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Electronic Supplementary Information for

Rapid and Scalable Production of High-Quality Phosphorene by Plasma-Liquid Technology

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Experimental details

Materials

The BP crystals were synthesized using a previously reported modified chemical vapor transport method. In brief, 400 mg of red phosphorus, 30 mg of Sn, and 10 mg of SnI_4 were weighed in a silica tube with a length of 12 cm, inner diameter of 1.0 cm, and wall thickness of 0.2 cm. The tube was evacuated, sealed, and placed horizontally in a muffle furnace with one end closer to the heating elements. The temperature was set to 650 °C and then cooled to 480 °C during 10 h followed by natural cooling. *N, N*-dimethylformamide (DMF, ≥99.9%) was purchased from Aladdin Ltd. (Shanghai, China) and isopropyl alcohol (IPA, ≥99.7%) was obtained from Shanghai Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

Plasma-liquid exfoliation of BP crystal to few-layer phosphorene

A home-made plasma-liquid system comprising a high-voltage power supply, two electrodes (a BP cathode and a plasma anode), and a glass cell filled with DMF solution was

used in the experiments. On the cathode side, the bulk BP crystal was partially immersed in the solution. The other electrode was the atmospheric-pressure argon plasma, which was generated from a stainless steel capillary tube with flowing argon gas (~ 30 sccm) and positioned 2 mm above the surface of the solution. Exfoliation was carried out by applying a high-voltage (from 1.8 to 2.5 kV) to the anode for only 5 minutes at room temperature (25 ^{o}C) and relative humidity of 80% $\pm$ 10%. Rapid release of fine particulates from the crystal to the solution was observed and after exfoliation, the materials were collected. In the synthesis, the voltage could be applied to change the electron number density [1] to prepare the phosphorene sheets with different thicknesses.

Preparation of the phosphorene film and fabrication of the photodetector

The phosphorene sheets were dispersed in isopropyl alcohol (IPA) (1 mg/mL) ultrasonically for a few seconds, centrifuged at 8,000 r/min for 5 min, and redispersed in IPA. 5 mL of the phosphorene solution were vacuum filtered with cellulose membranes (Diameter 50 mm, pore size 0.45 μm) and dried at 60 ^{o}C. The film was cut into several pieces with dimensions of 5×10 mm^2 and two pieces of conductive adhesive were used as the electrodes.

Characterization

High-resolution mass spectrometry (HRMS) was conducted on the Micromass Q-TOF mass spectrometer. The TEM and HR-TEM images were taken on the FEI Tecnai G2 F30 transmission electron microscope at an acceleration voltage of 200 kV and SEM was carried out on the ZEISS SUPRA 55 (Carl Zeiss, Germany) field-emission scanning electron microscope. AFM was performed on the drop-cast flakes on SiO_2 substrates on the Bruker Dimension Icon atomic force microscope (Bruker, USA) using the tapping mode and XPS was conducted on the Thermo Fisher ESCALAB 250Xi system. The XRD data was acquired by X-ray diffraction (XRD, D8 Advance, Cu K_α radiation). The Raman scattering spectra and optical images were obtained on a Horiba Jobin Yvon LabRam HR-VIS high-resolution confocal Raman microscope equipped with a 633 nm laser. The electrical data was recorded by a electrochemical workstation (CHI760e, Shanghai).

