# **Electronic Supplementary Information (ESI)**

## Hydrodynamics-assisted scalable production of boron nitride nanosheets and their application in improving oxygen-atom erosion resistance of polymeric composites

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## **TC1: Additional Experiment section**



Figure S1. Phtographs of neat epoxy and BNNSs/epoxy composites

## TC2: Yield and efficiency

The yield here is estimated as the ratio of output to input, i.e. the ratio of resultant BNNSs concentration to the initial concentration (3 mg/mL here). Because published works are all within the scope of laboratory research, the focuses are often put on the resultant concentration instead of the volume processed one time and the resultant product weight. Therefore, in order to compare the results from those published works, here a high efficiency means a high yield (not the weight of resultant BNNSs) in unit time. A comprison between our method and other published work are given in Table S1 and Figure S2.

The liquid-phase exfoliation methods for BNNSs are not that successful. For example, Han et al.<sup>s1</sup> and Warner et al.<sup>s2</sup> prepared thin few-layer BNNSs by several-hours sonication-assisted exfoliation in 1,2-dichloroethane, but their goal was investigating the microscopic or atomic structure, not establishing a scalable method; and no concentration or yield data were reported. Afterwards, Zhi et al.<sup>s3</sup> prepared BNNSs in dimethylformamide, but tip-type sonication for 10 h could only achieve a concentration of ~0.0125-0.025 mg/mL. Similarly, Coleman et al.<sup>s4</sup> used 24 h bath sonication, but only obtain 0.06 mg/mL dispersions in isopropanol. In 55 vol%

ethanol/water mixtures, Zhou et al.<sup>s5</sup> used 8 h sonication, but only obtain 0.075 mg/mL dispersions. Hence, these sonication-based works have drawbacks in low yield and efficiency. Meanwhile, in achieving high concentration or yield, Wang et al.<sup>s6</sup> sonicated h-BN powders in methanesulfonic acid (MSA) for 8 h and the resultant concentration reached 0.2-0.3 mg/mL, but as a strong acid MSA is high-boiling, difficult-handling, and environmentally unfriendly: Lin et al.<sup>s7</sup> sonicated the functionalized h-BN to obtain a concentration of 0.5-1 mg/mL, but the functionalization reaction of h-BN with octadecylamine or polyethylene glycol must be conducted in the melt for very long time (4-6 days) under a nitrogen atmosphere. Unfortunately, as for large-scale production in industry, environment-unfriendly MSA and 8 h sonication or 4-6 days reaction in one run are undesirable. Recently, some methods dominantly using shear force were reported to exfoliate h-BN. For example, Li et al<sup>s8</sup> used ball milling assisted by sonication to prepared BNNSs with a milling medium of benzyl benzoate which is high boiling. Chen et al.<sup>59</sup> reported shearing vortex fluidic films in a rotated tube for exfoliating h-BN in N-methyl-pyrrolidone (NMP), while these fluidic films are so thin that the exfoliation domain is rather limited to result in throughput problems.

