

Supporting information

**Synergic effect of graphene oxide and boron nitride on the  
mechanical properties of polyimide composite films**

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## 1. Evaluation of dispersibility

To confirm the dispersibility of each solution, only  $\text{BN}_{\text{NH}_2}(\text{G})$  and  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}$  in which  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}$  ratios were 10:1 and 100:1 suspensions were prepared. 52.5 mg of  $\text{BN}_{\text{NH}_2}(\text{G})$  and  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}$  (52.5 mg/0.525 mg or 5.25 mg) were dispersed in DMAc (20ml). After ultrasound treatment (1h),  $\text{BN}_{\text{NH}_2}(\text{G})$  and  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}$  are completely dispersed in suspension.

After 1 month, no change was observed.

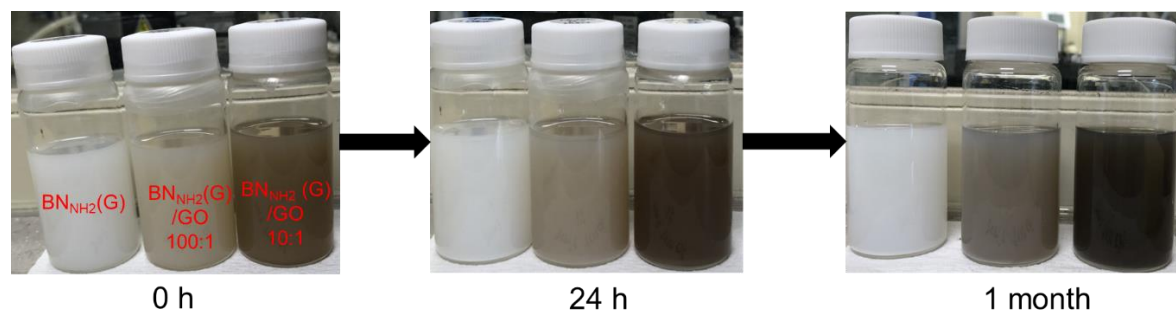


Fig. S1 Schematic illustration of dispersion process (in DMAc).

## 2. Structure analysis of functionalized BN

Series of  $\text{BN}_{\text{NH}_2}$  were prepared by using urea and guanidine hydrochloride. The products were analyzed by FT-IR to confirm N-H stretching at  $3400\text{ cm}^{-1}$ .<sup>1,2</sup>

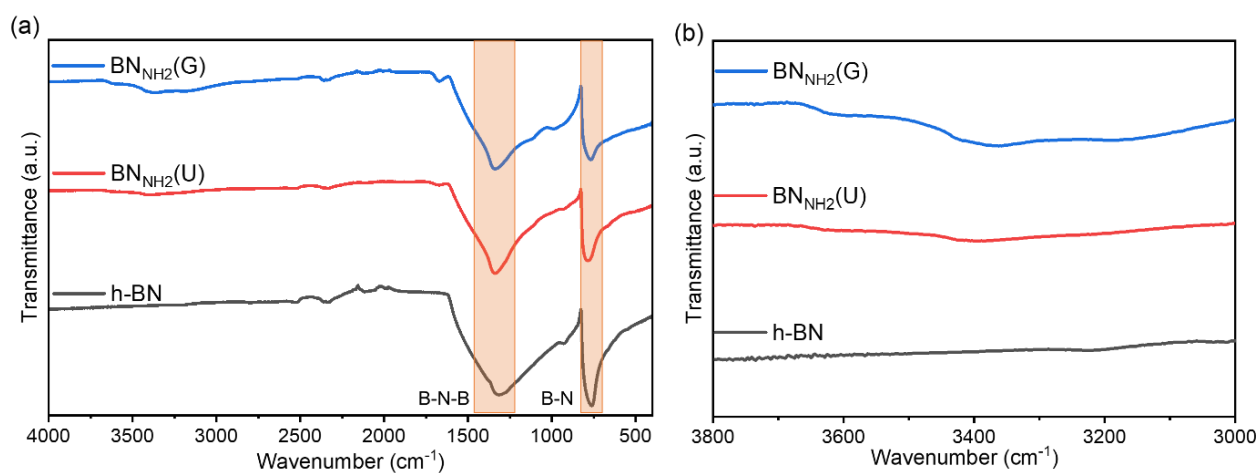


Fig. S2 FT-IR spectra of h-BN,  $\text{BN}_{\text{NH}_2}(\text{U})$ , and  $\text{BN}_{\text{NH}_2}(\text{G})$ : (a) full range and (b) narrow range.