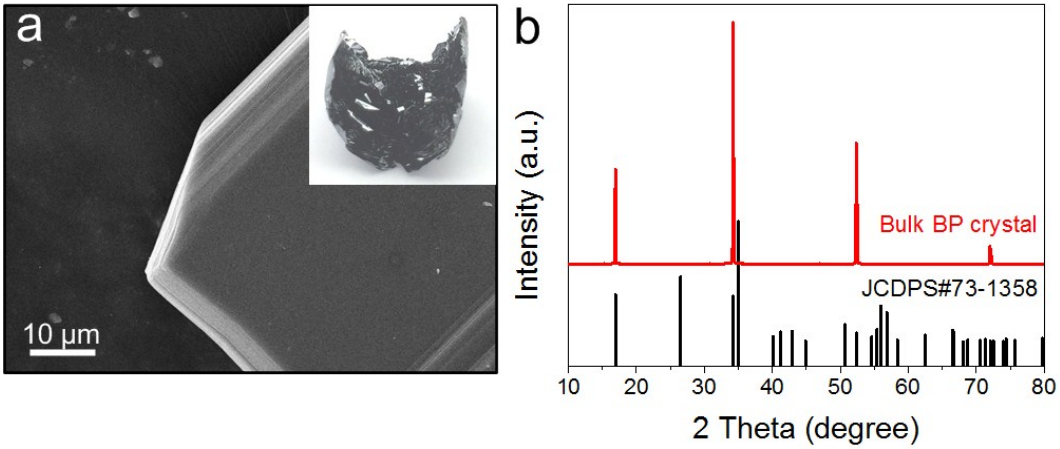

Fig S1. a) SEM image and photograph (inset) of the BP crystal; b) XRD spectrum of the BP crystal.

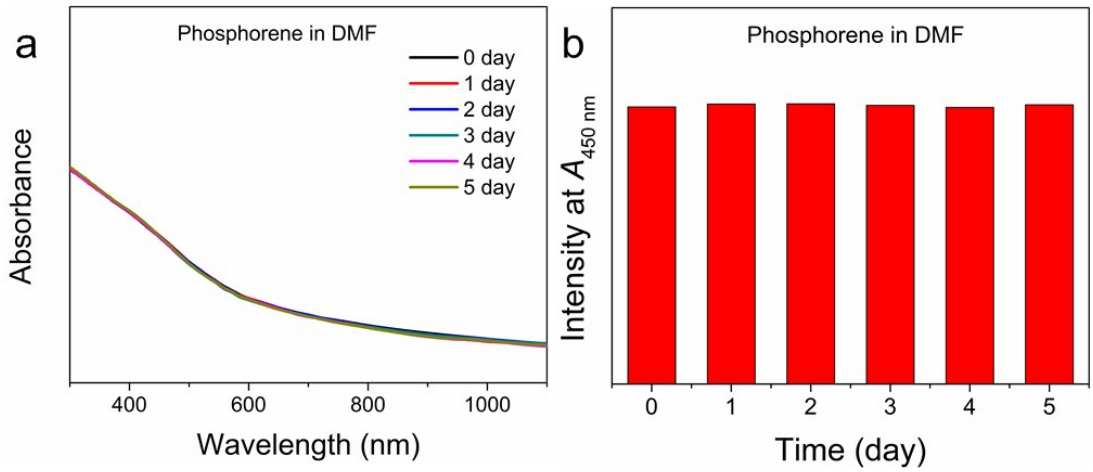

Fig S2. a) Absorption spectra and b) Variation of the absorption intensity at 450 nm (A450 nm) of phosphorene sheets with different dispersion time in DMF.

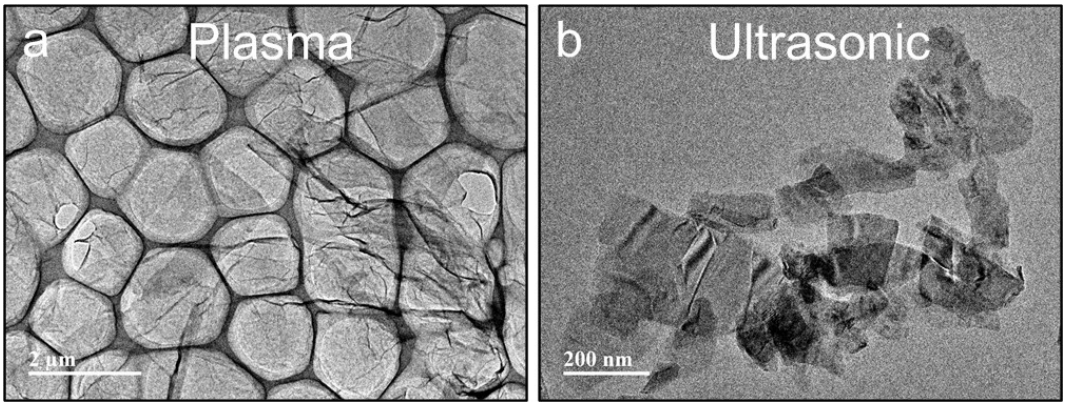

Fig S3. TEM images of the phosphorene sheets prepared by a) Plasma exfoliation and b) Ultrasonic exfoliation.

