

Supporting Information

Air stable conductivity of black phosphorous / graphitic carbon nitride blends

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Transmission electron microscopy

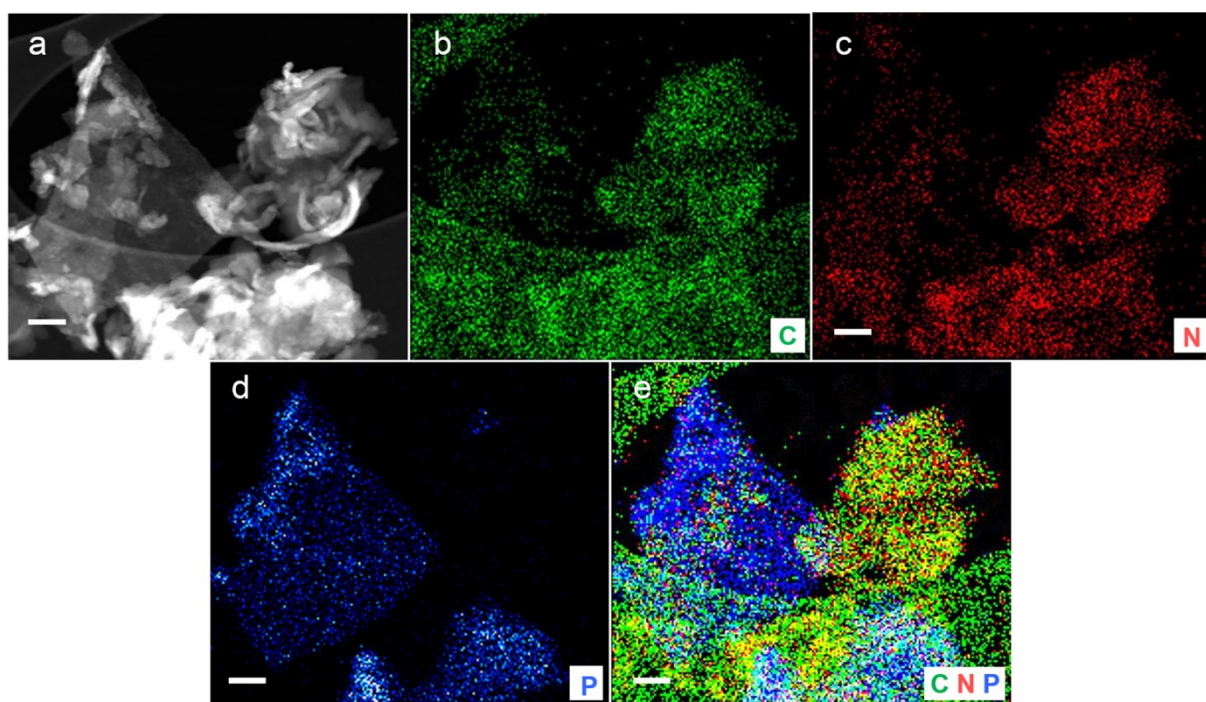


Figure S1 (a) High-angle annular dark field (HAADF) scanning TEM (STEM) image of 10 wt% BP/g-C₃N₄ sample. STEM-energy-dispersive X-ray (EDX) mapping of (b) C, (c) N, (d) P, and (e) the overlay of all the elements. Scale bars: 100 nm. The TEM grids used are lacey carbon film coated nickel grids.

Electrical characterization ($I_D V_D$ curves)

