Electronic Supplementary Information

Synthesis of High-Quality Black Phosphorus Sponges for All-Solid-State Supercapacitor

Min Wen[a], Danni Liu[a], Yihong Kang[a], Jiahong Wang[a,b], Hao Huang[a], Jia Li[a], Paul K Chu[b] and Xue-Feng Yu[a,*]

[a] *Center for Biomedical materials and Interfaces, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055 (P. R. China)*

[b] *Department of Physics and Department of Materials Science and Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong (P. R. China)*

E-mail: xf.yu@siat.ac.cn

Chemicals

The bulk BP crystals were purchased from Mophos (China). Tetrabutylphosphonium bromide (99.0 %), alcohol (99.5 %), n-hexane (99.5 %), and N,N-dimethylformamide (DMF, 99.5 %) were purchased from Aladdin. Poly(vinylalcohol) (PVA) and phosphoric acid (H_3PO_4) were obtained from Alfa Aesar. The silver plastic was purchased from TED PELLA, INC. Ultrapure water with a resistivity of 18.2 MΩ was used in the experiments and all the chemicals were used without further purification.

Instruments

Scanning electron microscopy (SEM) was performed on the Zeiss Supra 55 high-resolution field-emission scanning electron microscope at an accelerating voltage of 2.0 kV. Raman scattering spectra were acquired at room temperature on a Horiba Jobin-Yvon Lab Ram HR VIS high-resolution confocal Raman microscope equipped with a 633 nm laser as the excitation source. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Fisher ESCALAB 250Xi XPS. Atomic force microscopy (AFM) images were performed on the Bruker MultiMode 8. Transmission electron microscopy (TEM) images, high-resolution TEM (HR-TEM) images, and selected-area electron diffraction (SAED) patterns were acquired on the Tecnai G2 F20 S-Twin transmission electron microscope at 200 kV. The BP sponges were synthesized using an IT6123B workstation. The ICP elemental analysis was acquired on PE ICP-OES Optima 7000DV. The Au film on PET substrates for supercapacitor construction were evaporated on JSD 350. The electrochemical performance of the supercapacitors was evaluated on CHI-760E workstation (China, Shanghai) and cyclic voltamograms and galvanostatic charging/discharging curves were obtained to investigate the electrochemical properties.

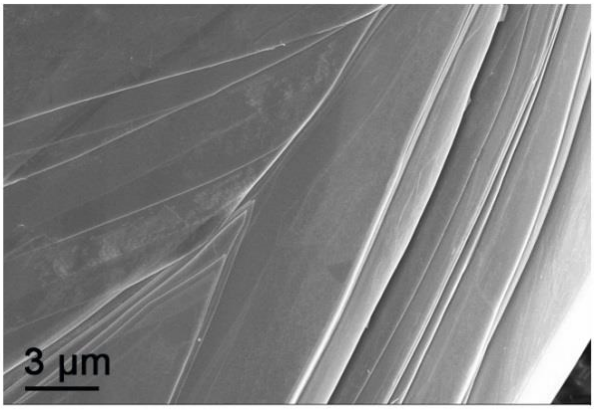

Fig. S1 SEM image of bulk BP crystal.