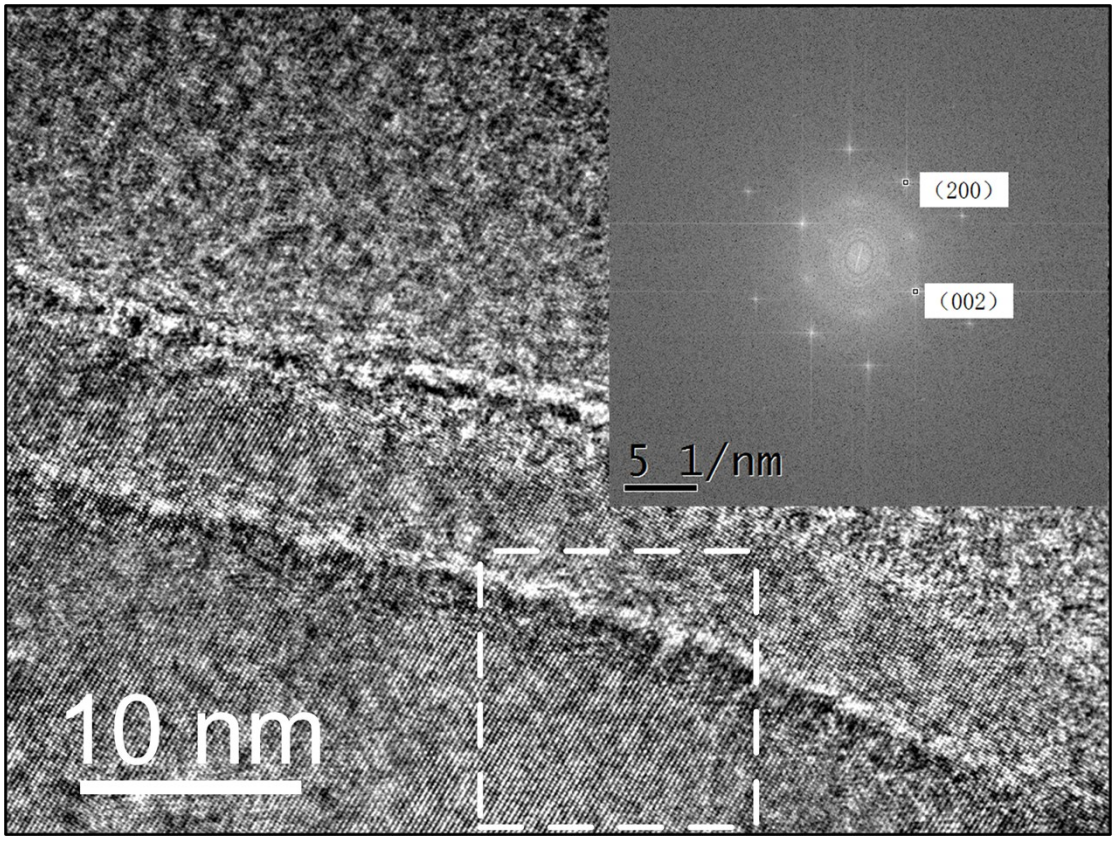

Fig S4. Magnified HR-TEM image to show the three layers of a phosphorene sheet, inset FFT image.