References	Initial concentratio n	Method	Solvent	Time	Resultant BNNSs concentrat ion	Yield	Efficiency (/h)	
Zhi et al. Adv.Mater.2009,21, 2889	25mg/mL	Tip-type sonication	DMF 10h 5000-8000rpm		0.0125-0. 025mg/m L	0.05-0 .1%	0.005-0.0%1	
Coleman et al. Science, 2011	3 mg/mL	Bath sonication (68W)	Isopropanol 24h 1500rpm (225g) 45min		0.06mg/m L	2.0%	0.083%	
Zhou et al. Angew. Chem. Int. Ed.2011,50,10839	3 mg/mL	Bath sonication	55% vol8hEthanol/water3000rpm 20min		0.075mg/ mL	2.5%	0.3125%	
Wang et al. J.Mater.Chem.2011,21,113 71	2 mg/mL	Bath sonication	Methanesulfonic acid 4000rpm 90min	8h	0.2-0.3mg /mL	10-15 %	1.25-1.875%	
Han et al. Appl.Phys.Lett.2008,93,22 3103	0.04 mg/mL	Bath sonication	1,2-Dichloroethane solution of poly(m-phenylenevi nylene-co-2,5-dictox y-p-phenylenevinyle ne)(1.2 mg/10 ml)	1h	Just investigated the microstructure by TEM. No concentration data were reported.			
Du et al. CrystEngComm, 2013,15,1782	1g BN powder mixed with Concentrate d H <sub>2</sub> SO <sub>4</sub>	Hummers-like process + stirring	Concentrated H <sub>2</sub> SO <sub>4</sub> , KMnO <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> 3000rpm 10min	12h	65mg (not dispersion )	6.5%	0.54%	
Lin et al. JPCc 2011,115,2679	2 mg/mL	Bath sonication	Deionized water	8h	0.05 mg/mL	2.5%	0.3125%	
Warner et al.ACS Nano,2010,4,1299	0.02 mg/mL	Bath sonication	1,2-Dichloroethane	3h	Just investigated the microstructure by TEM. No concentration data were reported.			
Lin et al. J. Phys.Chem.Lett., 2010,1,277	50mg	Functionalizati on with Octadecylamin e (ODA) or polyethylene glycol (PEG) [160-180 °C, N <sub>2</sub> flow]	Tetrahydrofuran (THF) or water	94-144 h	5-10mg	10-20 %	0.069-0.213 %	
Li et al. J. Mater.Chem.,2011,21,1186 2	500mg	Ball milling + bath sonication	Benzyl benzoate	15+0.5h	No data	9%	0.58-4.32%	
Chen et al. Chem.Commun.2012,48,3 703	0.1mg/mL	Vortex fluidic device	N-methyl-pyrrolidon e (NMP)	0.5h	No data	<5%	<10%	
Li et al. Adv. Mater. 2013, DOI: 10.1002/adma.201204031	248mg	Exfoliation by Molten Hydroxides (180 °C)	Molten sodium hydroxide (2.0600 g) and potassium hydroxide (2.7160 g)	2h	0.47mg	0.191 %	0.0955%	
Hydrodynamics method	3 mg/mL	Hydrodynamics	55% vol Ethanol/water 225g 45min	2h(45M Pa,100 Cycles)	0.35 mg/mL	11.67 %	5.83%	



Figure S2. Yield (a) and Efficiency (b) of our work and other published works.

## **TC3: Additional AFM results**



**Figure S3.** Typical AFM images of BNNSs prepared in the condition of a pressure of 45 MPa and 5 cycles (a, b), 20 cycles (b), 60 cycles (c), and 100 cycles (d). Based on the (a-e) AFM images, statistical analyses were performed with a sample size of 94 at 5 cycles, 89 at 20 cycles, 151 at 60 cycles, and 204 at 100 cycles. The number fraction of BNNSs thickness (f) and area (g) as a function of cycles.  $N_{t1.0}/N_T$ ,  $N_{t2.0}/N_T$ , and

 $N_{t3.5}/N_T$  denote the number fraction of BNNSs with thickness of  $\leq 1.0 \text{ nm}$ ,  $\leq 2.0 \text{ nm}$ , and  $\leq 3.5 \text{ nm}$ .  $N_{A4}/N_T$ ,  $N_{A9}/N_T$ , and  $N_{A16}/N_T$  denote the number fraction of BNNSs with area of  $\geq 4 \mu m^2$ ,  $\geq 9 \mu m^2$ , and  $\geq 16 \mu m^2$ .





**Figure S4.** Typical AFM images of BNNSs prepared in the condition of 10 cycles and pressure of 21 MPa (a, b, c), 77 MPa (d), and 127 MPa (e). Based on the (a-e) AFM images, statistical analyses were performed with a sample size of 22 at 21 MPa, 50 at 77 MPa, and 48 at 127 Mpa, to obtain the statistical histogram showing the thickness (e) and area (f) distribution. (j) Calculated average thickness <t> and average area <A> as a function of cycles. The number fraction of BNNSs thickness (h) and area (i) as a function of cycles. Nt<sub>1.0</sub>/N<sub>T</sub>, Nt<sub>2.0</sub>/N<sub>T</sub>, and Nt<sub>3.5</sub>/N<sub>T</sub> denote the number fraction of BNNSs with thickness of  $\leq 1.0$  nm,  $\leq 2.0$  nm, and  $\leq 3.5$  nm. N<sub>A4</sub>/N<sub>T</sub>, N<sub>A9</sub>/N<sub>T</sub>, and N<sub>A16</sub>/N<sub>T</sub> denote the number fraction of BNNSs with area of  $\geq 4 \mu m^2$ ,  $\geq 9 \mu m^2$ , and  $\geq 16 \mu m^2$ , respectively.