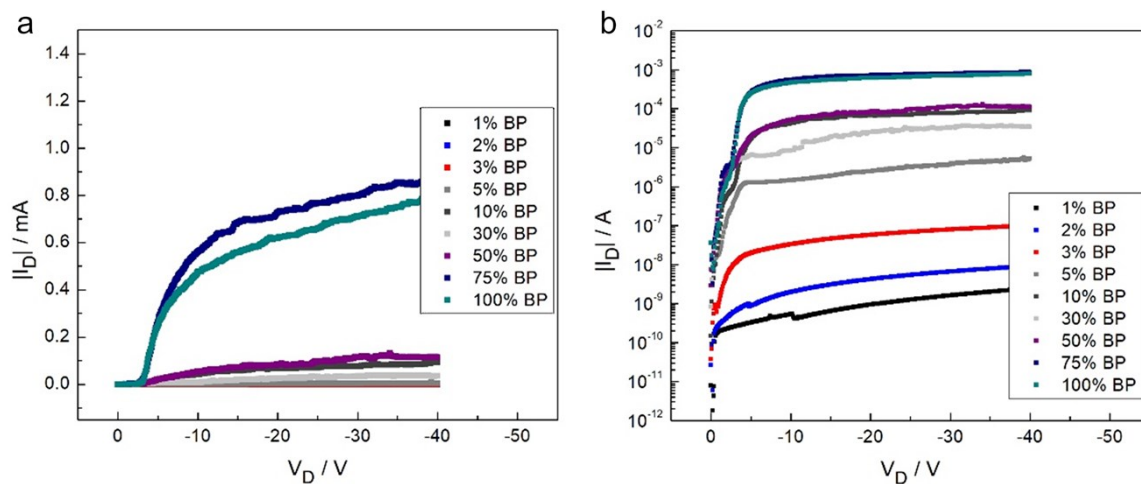


Figure S4 I-V curves of tested devices at varying contents of black phosphorous (BP) and carbon nitride (g-C₃N₄). Curves represented in (a) linear and (b) logarithmic scale.

Profilometer measurements and atomic force microscopy height plots

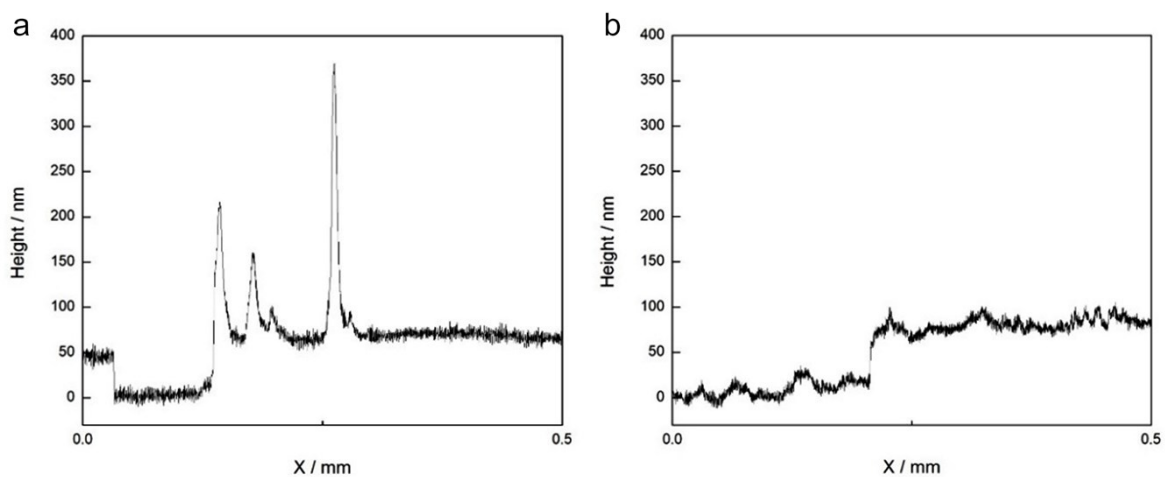


Figure S2 Profilometer measurements of films of (a) BP and (b) g-C₃N₄.