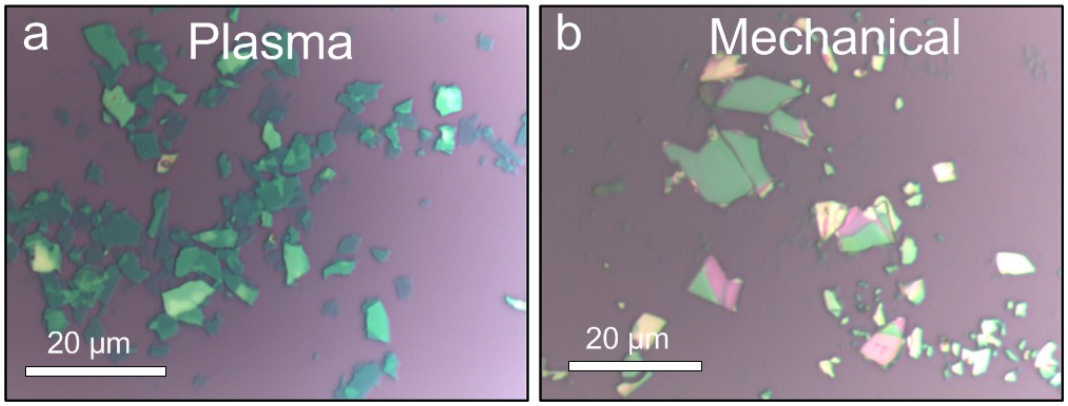

Fig S5. Optical images of the phosphorene sheets prepared by a) Plasma exfoliation and b) Mechanical exfoliation.

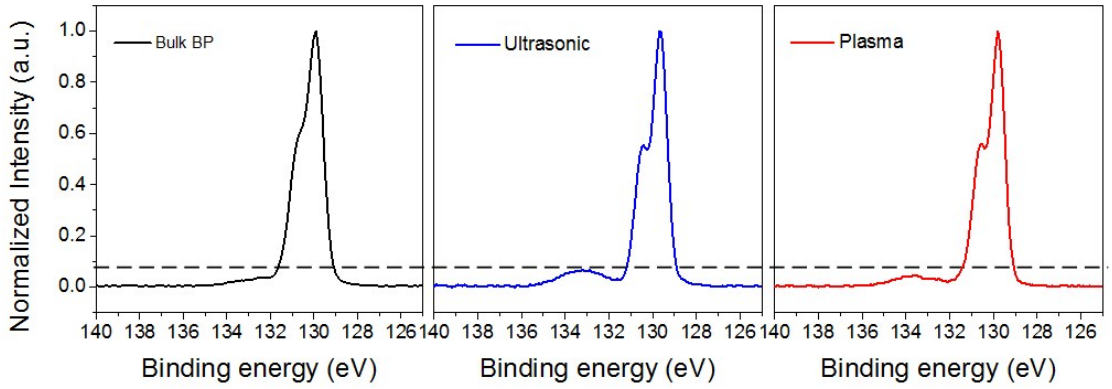

Fig. S6 XPS spectra of Bulk BP, ultrasonication method prepared BP, Plasma-liquid technology prepared BP.

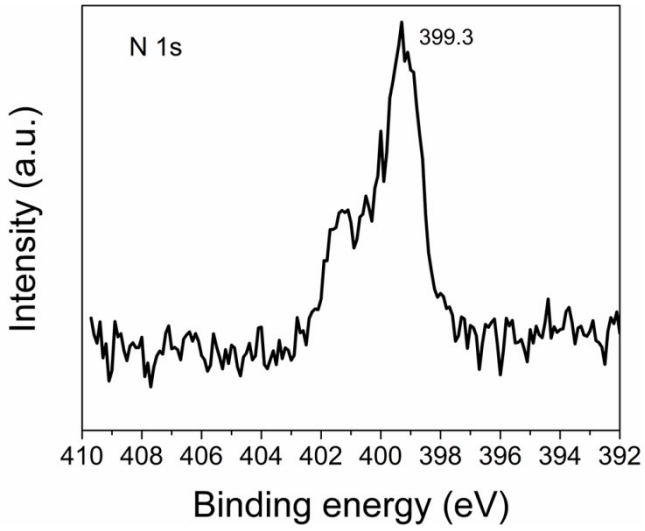

Fig. S7. XPS spectrum of N 1s of phosphorene sheets.

