# Supporting Information

## Size-dependent flame retardancy of black phosphorus nanosheets

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#### **Experimental Methods**

#### 1. Materials

The >99.99% pure bulk black phosphorus (BP) crystals were purchased from Mophos (*www.Mophos.cn*) and epoxy resin CER1000 and curing agent CEH500 were obtained from Guangzhou Weiyee Metallographic Test Instrument Co. Ltd. The epoxy resin (EP) with a Shore hardness of 80 HD is type CE1000 of epoxy resin which can be used for PCB microsectioning. *N*-methylpyrrolidone (NMP, 99.9%), acetone (99.5%), *N*, *N*-dimethylformamide (DMF, 99.9%), and tetrabutylammonium bromide (99.5%) were purchased from Aldrich. All the reagents were used without further purification.

## 2. Preparation of BP nanosheets with different sizes, BP/EP composites and bare EP

#### 2.1 Synthesis of BP nanosheets (sb-BP) by solid ball milling exfoliation

0.6 g of bulk BP crystals (pre-powdered into a powder of ca. 20  $\mu$ m), 20.0 g of 10 mm diameter balls, and 4.0 g of 3 mm diameter balls were put in a 100 mL ball-milling jar under argon. In the solid ball-milling treatment, the total time was 186 minutes (stopping for 2 minutes every 60 minutes) and speed was 400 rpm. The final solid ball-milled product was dispersed in 50 mL of NMP and centrifuged at 3,000 rpm for 10 mins. Afterwards, the supernatant was further centrifuged at 7,000 rpm to obtain precipitated sb-BP. The product was centrifuged four times with acetone to get rid of the remaining solvent and concentrated to form a nanosheet suspension with a concentration of 15 mg mL<sup>-1</sup>.

#### 2.2 Synthesis of BP nanosheets (lb-BP) by liquid ball milling exfoliation

The preparation process of lb-BP was similar to that of sb-BP, except that 50 mL of NMP were added to the ball-milling jar. After liquid ball milling, the product was collected by same procedure described in *Section 2.1*. In the synthesis of lb-BP (10 g scale), 200 g of 10 mm diameter balls, 400 g of 3 mm diameter balls, 1 L ball-milling jar and 500 mL of NMP were

used. The product was centrifuged four times with acetone to get rid of the remaining solvent NMP and concentrated to form a nanosheet suspension with a concentration of 15 mg mL<sup>-1</sup>.

## 2.3 Synthesis of BP nanosheets (us-BP) by ultrasonic exfoliation

0.1 g of bulk BP crystals was added to 100 mL of NMP to form a suspension which was sonicated for 15 h using a probe sonicator (power of 1,800 W) at 6 °C. During the sonication treatment, 40% of the total power was employed and the treatment stopped for 4 s after operation for 2 s. After the treatment, the product of us-BP was collected by same procedures described above. The product was centrifuged four times with acetone to get rid of the remaining solvent and concentrated to form a nanosheet suspension with a concentration of 15 mg mL<sup>-1</sup>.

## 2.4 Synthesis of BP nanosheets (ec-BP) by electrochemical exfoliation

The bulk BP crystals (cathode) and platinum foil (anode) were placed in parallel separated by a distance of 5 cm and immersed in DMF containing tetrabutylammonium bromide with a concentration of 40 g L<sup>-1</sup>. Electrochemical exfoliation was carried out at a constant current of 30 mA for 30 min and ec-BP was collected by the same procedures described before. The product was centrifuged four times with acetone to get rid of the remaining solvent (DMF, etrabutylammonium bromide, etc.) and concentrated to form a nanosheet suspension with a concentration of 15 mg mL<sup>-1</sup>.

#### 2.5 Preparation of BP/EP composites and bare EP

The concentration of exfoliated BP nanosheets in the BP/EP composite was 1.0 *wt*%. In the process, 10.0 mL of the 15 mg mL<sup>-1</sup> BP nanosheet suspension in acetone were mixed with 10.0 g of epoxy resin CER1000. The suspension was dispersed ultrasonically (1,000 W at 20 °C) for 5 min and then mixed using a vortex mixer (3,000 rpm) for 5 min. The mixture was vacuum-dried at 60 °C for 6 h to remove acetone and combined with 5.0 g of the curing agent CEH500 (3,000 rpm, 10 min). It was then poured quickly into a curing mold (length and width were 100 mm and height was 2 mm) and cured at 60 °C for 2 h. After curing, the sample was cooled to room temperature to obtain the BP/EP composite. To produce the bare EP, 10.0 g of the epoxy resin CER1000 and 5.0 g of the curing agent CEH500 were mixed and transferred quickly to a curing mold and cured at 60 °C for 2 h. The prepared samples with a length of 100 mm, width of 100 mm and thickness of 2 mm were used for cone calorimetry. For flame test, the sizes of all the four BP/EP composites and bare EP were 125 mm of length, 13 mm of width and 2 mm of thickness.