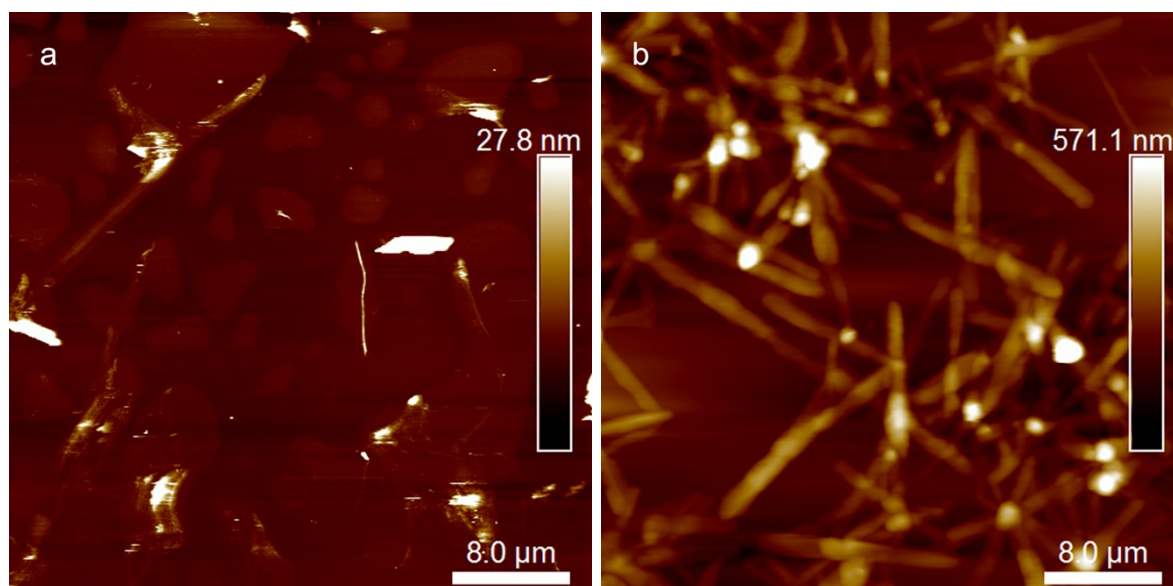


Figure S3 Atomic force microscopy height plots of films of (a) BP and (b) g-C₃N₄.

Conductivity measurements of pristine devices

Table S1 Measured current and conductivity values of films with varying contents of black phosphorous (BP) and carbon nitride (g-C₃N₄). Measurements performed in air on samples immediately after removal from nitrogen atmosphere.

BP (wt%)	g-C ₃ N ₄ (wt%)	I _D (A)	σ (S/m)	STDEV (S/m)
0	100	-1.35 × 10 ⁻⁸	3.38 × 10 ⁻⁶	2.25 × 10 ⁻⁷
1	99	-1.51 × 10 ⁻⁸	3.79 × 10 ⁻⁶	6.43 × 10 ⁻⁶
2	98	-2.08 × 10 ⁻⁸	5.21 × 10 ⁻⁶	1.55 × 10 ⁻⁶
3	97	-1.39 × 10 ⁻⁷	3.48 × 10 ⁻⁵	2.33 × 10 ⁻⁵
5	95	-5.90 × 10 ⁻⁶	1.48 × 10 ⁻³	1.35 × 10 ⁻³
10	90	-3.54 × 10 ⁻⁵	8.86 × 10 ⁻³	5.71 × 10 ⁻³
30	70	-1.22 × 10 ⁻⁴	3.06 × 10 ⁻²	9.24 × 10 ⁻³
50	50	-6.32 × 10 ⁻⁴	1.58 × 10 ⁻¹	1.46 × 10 ⁻²
75	25	-1.15 × 10 ⁻³	2.86 × 10 ⁻¹	3.47 × 10 ⁻²
100	0	-1.31 × 10 ⁻³	3.28 × 10 ⁻¹	6.50 × 10 ⁻²