### TC4: Computational Fluid Mechanics (CFD) calculations

For simplification and qualitatively revealing the fluid dynamics events involved in the hydrodynamics apparatus, we used a 2D axisymmetric model to perform CFD calculations (FLUENT 6.3.26) for the case of 45 MPa. The model is shown in Figure S5. We adopted structured meshes to numerically simulate the flow field. The number of total cells was approximately 139 0000 for half of the axisymmetric model. A two phases (liquid and vapor), incompressible, continuous flow with Newtonian viscosity is assumed. The specific values of parameters are set as follow: density 920 kg/m<sup>3</sup>, viscosity 0.00241 Pa s, vapor density 0.02558 kg/m<sup>3</sup>, viscosity 1.26×10<sup>-6</sup> Pa s, vaporization pressure 10000Pa, surface tension coefficient 0.0294 N/m, non-condensable gas mass fraction  $1.0 \times 10^{-4}$ . The inlet and outlet were set as pressure inlet (45MPa) and pressure outlet (1atm) conditions, respectively. The standard k- $\varepsilon$ turbulence model was used, with a segregated solver. In order to obtain a converged solution, we intentionally computed an initial field with 1<sup>st</sup>-order discretization and small under-relaxation factor. In fact, it is important to set the value of source terms as small as possible for this large pressure-gradient turbulent flow.



**Figure S5.** (a) Geoemtry of the apparatus. Unit: mm. (b) Cavitation of region P in (a). (c) Cavitation of region F in (a). (d) Pressure variation along the path M-N in (a). (e) Pressure , turbulence intensity, turbulence kinetic energy, and strain rate of the regions indicated in (a).

# TC5: Exfoliation mechanism



**Figure S6**. **Illustrations of the exfoliation mechanism in the published works**. The mechanism of all these three techniques is single.

(a) The most widely used sonication technique mainly generates liquid cavitation to exfoliate BN. The cavitation-induced micro jets and compressive shock stress waves exert on the BN surfaces to generate a compressive stress wave. When this

compressive stress wave propagates to the other side surface, it will reflect as a tensile stress wave to exfoliate BN. This results in a normal-force-dominated way.

(b) Ball milling technique utilizes the rotating ball to generate shear force on the BN surface to exfoliate BN, resulting in a shear-force-dominated way.

(c) Sear fluidic film technique utilizes the shear force within the fluidic film to exfoliate BN, resulting a lateral-force-dominated way.

It should be noted that all these three techniques can fragment BN into smaller pieces. The fragmentation effects also facilitate exfoliating BN, because smaller BN flakes are easier to exfoliate than larger ones for the smaller collective interaction force between layers in the smaller BN flakes.



Figure S7. Illustrations of the exfoliation mechanism in the hydrodynamic

method. In our hydrodynamic method, the exfoliation mechanism is multiple. There

are two fluid dynamics events (a, b) responsible for normal-force-dominated way and four fluid dynamics events (c, d, e, f) responsible for lateral-force-dominated way.

(a) Hydrodynamics cavitation generates a normal-force-dominated way, as elucidated previously in Figure S6a.

(b) According to Bernoulli equation,  $\rho*v^2+2*P = \text{constant}$ , and flow conservation equation, v\*A = constant, in large channel, BN is in a state of high pressure. When BN suddenly flows into the small channel, the fluid will speed up and fall into a state of low pressure. However, during this abrupt change, high pressure inherited from the high pressure in large channel still remains. Therefore, the pressure difference between the outside low pressure (fluid) and the inside high pressure (BN) will generate a pressure release effect to exfoliate BN, resulting in a normal-force-dominated way.

(c) Owing to the boundary layer effect, the flow velocity grows rapidly from the wall to the liquid. This induces a very large velocity gradient and thus a very large viscous shear stress to exfoliate BN, resulting a lateral-force-dominated way.