### 3. Crystal analysis of functionalized BN

Series of  $\text{BN}_{\text{NH}_2}$  were prepared by using urea and guanidine hydrochloride. The products were analyzed by XRD to confirm (002) peak at  $26^\circ\text{C}$

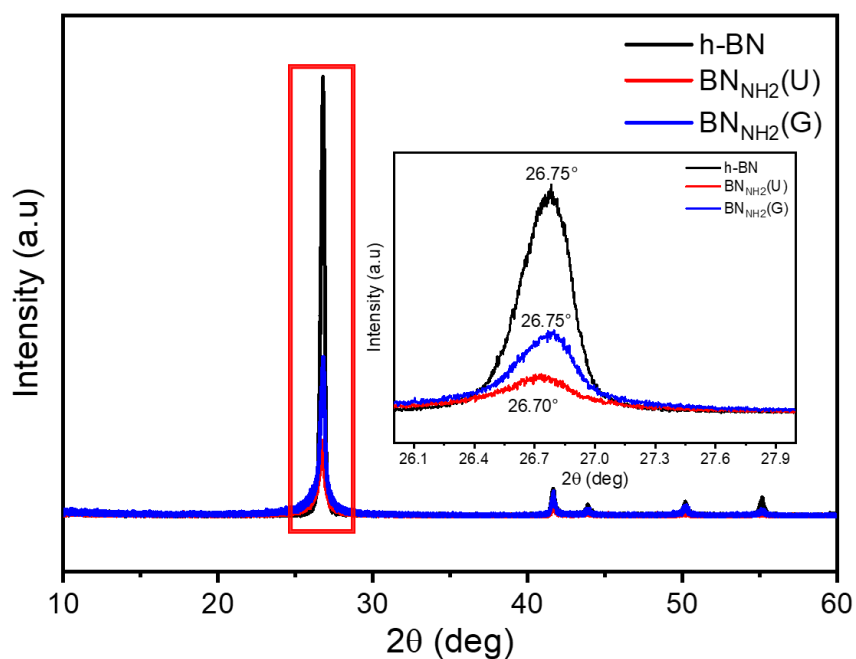


Fig. S3 XRD patterns of  $\text{BN}_{\text{NH}_2}(\text{G})$ ,  $\text{BN}_{\text{NH}_2}(\text{U})$ , and pristine h-BN zoom at (002) peak

#### 4. Structure analysis of functionalized BN with acid anhydride

After reaction with BTDA, to confirm the amide bond between amino group of  $\text{BN}_{\text{NH}_2}(\text{G})$  and acid anhydride, FT-IR was measured. According to the result, C=O group originated from amide bond was observed at  $1720\text{ cm}^{-1}$ .<sup>3,4</sup>

