



# Black Phosphorus/Carbon Nanoframes for Efficient Flexible All-Solid-State Supercapacitor

Zunbin Duan <sup>1,†</sup>, Danni Liu <sup>1,†</sup>, Zhaoer Ye <sup>1,3</sup>, Caixia Sun <sup>1,4</sup>, Zikun Wang <sup>1,3</sup>, Kezhen Chen <sup>1,5</sup>, Yang Li <sup>1</sup>, Hao Huang <sup>1</sup>, Xiaoliang Zeng <sup>2</sup>, Jiahong Wang <sup>1,\*</sup>, Rong Sun <sup>2,\*</sup> and Xue-Feng Yu <sup>1,\*</sup>

<sup>1</sup> Shenzhen Engineering Center for the Fabrication of Two-Dimensional Atomic Crystals, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

<sup>2</sup> Shenzhen Institute of Advanced Electronic Materials, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China

<sup>3</sup> Nano Science and Technology Institute, University of Science and Technology of China, Suzhou 215125, China

<sup>4</sup> Department of Hematology, Zhanjiang Central Hospital, Guangdong Medical University, Zhanjiang 524045, China

<sup>5</sup> University of Chinese Academy of Sciences, Beijing 100049, China

\* Correspondence: jh.wang1@siat.ac.cn (J.W.); rong.sun@siat.ac.cn (R.S.); xf.yu@siat.ac.cn (X.-F.Y.)

† These authors contributed equally to this work.

## 1. Instruments and calculations of electrochemical properties

Scanning electron microscopy (SEM) was performed on a Zeiss Supra 55 high-resolution field-emission scanning electron microscope at 2.0 kV and a distance of 5.0 mm. Transmission electron microscopy (TEM) was acquired on a Tecnai G2 F20 S-Twin transmission electron microscope at 200 kV. Atomic force microscopy (AFM) was performed on an Oxford AR Cypher S atomic force microscope using the tapping mode. Optical microscopy was employed to observe the dispersed BP microplates. Powder X-ray diffraction (XRD) was performed on a Rigaku SmartLab diffractometer at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher ESCALab 250Xi spectrometer with Al K $\alpha$  radiation. The BP microplates were prepared by using an IT6123B workstation. Raman scattering microscopy was conducted on the Horiba Jobin-Yvon Lab Ram HR VIS Raman microscope (633 nm laser as the excitation; RT). The spraying process was performed using an HF-600 air pump sprayer with an airbrush. The electrochemical performance of the supercapacitors BP/C SC and BP SC was evaluated on a CHI-760E workstation (China, Shanghai). The cyclic voltamograms (CV) and galvanostatic charging-discharging curves were obtained to investigate the electrochemical properties. The electrochemical evaluations were performed in two environmental conditions, including a conventional environment of 25 °C and 40% RH and a harsh environment with a high temperature of 50 °C and a high relative humidity of 65%. The cycle stability of BP/C SC was evaluated by using a 10,000 galvanostatic charge-discharge cycles under a high current density of 4 A g<sup>-1</sup>. The bending angle is 180° in 10,000 flat-bend cycles.

The specific capacitance of the device was calculated from the CV curves with the following Eq. S1,

$$C_m = \int i(V)dV / mv\Delta V \quad (S1)$$

where  $C_m$  is the mass capacitance of the device,  $m$  is the mass of the electrode material,  $v$  is the scanning rate, and  $\Delta V$  is the potential window.