(d) In our hydrodynamics method, turbulence exists in the flow channel. According to turbulence theory, apart from the shear stress stemmed from fluid viscosity, the velocity fluctuation in turbulence will generate another kind of shear stress, i.e. Reynolds shear stress. The Reynolds shear stress can also exfoliate BN, resulting a lateral-force-dominated way.

(e) In turbulence, the Reynolds number which physically defines the ratio of inertial force to viscous force is very large. This means that the inertial force is much larger

than viscous. The extremely large inertial force endues BN with great kinetic energy which will enhance the BN-BN collisions. Through the BN self-lubricating ability, these BN-BN collisions can lead to BN self-exfoliation down to few layers even single layer. This process also generates a lateral-force-dominated way.

(f) The designed flow channel here can also induce enhancement in BN-BN collisions to facilitate BN exfoliation, leading to a lateral-force-dominated way.

### TC6: Raman, XRD, XPS, and TGA results

In contrast to pristine h-BN powder, the XRD pattern of the film made from the h-BN nanosheet dispersion obtained by jet cavitation exfoliation only exhibits a weak peak corresponding to the (0002) planes and the corresponding FWHM increases due to Scherrer broadening, as shown in Figure S8. This may be attributed to very thin h-BN nanosheets due to high degree of exfoliation by jet cavitation. Because the collapse of cavitation bubbles induced by jet cavitation in liquid can result in shockwaves and shear waves to exfoliate thicker and larger h-BN flakes into thinner and smaller nanosheets. Moreover, no (0004) and other peaks can be detected for the filtered film, stating that the sublattices in the filtered film almost completely exclude the long-range order greater than four-layer.<sup>s10</sup>



**Figure S8**. XRD spectra of pristine h-BN powder and film made from BNNSs dispersions.

Figure S9 shows the typical Raman spectra of pristine h-BN powder and the filtered film. BN exhibits a characteristic peak that is due to the  $E_{2g}\xspace$  phonon mode and analogous to the G peak in graphene. It is clear that the peak in the pristine powder is much stronger than that in the filtered film. This phenomenon is consistent with the recently reported statement that the peak becomes progressively weaker as the layer number of h-BN decreases. In the pristine h-BN powder, the Raman peak occurs at ~1363.6 cm<sup>-1</sup>. However, the Raman peak of the filtered film is located at ~1364.6  $cm^{-1}$ , showing an upward shift of ~1  $cm^{-1}$ . In addition, the FWHM increases from 9.5 cm<sup>-1</sup> in bulk BN to 11.3 cm<sup>-1</sup> in the filtered film. Generally, a Raman peak would shift to higher and lower position under compressive and tensile stress, respectively. Thus, it can be speculated that the upward shift is due to compressive stress in the filtered film, which may be generated by the dynamic flow induced compaction, tear and fold of nanosheets during the vacuum filtration. Nevertheless, according to the reported Raman analysis of monolayer and few-layer BN, the Raman information here is reminiscent of few-layer h-BN. Combined with the XRD result, it can be believed that the filtered film is intrinsically different from the bulk BN and is constituted by a disordered array of few-layer h-BN.



**Figure S9**. Raman spectra of pristine bulk BN and filtered film. The inset picture illustrates the phonon mode in BN responsible for the Raman peak.

The chemical composition of h-BN and BNNSs was investigated by XPS, a surface-sensitive tool for detecting the chemical status of a material sample. It can be seen from XPS survey spectra in Figure S10 that the composition of the BNNSs (N~41.6%, B~45.3%, C~10.3%, and O~2.8%) is similar to the composition of pristine h-BN powder (N~41.7%, B~45.8%, C~10.3%, and O~2.2%). Figure S10 summarizes the results of B1s, N1s, and C1s XPS spectra of pristine BN and BNNSs. B1s and N1s peaks in both h-BN and BNNSs are located at ~190.6 eV and ~398.1 eV, respectively, in agreement with the literature value of boron and nitrogen atoms in BN material. In addition, the both B1s and N1s spectra are symmetric while the possible component of B-O bond cannot be resolved in B1s spectra. It is common that BN materials often suffer from B<sub>2</sub>O<sub>3</sub> and carbon contamination, so the appearance of C and O in the XPS spectra is expectable. The atomic ratio of O increases from 2.2% in pristine BN to 2.8% in BNNSs, indicating some oxygen-containing groups introduced during the hydrodynamics process. However, both N1s and B1s spectra are symmetric while the C1s spectra (Figure S10d) are not symmetric and present additional peaks corresponding to oxygen-related groups. Therefore, the oxidation happens in the carbon contaminants and the hydrodynamics-assisted exfoliation does not cause heavy oxidation of BNNS for the excellent oxidative resistance of BN materials



**Figure S10**. (a) XPS survey spectra of pristine BN powder and BNNSs film. High resolution XPS spectra of B1s (b), N1s (c), and C1s (d).