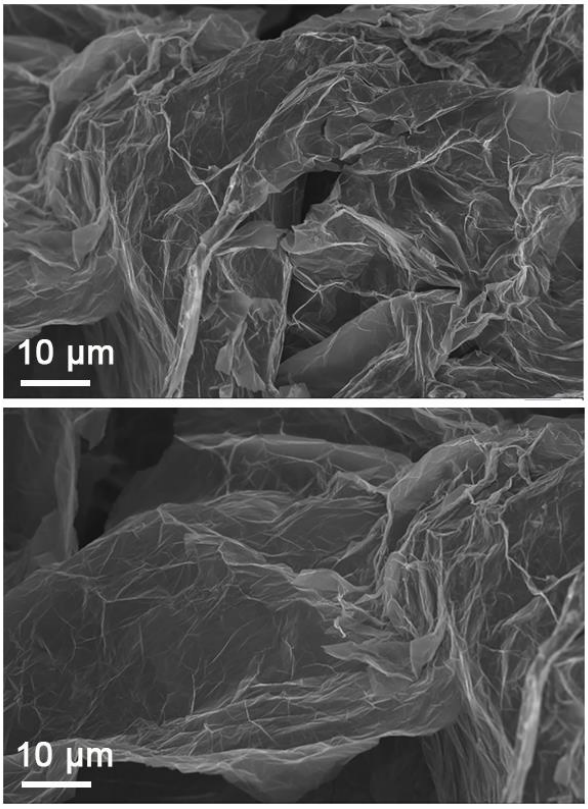

Fig. S2 Magnified SEM images of BP sponge.

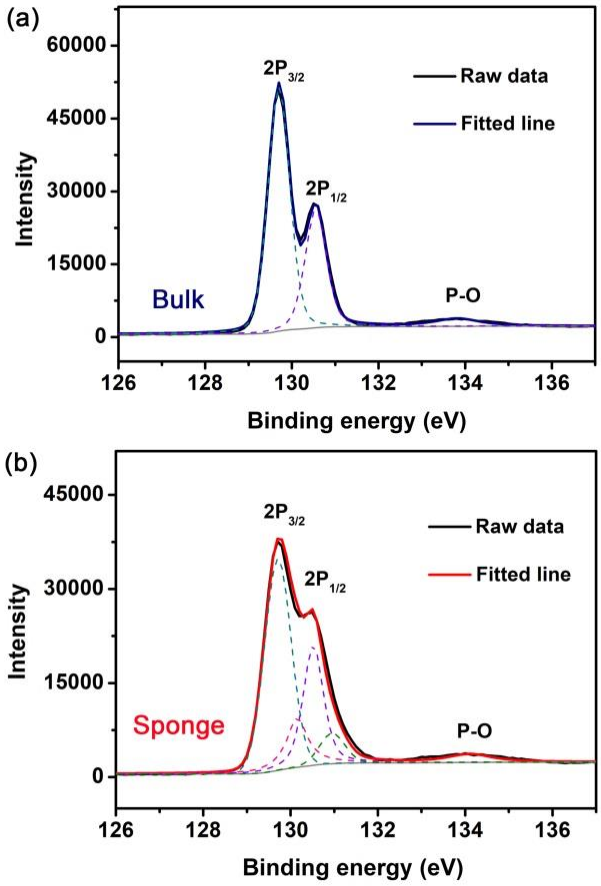

Fig. S3 Original XPS spectra (P 2p) of the bulk BP (a) and BP sponge (b).