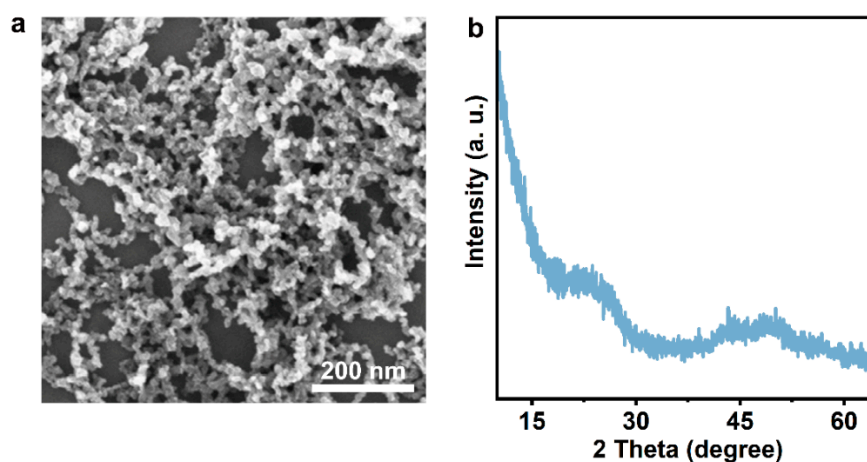
The specific capacitance of BP/C SC in galvanostatic charging-discharging process was calculated by using Eq. S2,

$$C_m = \frac{I\Delta t}{m\Delta V} \quad (S2)$$

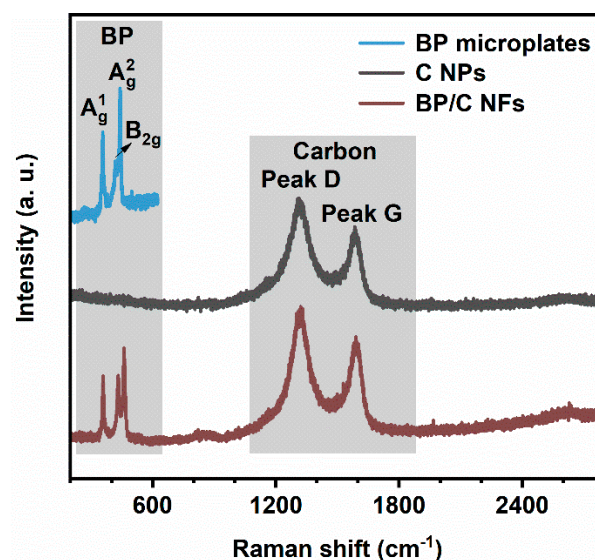
where  $I$  is the current density, and  $\Delta t$  is the discharge time.

The power density of BP/C SC is calculated by using the following Eq. S3,

$$P = I\Delta V / m \quad (S3)$$



**Figure S1.** Characterization of C NPs. (a) SEM image. (b) XRD pattern.



**Figure S2.** Raman scattering spectra of BP microplates, C NPs, and BP/C NFs.

In the Raman spectra shown in Figure S2, the BP/C NFs possess characteristic peaks of BP near  $360.6\text{ cm}^{-1}$  of  $A_g^1$ ,  $439.7\text{ cm}^{-1}$  of  $B_{2g}$ , and  $466.2\text{ cm}^{-1}$  of  $A_g^2$  [S1, S2] and characteristic peaks of carbon around  $1365\text{ cm}^{-1}$  of peak D and  $1596\text{ cm}^{-1}$  of peak G [S3], which are not much different from BP microplates and C NPs alone. This may mean that the BP microplates and C NPs are only physically mixed in the BP/C NFs.

### Supplementary references

- S1. Zeng, L.; Zhang, X.; Liu, Y.; Yang, X.; Wang, J.; Liu, Q.; Luo, Q.; Jing, C.; Yu, X.; Qu, G.; Chu, P. K.; Jiang, G. Surface and interface control of black phosphorus. *Chem* **2022**, *8*, 632-662.
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- S3. Duan, Z.; Wang, Y.; Bian, S.; Liu, D.; Zhang, Y.; Zhang, X.; He, R.; Wang, J.; Qu, G.; Chu, P. K. Size-dependent flame retardancy of black phosphorus nanosheets. *Nanoscale* **2022**, *14*, 2599-2604.