We investigated the thermal performance BNNSs/epoxy also of thermogravimetric nanocomposites by analysis (TGA) and differential thermogravimetric (DTG) analysis, as shown in Figure S11 and Table S2. The thermal degradation process mainly occurs at 340-400°C. The onset decomposition temperature, T<sub>onset</sub>, the maximum decomposition temperature defined as the peak on DTGA curve, T<sub>max</sub>, the end decomposition temperature, T<sub>end</sub>, the maximum decomposition rate, Max<sub>dr</sub>, and the residue at 500 °C and 700 °C are listed in Table S2. BNNSs incorporation in epoxy resin slightly increases T<sub>onset</sub>, T<sub>max</sub>, and T<sub>end</sub> by 1-7°C; The char residues at 500 °C and 700 °C increase with BNNSs laodings; A ~26% reduction in the maximum decomposition rate occurs in the 0.5 and 1.0 wt% BNNSs/epoxy nanocomposties. All those improvements indicate enhanced thermal

stability, which may be attributed to the physical barrier effect of BNNSs and the increased interaction between BNNSs and epoxy matrix. Additionally, the increase of char residual can form char barrier to protect the nanocomposite surface from oxygen, as a mass and heat barrier which may also enhance the thermal stability.



**Figure S11**. TGA (a) and DTGA (b) curvers of BNNSs/epoxy nanocomposites with different BNNSs loading contents. (c) Details about determining  $T_{onset}$ ,  $T_{max}$ ,  $T_{end}$ ,  $Max_{dr}$ , and Char residue.

BNNSs (wt%)	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	$T_{end}(^{o}C)$	Max <sub>dr</sub> (%/°C)	Char residue (wt%)	
					500°C	700°C
Neat Epoxy	342.2	365.2	395.5	1.91	17.43	14.42
0.05	349.6	364.0	392.9	1.59	17.50	15.67
0.5	344.3	366.2	395.6	1.43	20.80	18.69
1.0	346.6	367.7	402.8	1.42	21.87	19.78

Table S2. Thermal stability factors of the BNNSs/epoxy nanocomposites

T<sub>onset</sub>: The onset decomposition temperature, determined by the method in Figure S11c

 $T_{max}$ : the maximum decomposition temperature, defined as the peak on the derivation of the TGA curve

 $T_{end}$ : The end decomposition temperature, determined by the method in Figure S11c Max<sub>dr</sub>: The maximum decomposition rate

Though it is impossible to directly capture the embedded BNNSs in epoxy after atomic oxygen exposure, we can use Raman spectrum to identify the existence of the exposed BNNSs, as shown in Figure S12. There is no signal corresponding to BN  $E_{2g}$ mode in the Raman spectrum of the surface of BNNSs/epoxy nanocomposites. However, after the BNNSs/epoxy nanocomposites were exposed into atomic oxygen, Raman spectrum measurement of the exposed surface shown definitive BN  $E_{2g}$  mode at 1364.6 cm<sup>-1</sup>, indicating that epoxy matrix was eroded way while BNNSs remained.



Figure 12. Raman spectra of the surface of BNNSs/epoxy nanocaomposites before



and after atomic oxygen exposure.

Naked polymeric membrane Polymeric membrane coated with BNNSs film **Figure S13**. Mass loss of naked polymeric membrane and BNNSs film coated polymeric membrane. AO flux is  $5.5 \times 10^{20}$  atoms/cm<sup>2</sup>. The polymeric membrane is the widely used membrane for filtering nanomaterials dispersed in organic slovents. The BNNSs film coated polymeric membrane is directly simply fabricated by vacuum filtrating the BNNSs dispersions onto the polymeric membrane. Throng vacuum filtration, BNNSs from the dispersions were deposited on the membrane to form a uniform and compact BNNSs film.

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