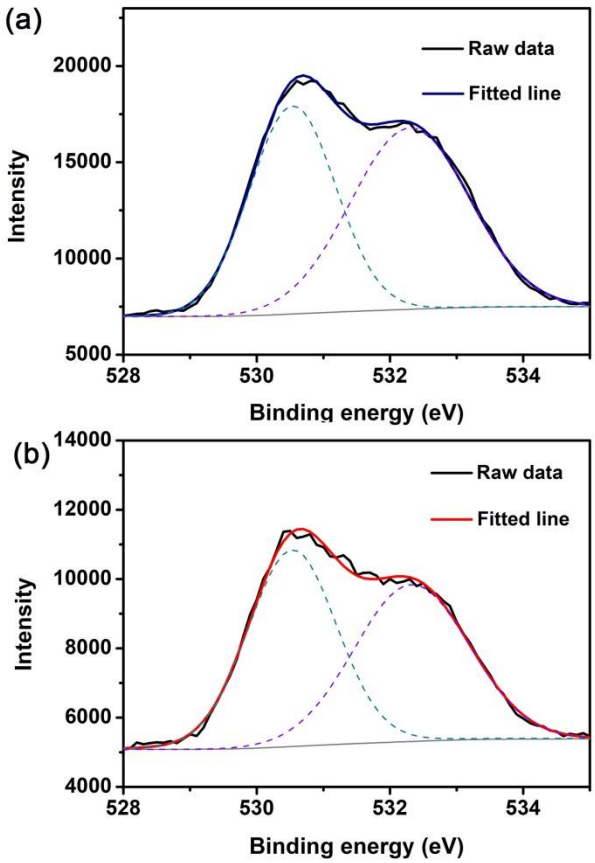

Fig. S4 XPS spectra (O 1s) of the bulk BP (a) and BP sponge (b).

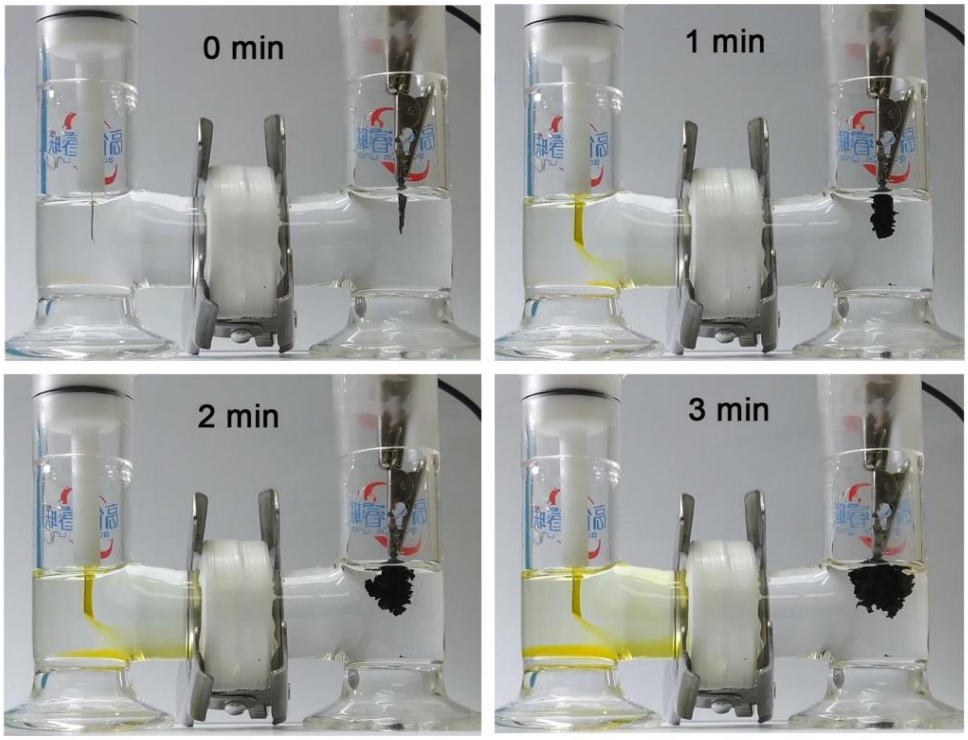

Fig. S5 Color change of the electrolyte in the anode and cathode at time points of 0, 1, 2, and 3 mins during synthesis of BP sponge.

