected here.¹

This DLS data is plotted in Figure S3 (hBN- I) and Figure S4 (hBN- II). The observed final flake size depends on the initial flake size, which indicates that the dispersed nanosheets have not reached a "terminal flake size" analogous to those observed for sonicated carbon nanotubes.² The average particle size for hBN-I is 198, 225, and 253.6 nm after 0 hour, 0.5 hours, and 1 hour of sonication time, respectively (Table S1). The average particle size for hBN-II is 204, 174, and 206 nm after 0 hour, 0.5 hours, and 1 hour of sonication time, respectively (Table S1). These values are comparable to those of Nazarov *et al.*, who reported an average hydrodynamic radius of 334 nm for acid-functionalized BNNSs in DMF.³ The effect of longer sonication time results in a reduction of the large-nanosheet-size tail of the distribution in all cases. (The number-average fluctuates because the breakage of a large sheet creates additional sheets that may still be larger than the average.)

 Table S1. Average and maximum sheet hydrodynamic radius of BN nanoparticle with sonication time.

Sample	Additional Sonication	Number-average hydrodynamic radius (nm)			
	time (hour)	hBN-I	hBN-II		
	0	198	204		
BNNSs/PVP/water	0.5	225	174		
	1	253	206		



Figure S3. Hydrodynamic radius distribution of hBN- I in PVP solution after additional sonication of (a) 0 hours, (b) 0.5 hour sonication, and (c) 1 hour. (The starting, centrifuged dispersion was prepared with 1 hour sonication as described in the methods section; the later samples were prepared by sonicating the centrifuged samples for 0.5 and 1 hour.) The black curve (cumulative distribution) corresponds to the left y-axis, while the blue probability distribution corresponds to the right y-axis.



Figure S4. Hydrodynamic radius distribution of hBN- II in PVP solution after additional sonication of (a) 0 hours, (b) 0.5 hour sonication, and (c) 1 hour. (The starting, centrifuged dispersion was prepared with 1 hour sonication as described in the methods section; the later samples were prepared by sonicating the centrifuged samples for 0.5 and 1 hour.) The black curve (cumulative distribution) corresponds to the left y-axis, while the blue probability distribution corresponds to the right y-axis.

Section S4: Error Estimations

For each of the inorganic nanomaterials, a fractional error was calculated to determine the variation in the concentration values obtained by the UV-vis spectrophotometer. This variation was calculated by sonicating four samples of each nanomaterial, each with identical concentrations of ~20 mg mL⁻¹ of parent material and ~10 mg mL⁻¹ of PVP stabilizer. The average nanomaterial concentration and standard deviation for each nanomaterial set were calculated, and the fractional error was determined by dividing the standard deviation by the average concentration. These calculated fractional errors were then applied to all other data points. The fractional value for error was used because the main source of error for this experiment is likely to be variation in sonication efficiency. Prior measurements show that the error in absorbance measurement is relatively low, so variations in the dispersion itself are the cause of variable absorbance (and thus, concentration) values.



Figure S5. Figure 6 in the main manuscript is shown with error bars (standard deviation from 5 experiments where separate samples were made and absorbance was measured), (a) BNNSs, (b) MoS_2 , and (c) WS_2 .



Figure S6. Figure 7 in the main manuscript is shown with error bars (standard deviation from 5 experiments where separate samples were made and absorbance was measured) (a) BNNSs, (b) MoS_2 , and (c) WS_2 .