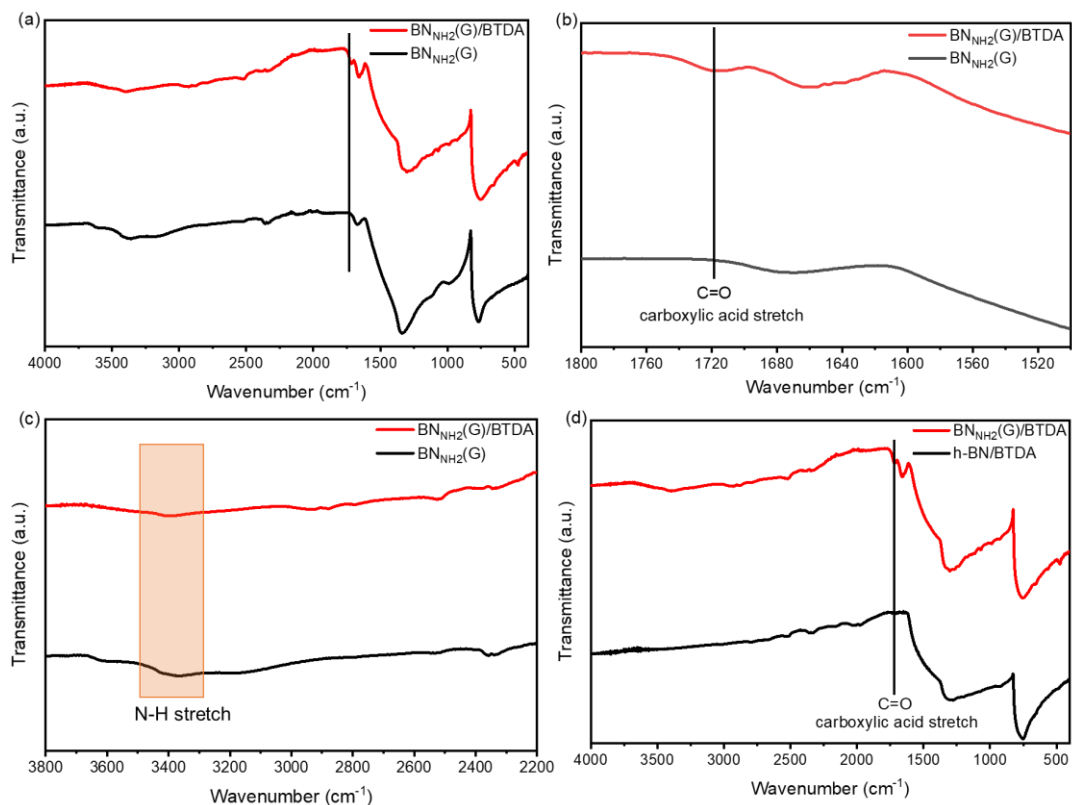


Fig. S4 FT-IR spectra of  $\text{BN}_{\text{NH}_2}(\text{G})$ ,  $\text{BN}_{\text{NH}_2}(\text{G})/\text{BTDA}$ : (a)~(c).  $\text{BN}_{\text{NH}_2}(\text{G})/\text{BTDA}$  and h-BN/BTDA comparison: (b). (a) full range, (b) narrow range around C=O peak, (c) narrow range around NH stretch peak, (d)  $\text{BN}_{\text{NH}_2}(\text{G})/\text{BTDA}$  and h-BN/BTDA full range.

#### 5. Particle size analysis

To confirm the particle size, suspensions of  $\text{BN}_{\text{NH}_2}(\text{G})$ ,  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}(10:1)$ , and  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}(100:1)$  were prepared. The particle size of  $\text{BN}_{\text{NH}_2}(\text{G})$  and  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}$  were observed by the ELSZ-2000N (Photal Otsuka Electronics, Japan) at a cumulative number of 25 times.

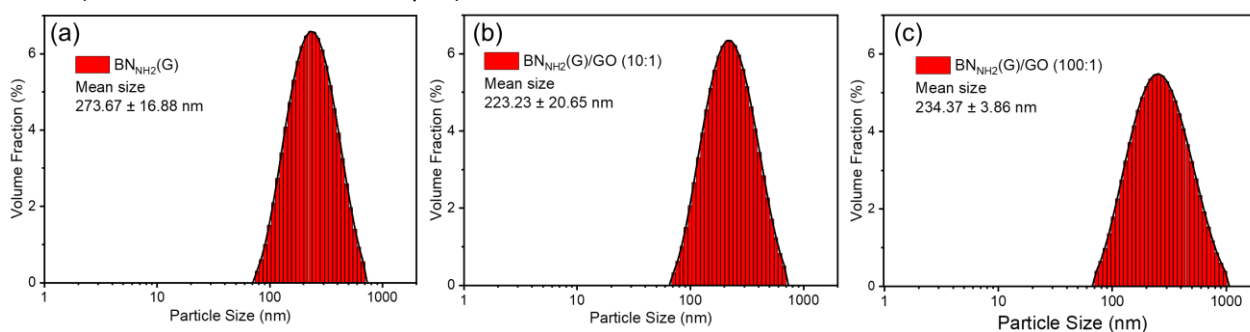


Fig. S5 The particle size analyses of (a)  $\text{BN}_{\text{NH}_2}(\text{G})$ , (b)  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}(10:1)$ , (c)  $\text{BN}_{\text{NH}_2}(\text{G})/\text{GO}(100:1)$ .

## 6. Surface observation of h-BN and BN<sub>NH2</sub>(G)

To measure the thickness of BN<sub>NH2</sub>(G), SEM measurement was carried out. the specimen was prepared by spin coating method on a silicon substrate.

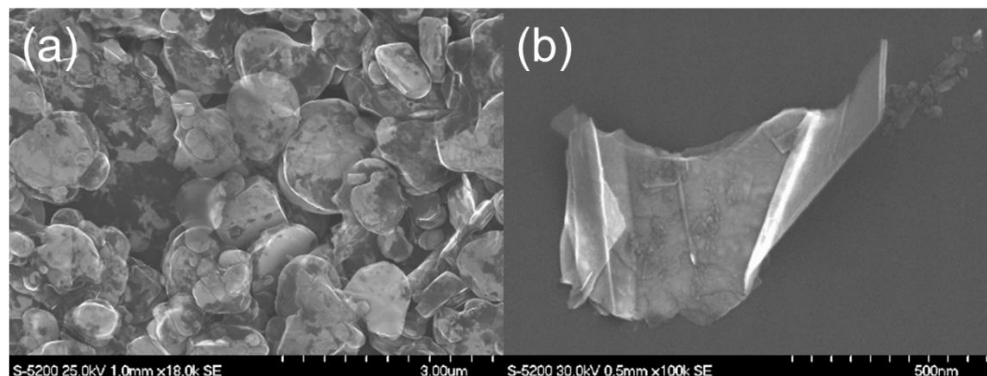


Fig. S6 SEM images of fractured surface of (a)h-BN powder (b) Dispersion of h-BN via ultrasound in DMAc