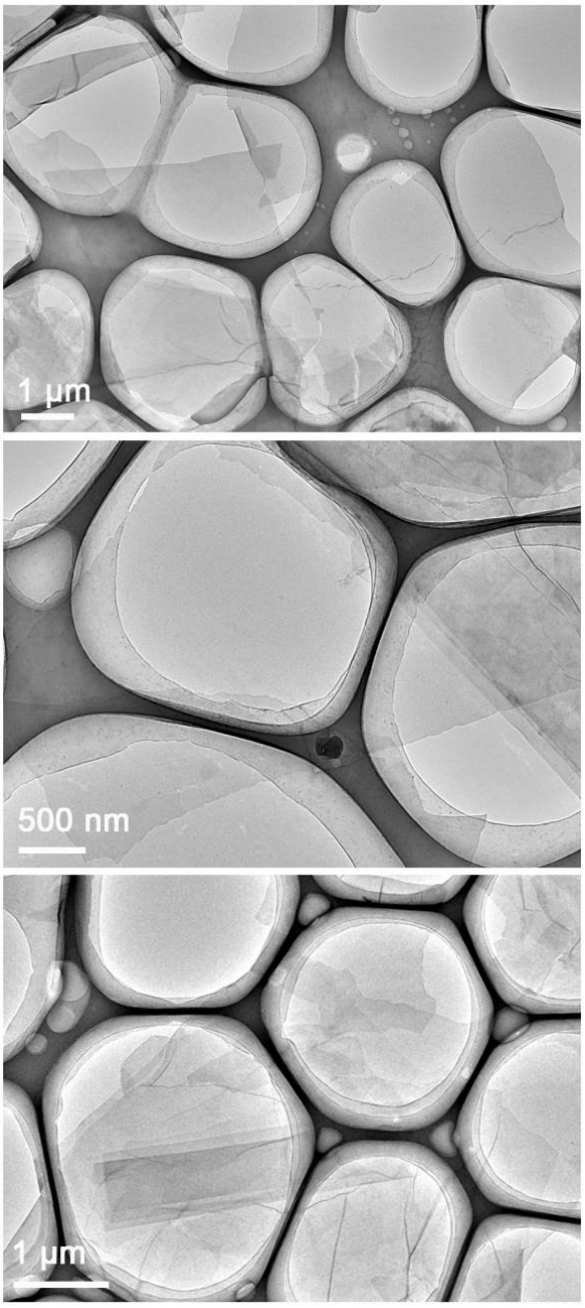

Fig. S6 TEM images of nanosheets in BP sponge.

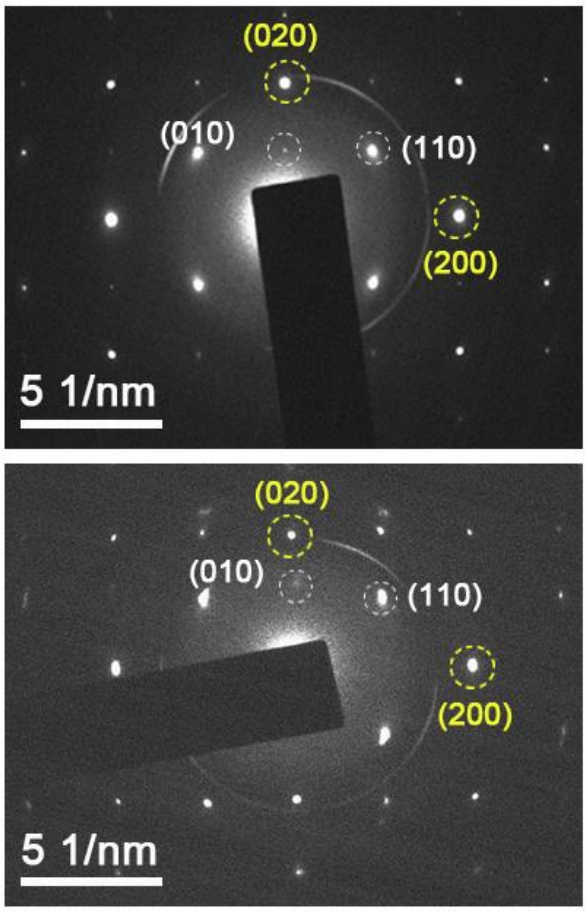

Fig. S7 SAED patterns of the nanosheets in BP sponge.