Section S5: Absorbance plot before and after freeze drying



Figure S7. UV-vis absorbance spectra in water before and after freeze-drying (a) BNNSs, (b) MoS₂, and (c) WS₂. (This figure supports Figure 8 in the main manuscript)

Section S6: Nanomaterial dispersion in organic solvents

Table S2: Concentration of nanomaterial and extinction coefficient values in different solvent
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		Methanol	Ethanol	Isopropanol	Chloroform	DMF	DMSO	NMP
BNNSs	Conc (mg mL ⁻¹)	0.23	0.24	0.25	0.17	0.15	0.030	1.1
	alpha (mL mg ⁻¹ m ⁻¹)	1.2 x 10 ³	4.2 x 10 ²	2.9 x 10 ³	2.5 x 10 ²	1.5 x10 ³	2.0 x 10 ³	1.1x 10 ³
MoS ₂	Conc (mg mL ⁻¹)	0.080	0.26	0.030	0.10	0.10	0.10	0.68
	alpha (mL mg ⁻¹ m ⁻¹)	6.9 x 10 ²	8.5 x 10 ²	1.3 x 10 ³	5.9 x 10 ¹	4.2 x 10 ³	2.3 x 10 ³	1.9 x 10 ²
WS ₂	Conc (mg mL ⁻¹)	0.13	0.33	0.070	0.28	0.30	0.050	0.13
	alpha (mL mg ⁻¹ m ⁻¹)	8.3 x 10 ²	3.4 x 10 ¹	2.2×10^2	3.2 x 10 ¹	5.5 x 10 ²	1.2 x 10 ³	5.0 x 10 ²



Figure S8: Digital photographs of PVP-stabilized nanomaterial dispersion in methanol. (a) BNNSs, (b) MoS_2 , and (c) WS_2 ; the absorbance spectra of (d) BNNSs, (e) MoS_2 , (f) WS_2 ; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS_2 , (i) WS_2 .



Figure S9: Digital photographs of PVP-stabilized nanomaterial dispersion in ethanol. (a) BNNSs, (b) MoS₂, and (c) WS₂; the absorbance spectra of (d) BNNSs, (e) MoS₂, (f) WS₂; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS₂, (i) WS₂.



Figure S10: Digital photographs of PVP-stabilized nanomaterial dispersion in isopropanol. (a) BNNSs, (b) MoS_2 , and (c) WS_2 ; the absorbance spectra of (d) BNNSs, (e) MoS_2 , (f) WS_2 ; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS_2 , (i) WS_2 .



Figure S11: Digital photographs of PVP-stabilized nanomaterial dispersion in chloroform. (a) BNNSs, (b) MoS₂, and (c) WS₂; the absorbance spectra of (d) BNNSs, (e) MoS₂, (f) WS₂; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS₂, (i) WS₂.



Figure S12: Digital photographs of PVP-stabilized nanomaterial dispersion in DMF. (a) BNNSs, (b) MoS_2 , and (c) WS_2 ; the absorbance spectra of (d) BNNSs, (e) MoS_2 , (f) WS_2 ; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS_2 , (i) WS_2 .



Figure S13: Digital photographs of PVP-stabilized nanomaterial dispersion in DMSO. (a) BNNSs, (b) MoS_2 , and (c) WS_2 ; the absorbance spectra of (d) BNNSs, (e) MoS_2 , (f) WS_2 ; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS_2 , (i) WS_2 .



Figure S14: Digital photographs of PVP-stabilized nanomaterial dispersion in NMP. (a) BNNSs, (b) MoS_2 , and (c) WS_2 ; the absorbance spectra of (d) BNNSs, (e) MoS_2 , (f) WS_2 ; and Lambert-Beer plot of PVP-stabilized nanomaterial dispersion to determine the extinction coefficient (g) BNNSs, (h) MoS_2 , (i) WS_2 .

Section S7: Scanning Electron Microscopy (SEM) images of crumpled nanosheets



Figure S15. Additional SEM images of crumpled nanosheets (a, b, c) BNNSs, (d, e, f) MoS₂, and (g, h, i) WS₂. (This supports Figure 10 in the main manuscript.)

Section S8: Schematic illustration of nanosheet crumpling process



Figure S16. Schematic diagram of the crumpling process of nanomaterial; (a) water droplet with nanosheets from atomizer, (b) shell of nanosheets formation by clustering of nanosheets, (c) coalescence and aggregation of nanosheets, (d) evaporation of water from shell and crumpling of nanosheets with dimples, and (e) crumpled particles with dimples.

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