## 7. Fracture surface analysis

The specimens after the tensile strength test were observed by SEM. To impose conductivity, Au was coated on the samples before measurement.

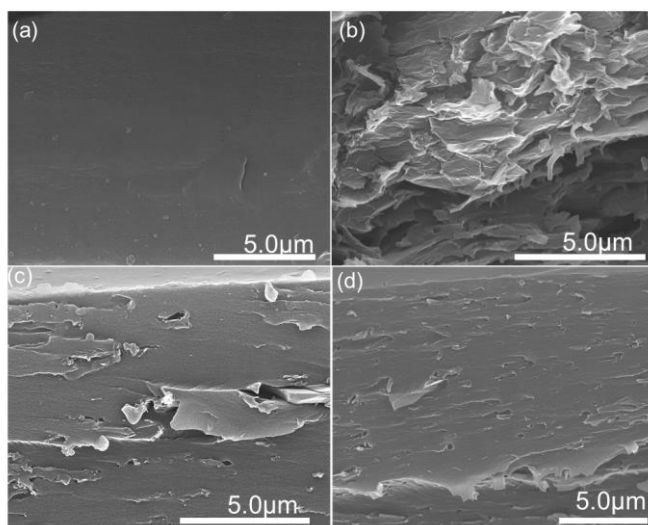


Fig. S7 SEM images of fractured surface of (a) pristine PI, (b) PI-GO 1wt%, (c) PI- BN<sub>NH2</sub>(G) 1wt%, (d) PI- BN<sub>NH2</sub>(G)/GO (100:1) 1wt% films.

## 8. Thickness analysis of BN<sub>NH2</sub>(G)

To measure the thickness of BN<sub>NH2</sub>(G), AFM measurement was carried out. The specimen was prepared by spin coating method on a silicon substrate with a thermally oxidized layer of 300 nm.

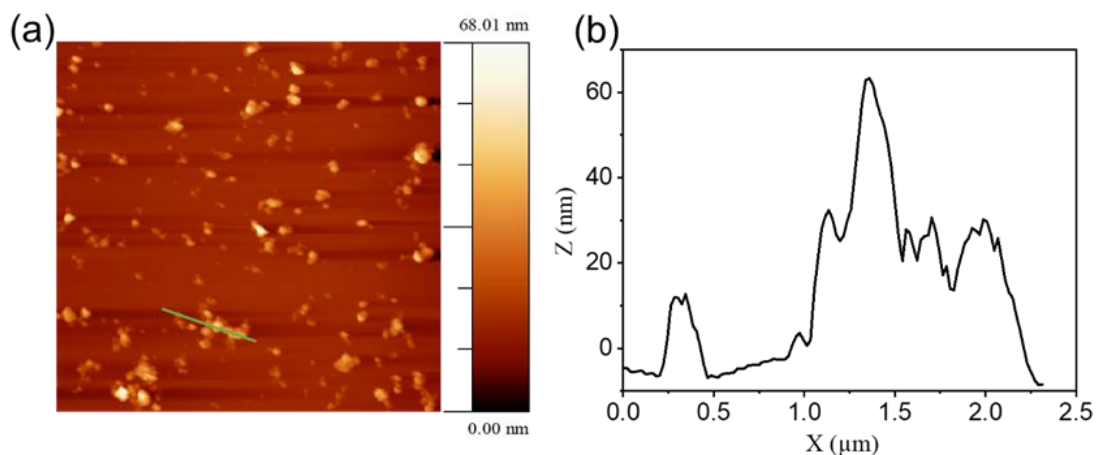


Fig. S8 (a) AFM images of BN<sub>NH<sub>2</sub></sub>(G) flakes, (b) the height profile along the green line in (a).