#### 3. Characterization

Cone calorimetry was performed to determine the flame retardancy of the EP composites and bare EP according to ASTM E1354/ISO 5660 (heat flux of 35 kW m<sup>-2</sup>; nominal duct flow rate of 0.024 m<sup>3</sup> s<sup>-1</sup>; separation distance of 60 mm; sampling interval of 5 s; sample weight of 14.5 g). Thermogravimetric analysis (TG) was performed on the TA Q600 thermo-analyzer (heating rate of 10 °C min<sup>-1</sup>; nitrogen atmosphere of 100 mL min<sup>-1</sup>). The thermogravimetric and infrared analysis (TG-IR) was carried out on the TGA Q5000 thermo-analyzer (heating rate of 10 °C min<sup>-1</sup>; purge gas flow of 50 mL min<sup>-1</sup>; protective gas flow of 20 mL min<sup>-1</sup>) in combination with the Nicolet 6700 spectrometer (scan number of 12; detector of DTGS KBr; sample spacing of 1 cm<sup>-1</sup>). Scanning electron microscopy (SEM) was used to examine the BP nanosheets, BP/EP composites, bare EP, and carbon residue (Zeiss Supra 55 Sapphire fieldemission scanning electron microscope) at 2.0 kV and a distance of 5.0 mm. Powder X-ray diffraction (XRD) was performed on the Rigaku SmartLab diffractometer (Cu K<sub>a</sub> radiation; 40 kV, 30 mA) and Raman scattering microscopy was conducted on the Horiba Jobin-Yvon Lab Ram HR VIS Raman microscope (633 nm laser as the excitation; RT). Atomic force microscopy (AFM) was performed on the Oxford AR Cypher S atomic force microscope using the tapping mode and X-ray photoelectron spectroscopy (XPS) was carried out on the Thermo Fisher ESCALab 250Xi spectrometer with Al K<sub>a</sub> radiation. Optical microscopy was employed to observe the dispersed BP nanosheets in the EP matrix and the samples were prepared by rapid slicing.

## Calculation

The parameters to assess the fire retardancy including the peak of the heat release rate (pHRR), total heat release (THR), peak of smoke production rate (pSPR), total smoke production (TSP), peak of the CO production rate (pCOPR), and total CO production (TCOP) were calculated by the following equations:

$$\varphi_{pHRR} = \frac{pHRR_m - pHRR}{pHRR_m \times wt\%} \times 100\%$$
(S1)

$$\varphi_{THR} = \frac{THR_m - THR}{THR_m \times wt\%} \times 100\%$$
(S2)

$$\varphi_{pSPR} = \frac{pSPR_m - pSPR}{pSPR_m \times wt\%} \times 100\%$$
(S3)

$$\varphi_{TSP} = \frac{TSP_m - TSP}{TSP_m \times wt\%} \times 100\%$$
(S4)

$$\varphi_{pCOPR} = \frac{pCOPR_m - pCOPR}{pCOPR_m \times wt\%} \times 100\%$$
(S5)

$$\varphi_{TCOP} = \frac{TCOP_m - TCOP}{TCOP_m \times wt\%} \times 100\%$$
(S6)

where  $pHRR_m$ ,  $THR_m$ ,  $pSPR_m$ ,  $TSP_m$ ,  $pCOPR_m$ , and  $TCOP_m$  are the pHRR, THR, pSPR, TSP, pCOPR, and TCOP of the matrix, pHRR, THR, pSPR, TSP, pCOPR, and TCOP are the corresponding values for the composites, and wt% is the mass fraction of the nanofillers in the composites.



Figure S1. Lateral thickness of BP nanosheets: (a) sb-BP, (b) lb-BP, (c) us-BP, and (d) ec-BP; (x-1, x = a, b, c, d) AFM images; (x-2) Lateral thickness profiles in Figure S1 x-1; (x-3) Thickness distributions in Figure S1 x-2. All the scale bars are 1  $\mu$ m.



Figure S2. Lateral Length of BP nanosheets: (a) sb-BP, (b) lb-BP, (c) us-BP, and (d) ec-BP; (x-1, x = a, b, c, d) SEM images; (x-2) Lateral length profiles in Figure S2 x-1; (x-3) Length distributions in Figure S2 x-2. All the scale bars are 1  $\mu$ m. For sb-BP, lb-BP and us-BP, the lateral length profiles are obtained from 50 random nanosheets in the corresponding SEM images.



Figure S3. XRD patterns of sb-BP, lb-BP, us-BP, ec-BP and bulk BP.



Figure S4. Raman scattering spectra of sb-BP, lb-BP, us-BP, ec-BP and bulk BP.



Figure S5. TEM image of lb-BP.



Figure S6. P 2p XPS spectra of (a) sb-BP, (b) lb-BP, (c) us-BP, and (d) ec-BP.



**Figure S7. Thermal stability of BP/EPs and bare EP under nitrogen:** (a) Thermogravimetric curves, (b) Differential thermal gravity curves, and (c) Residual weights at 800 °C and maximum weight loss rates (max deriv. weight) derived from Figure S7a and S7b.