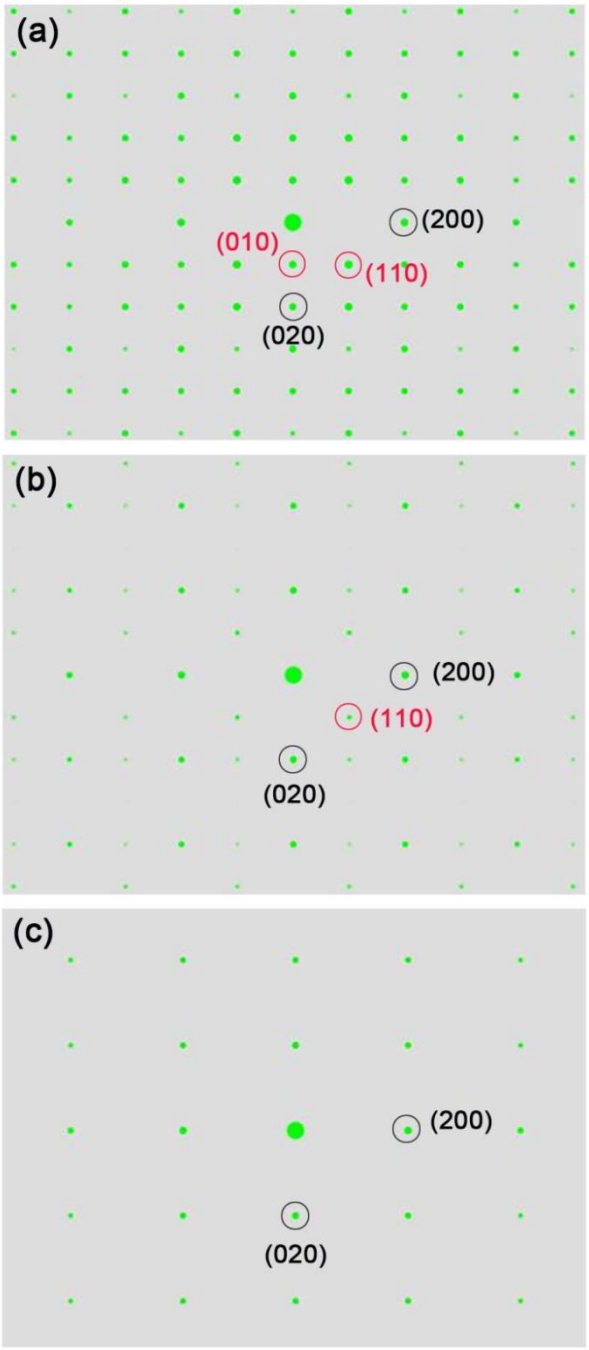

Fig. S8 Simulated SAED patterns: (a) Single-layer, (b) Two-layer, and (c) Multi-layer BP. The BP crystal structure from reference[1] is used and simulated using CrystalMaker Software LTD.

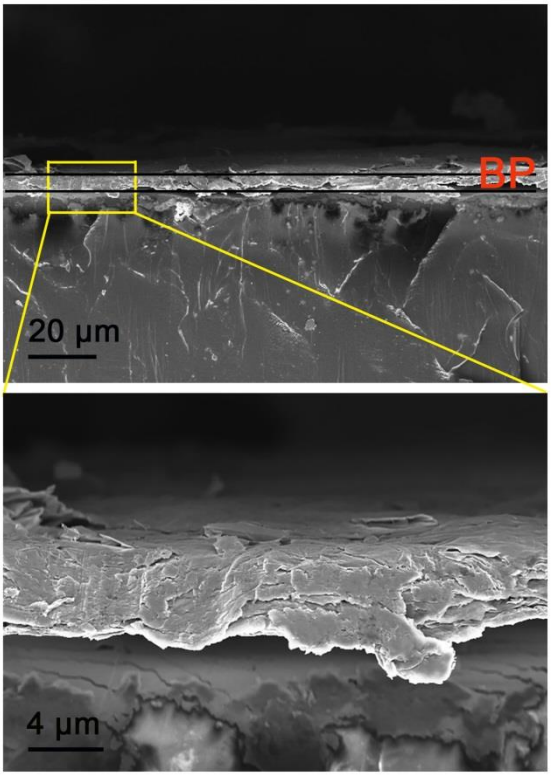

Fig.S9 The cross-section SEM image of the electrode.