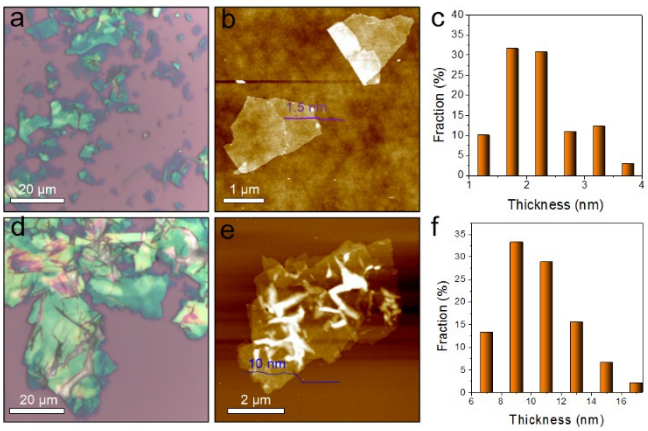

Fig S8. Optical and AFM images. a, b,c) Phosphorene sheets with thickness of about 1.5 nm and thickness statistics, d,e,f) Phosphorene sheets with thickness of about 10 nm and thickness statistics.

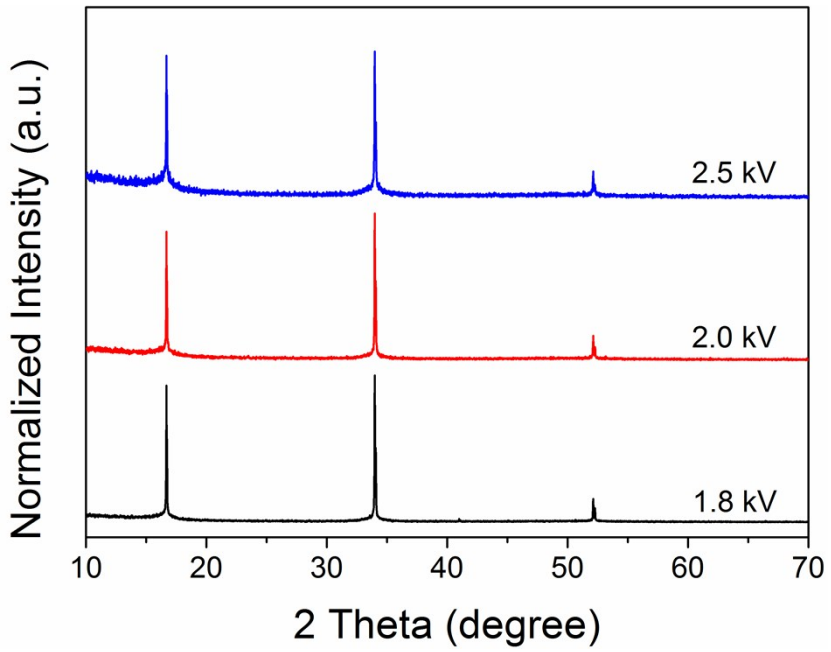

Fig. S9 XRD patterns of phosphorene produced with different voltages