**Figure S8.** Infrared absorbance of the pyrolysis products of BP/EPs and bare EP determined by TG-IR analysis.



**Figure S9.** Analysis of the residual carbons after combustion by using Raman scattering microscopy: (a-e) Raman scattering spectra of the the residual carbons on (a) bare EP, (b) sb-BP/EP, (c) lb-BP/EP, (d) us-BP/EP, and (e) ec-BP/EP; (f) Integral area ratio of peak D and peak G.



Figure S10. XPS survey spectrum of the residual carbon on lb-BP/EP.



**Figure S11.** Photograph of the NMP suspension containing lb-BP with a concentration of 10 mg mL<sup>-1</sup>.

	bare EP	sb-BP/EP	lb-BP/EP	us-BP/EP	ec-BP/EP	
pHRR (kW m <sup>-2</sup> )	1182.3	852.4	775.9	1004.7	1027.0	
THR (MJ m <sup>-2</sup> )	27.55	23.80	20.12	25.35	26.65	
pSPR (m <sup>2</sup> s <sup>-1</sup> )	0.5615	0.2345	0.1728	0.2828	0.3646	
TSP (m <sup>2</sup> )	10.35	8.42	7.31	9.26	9.31	
pCOPR (g s <sup>-1</sup> )	0.07021	0.03002	0.02839	0.04233	0.05724	
TCOP (g)	1.576	1.027	0.776	1.145	1.345	
AEHC (MJ kg <sup>-1</sup> )	27.79	23.67	18.79	24.97	25.36	
TTI (s)	18	17	15	17	15	

Table S1. Related results of cone calorimeter measurements.

Notes: pHRR, peak of the heat release rate; THR, total heat release; pSPR, peak of smoke production rate; TSP, total smoke production; pCOPR, peak of the CO production rate; TCOP, total CO production; AEHC, average effective heat combustion; TTI, time to ignition.

Basic information in cone test is listed in Table S1. Compared to the bare EP, the four BP/EP composites possess different degrees of reduction in all the parameters (pHRR, THR, pSPR, TSP, pCOPR, TCOP, TTI, and AEHC), showing that BP nanosheets can indeed improve the flame-retardant properties of the material.

Nanofillers	Fractions (wt%)	φ <sub>pPHR</sub>	$\varphi_{_{THR}}$	φ <sub>pSPR</sub>	φ <sub>TSR</sub>	φ <sub>pCOPR</sub>	φ <sub>TCOP</sub>	Matrices	Refs.
lb-BP	1.0	34.4%	27.0%	69.2%	29.4%	59.6%	50.8%	EP	This work
BP-G	3.5	13.6%	10.9%					WPU	[1]
<b>BP-PZN</b>	2.0	29.7%	31.8%					EP	[2]
<b>BP-EC-Exf</b>	3.0	14.8%	11.5%					PUA	[3]
BP	6.0	1.1%	1.3%					CNF	[4]
<b>BP-MCNTs</b>	2.0	27.9%	20.6%					EP	[5]
<b>BP-MF</b>	1.2	36.1%						EP	[6]
<b>BP-IL</b>	2.0	19.1%	9.8%			13.2%	5.1%	TPU	[7]
BP-TA	2.0	28.3%	21.5%			18.9%		TPU	[8]
<b>BP-CTAB</b>	2.0	19.4%	4.1%					PLA	[9]
<b>BP-RGO</b>	2.0	27.6%	27.2%		14.2%			EP	[10]
BP-RuL <sub>3</sub>	3.0	20.7%	11.7%	13.2%	13.1%			EP	[11]
<b>BP-NH-TOF</b>	2.0	30.6%	22.2%					EP	[12]
<b>BP-OH</b> <sub>x</sub>	40.0	1.2%	0.9%					NFC	[13]
BP-PDA	5.0	11.4%	9.6%					PVA	[14]
<b>BP-PEI</b>	2.0	17.2%	10.6%	18.2%	11.2%		25.1%	WPU	[15]
BP-	20.0	1.9%	2.2%	2.5%	1.8%	2.5%		CNF	[16]
MWCNTs									
BP-PDA	1.2	26.8%	17.8%					PU	[17]
BP	2.7	19.4%	12.9%	17.4%	17.3%			PET/GF	[18]
<b>BP-CN</b> <sub>x</sub>	2.0	23.9%	24.8%		4.2%			EP	[19]
<b>BP-NH</b> <sub>2</sub>	20.0	4.8%						RGO	[20]
BP-MoS <sub>2</sub>	20.0	2.7%						GO	[21]
BP-HAN	2.0	28.0%	24.1%		25.4%		25.0%	EP	[22]
BP-NH-	2.0	23.6%	21.2%					EP	[23]
MCA									
<b>BP-HPL</b>	2.0	25.0%	24.5%		22.9%		23.5%	TPU	[24]

**Table S2.** Comparison of the flame retarding characteristics of lb-BP and previously reportedBP-based flame retarding nano-additives.

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