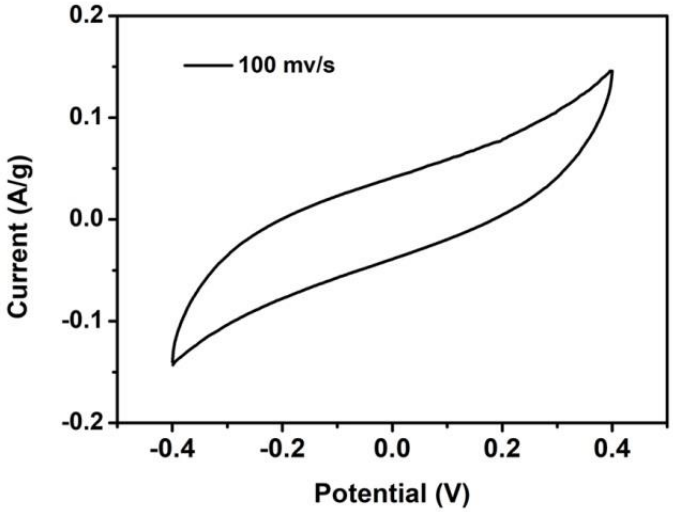

Fig. S10 Cyclic voltammogram of all-solid-state supercapacitor with bulk BP as the electrode materials acquired at a scanning rate of 100 mV/s.

Accoridng to Eq. 1, the specific mass capacitance of the all-solid-state supercapacitor with bulk BP as the electrode materials is calculated to be 0.7 F/g at 100 mV/s which is smaller than that of BP-ASSP (28 F/g at 100 mV/s).

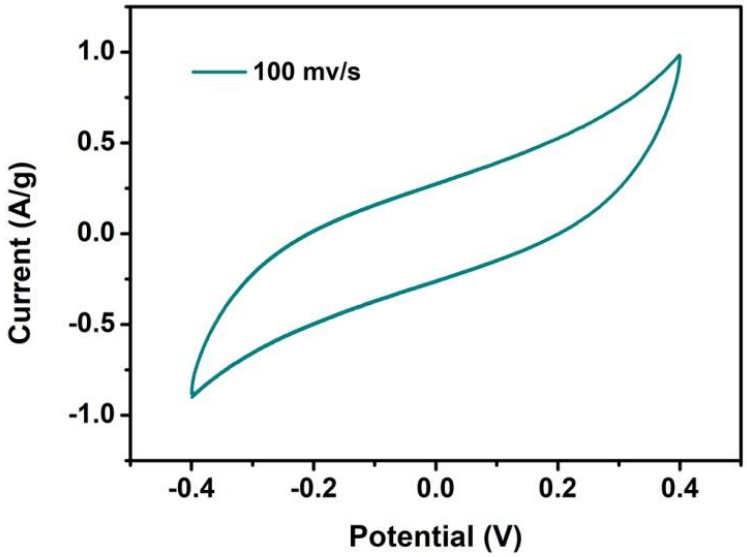

Fig. S11 Cyclic voltammogram of the all-solid-state supercapacitor composed of BP nanosheets as the electrode materials obtained at a scanning rate of 100 mV/s.

Accoridng to Eq. 1, the specific mass capacitance of the all-solid-state supercapacitor composed of BP nanosheets as the electrode materials is 4.7 F/g at 100 mV/s and less that of BP-ASSP (28 F/g at 100 mV/s).

Reference

1. R. Hultgren, N. S. Gingrich, B. E. Warren, *J. Chem. Phys.* **1935**, *3*, 351.