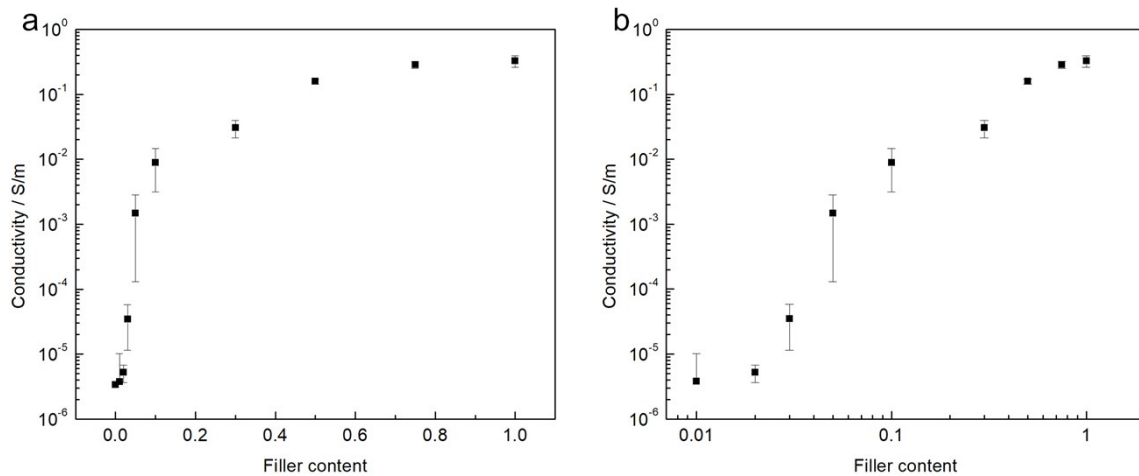


Figure S5 (a) Conductivity as a function of the percentage (mass fraction) of black phosphorous (BP) in the BP/g-C₃N₄ blend. The curve is represented in (a) logarithmic scale and (b) log-log scale. Averages over 4 identical devices. The error bars represent the standard deviation.

Fitting parameters

Table S2 Values of the parameters of the Sigmoidal-Boltzmann fitting of the conductivity as a function of the percentage of black phosphorous (BP) in the BP/g-C₃N₄ blend.

Parameter	Value	STDEV
A ₁	2.57 × 10 ⁻⁶	8.70 × 10 ⁻⁷
A ₂	0.00886	1.41 × 10 ⁻⁶
x ₀	0.05802	1.05 × 10 ⁻⁵
Δx	0.00498	6.61 × 10 ⁻⁵

Table S3 Values of the parameters of the linear fitting of the double-logarithmic plot of electrical conductivity vs. $\varphi - \varphi_c$. R² = 0.914.

Parameter	Value	STDEV
Interception	-0.45506	0.13017
Slope	1.23182	0.18683

Conductivity measurements of devices subjected to air atmosphere

Table S4 Measured conductivity values of films with varying contents of black phosphorous (BP) and carbon nitride (g-C₃N₄). Conductivity measurements performed in air on samples immediately after removal from nitrogen atmosphere (σ_{pristine}), after storage in air for 1 month ($\sigma_{\text{1 month}}$) and after storage in air for 4 months ($\sigma_{\text{4 months}}$).

BP (wt%)	g-C ₃ N ₄ (wt%)	σ_{pristine} (S/m)	$\sigma_{\text{1 month}}$ (S/m)	$\sigma_{\text{4 months}}$ (S/m)
1	99	3.79×10^{-6}	1.87×10^{-6}	1.89×10^{-6}
2	98	5.21×10^{-6}	4.93×10^{-6}	1.50×10^{-5}
3	97	3.48×10^{-5}	3.73×10^{-5}	3.64×10^{-5}
5	95	1.48×10^{-3}	1.27×10^{-3}	1.22×10^{-3}
10	90	8.86×10^{-3}	7.63×10^{-3}	7.69×10^{-3}
30	70	3.06×10^{-2}	2.69×10^{-2}	2.30×10^{-2}
50	50	1.58×10^{-1}	1.43×10^{-1}	1.37×10^{-1}
75	25	2.86×10^{-1}	1.74×10^{-1}	9.91×10^{-2} (1)
100	0	3.28×10^{-1}	6.00×10^{-2}	3.05×10^{-4} (2)

(1) Two devices failed to perform.

(2) Four devices failed to perform.

Materials and Methods

Materials: Bulk black phosphorus (BP, ~99.998%) was purchased from Smart Elements. Urea, HNO₃, N-Methyl-2-pyrrolidone (NMP, 99.5%, anhydrous), and isopropanol (IPA, 99.5%, anhydrous) were purchased from Sigma-Aldrich.

Preparation of graphitic carbon nitride (g-C₃N₄) nanosheets: A previously reported method was used for the preparation of g-C₃N₄ nanosheets.^[1] In a typical synthesis, 30 g of urea was placed in an alumina crucible with a cover and then underwent a programmed heating treatment in a tube furnace. With a heating rate of 2 °C min⁻¹, the temperature was increased to 250, 350, and 550 °C, and preserved at the three temperatures for 1, 2, and 2 h, respectively. After cooling down to room temperature, the obtained yellow powder in the crucible was washed with dilute HNO₃ solution and deionized water for three times. The solid precipitates collected by centrifugation were dried at 80 °C in an oven for 12 h.