### 9. Purification of BN<sub>NH<sub>2</sub></sub>(G) by dialysis

To confirm the purification of BN<sub>NH<sub>2</sub></sub>(G) by dialysis, three different dialysis times (5h, 24h, 1 week) were conducted. Focusing on FT-IR peaks from 400 cm<sup>-1</sup> to 1800 cm<sup>-1</sup>, the peaks originating from guanidine hydrochloride were removed by dialysis and 24h-treatment was enough for the purification.<sup>5</sup>

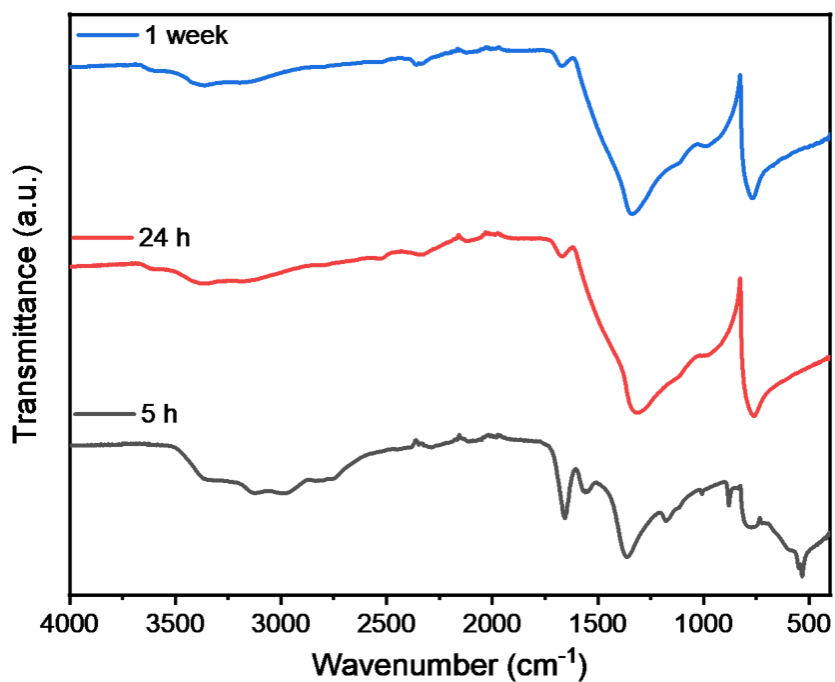


Fig. S9 FT-IR spectra of BN<sub>NH<sub>2</sub></sub>(G) by three different dialysis times (5h, 24h, and 1 week).

## 10. Comparison of mechanical properties

**Table S1.** Mechanical properties of PI-BN<sub>NH<sub>2</sub></sub>(G) films, and PI-BN<sub>NH<sub>2</sub></sub>(G)/GO films.

Entry	Sample	Percentage of sample in PI	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
1	PI-BN <sub>NH<sub>2</sub></sub> (G)	0.5	114.9 ± 5.9	3.1 ± 0.1	7.8 ± 3.1
2	PI-BN <sub>NH<sub>2</sub></sub> (G)	3	126.8 ± 6.3	3.3 ± 0.1	6.4 ± 0.8
3	PI-BN <sub>NH<sub>2</sub></sub> (G)	5	109.5 ± 7.1	2.8 ± 0.3	6.6 ± 1.1
4	PI-BN <sub>NH<sub>2</sub></sub> (G)/GO (100:1)	0.5	118.9 ± 4.1	2.1 ± 0.2	13.9 ± 3.2
5	PI-BN <sub>NH<sub>2</sub></sub> (G)/GO (100:1)	3	138.0 ± 5.1	3.3 ± 0.2	8.4 ± 1.4
6	PI-BN <sub>NH<sub>2</sub></sub> (G)/GO (10:1)	0.5	119.9 ± 4.7	2.4 ± 0.3	9.3 ± 2.3
7	PI-BN <sub>NH<sub>2</sub></sub> (G)/GO (10:1)	1	137.3 ± 3.2	3.3 ± 0.1	7.2 ± 1.5
8	PI-BN <sub>NH<sub>2</sub></sub> (G)/GO (10:1)	3	129.8 ± 4.2	2.9 ± 0.4	7.9 ± 0.9

## References

- 1 R. Geick, C. H. Perry and G. Rupprecht, *Phys. Rev.*, 1966, **146**, 543–547.
- 2 Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z. Y. Juang, M. S. Dresselhaus, L. J. Li and J. Kong, *Nano Lett.*, 2010, **10**, 4134–4139.
- 3 S. Shin, J. Jang, S. H. Yoon and I. Mochida, *Carbon.*, 1997, **35**, 1739–1743.
- 4 O. Gershevitc and C. N. Sukenik, *J. Am. Chem. Soc.*, 2004, **126**, 482–483.
- 5 L. Shi, L. Liang, F. Wang, J. Ma and J. Sun, *Catal. Sci. Technol.*, 2014, **4**, 3235–3243.