Preparation of BP nanosheets: An “NMP-ice-assisted” exfoliation approach was used for the preparation of BP nanosheets, which was previously developed by our group.^[2] Briefly, 25 mg of bulk BP was meticulously ground into ultrafine black powder in a N₂-filled glove box and ultrasonicated into 25 mL of NMP solvent until getting a homogeneous dispersion. The dispersion was frozen with a liquid N₂ bath and then sonicated in a BRANSONIC bath sonicator. These two procedures were repeated for three times. The dispersion was then centrifuged at 4000 rpm for 15 min to remove the un-exfoliated BP. The light yellow supernatant was further centrifuged at 12000 rpm for 20 min to get the BP nanosheets, which were then washed and dispersed into 25 mL of IPA. The concentration of BP in the final IPA dispersion was measured to be 0.75 mg mL⁻¹ by an Inductively Coupled Plasma-Atomic Emission Spectroscopy. The obtained solutions were stable for months in isopropanol. As shown in **Figure S6**, BP dispersions in isopropanol are light yellow and very stable, and there is no precipitation and color change over four weeks during storage.

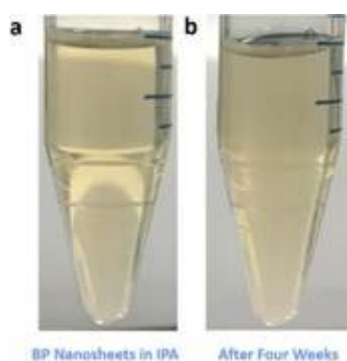


Figure S6. Photographs of BP nanosheets in isopropanol (a) at the first day and (b) after four weeks.

Preparation of BP/g-C₃N₄ devices: BP/g-C₃N₄ composites with different weight percentages of BP were prepared according to our previously reported method.^[2] Typically, 5 mg of g-C₃N₄ powder was dispersed into 10 mL of IPA, which was then added with 67 µL of BP dispersion and stirred for 2 h under the bubbling of N₂ gas. Afterwards, the precipitates were collected by centrifugation at 6500 rpm for 10 min, and then washed with IPA. The final

BP/g-C₃N₄ product contained 1 wt% BP was prepared and then dispersed in 10 mL of IPA for further use. By varying the addition volumes of BP dispersion, 2, 3, 5, 10, 30, 50, and 75 wt% BP/g-C₃N₄ solutions were prepared. The 100 wt% BP sample was obtained by adding 6.7 mL of BP dispersion into 3.3 mL of IPA. Subsequently, 400 μ L of the above dispersion solutions were drop-casted onto the patterned substrates inside a N₂-filled glove box and the 1, 2, 3, 5, 10, 30, 50, 75, and 100 wt% BP/g-C₃N₄ devices were fabricated, respectively.

Conductivity measurements: The conductivity measurements were performed using 2-terminal devices in a bottom-contact geometry. A Keithley 2636 sourcemeter was used to measure the current between the two electrodes. The conductivity was measured at $V_D = -40V$ using the equation $\sigma = L/RA$ where L is the channel length, R is the measured resistance and A is the area of the film cross-section. $A = \text{channel width (10 mm)} \times \text{film thickness (50 nm)}$.

Device storage: The samples were stored in a N₂-filled glove box prior to the first measurement. After the first measurement, the samples were stored in dark and in air environment (relative humidity ranging from 30% to 50%).

Morphological properties and thickness measurements: Morphological properties studied on Atomic Force Microscopy (AFM, Multimode AFM, controller Nanoscope V (Bruker), Nanoscope software version 7.30 was used to treat the images. Ambios XP-2 Profiler was used to measure thicknesses of prepared films.

- [1] a) Z. Xu, M. G. Kibria, B. AlOtaibi, P. N. Duchesne, L. V. Besteiro, Y. Gao, Q. Zhang, Z. Mi, P. Zhang, A. O. Govorov, L. Mai, M. Chaker, D. Ma, *Appl. Catal. B* **2018**, *221*, 77; b) Q. Zhang, J. Deng, Z. Xu, M. Chaker, D. Ma, *ACS Catal.* **2017**, *7*, 6225; c) Q. Zhang, F. Yang, S. Zhou, N. Bao, Z. Xu, M. Chaker, D. Ma, *Appl. Catal., B* **2020**, *270*, 118879.
- [2] Q. Zhang, S. Huang, J. Deng, D. T. Gangadharan, F. Yang, Z. Xu, G. Giorgi, M. Palummo, M. Chaker, D. Ma, *Adv. Funct. Mater.* **2019**, *29*, 1902486.