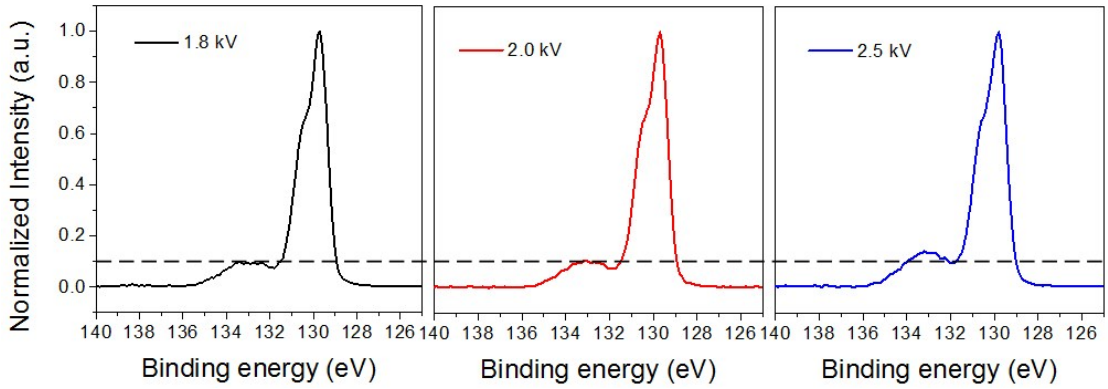

Fig. S10 XPS spectra of phosphorene produced with different voltages

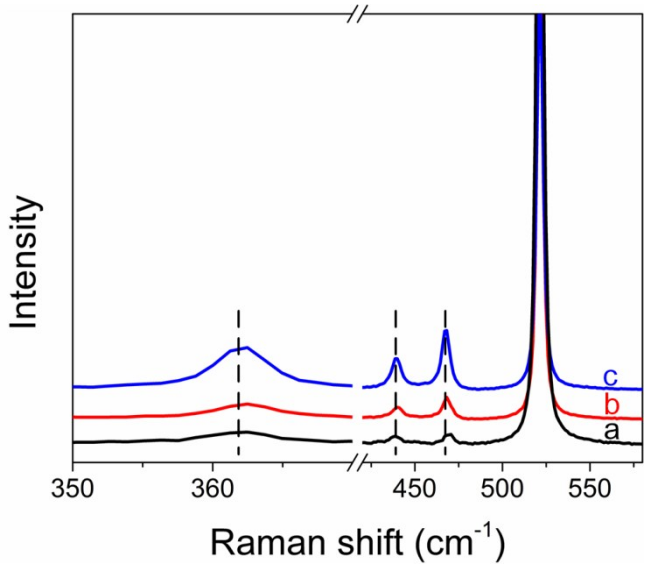

Fig S11. Raman spectra of phosphorene sheets with different thicknesses (a: 1.5 nm, b: 4 nm, c: 10 nm).

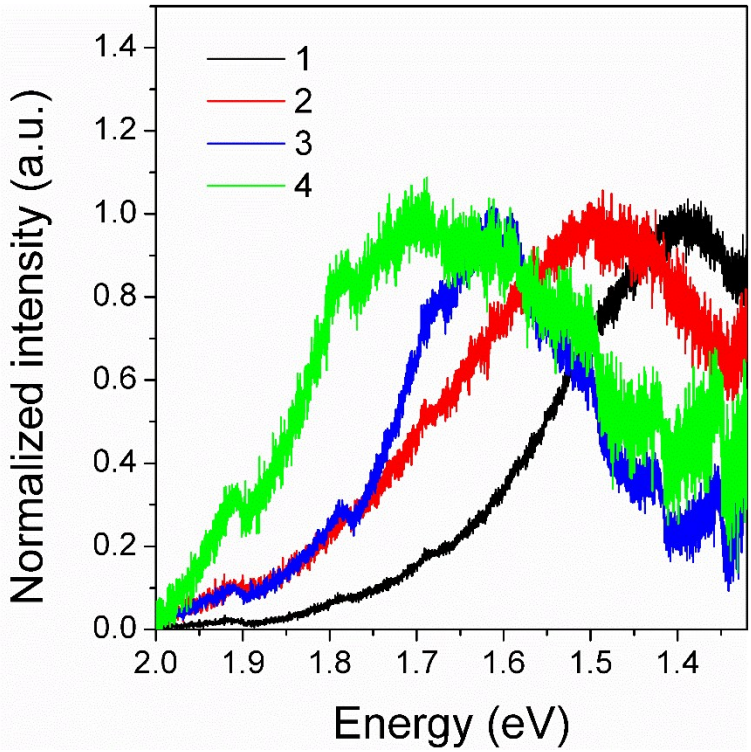

Fig S12 Emission spectra of different phosphorene sheets (2.5 kV sample).

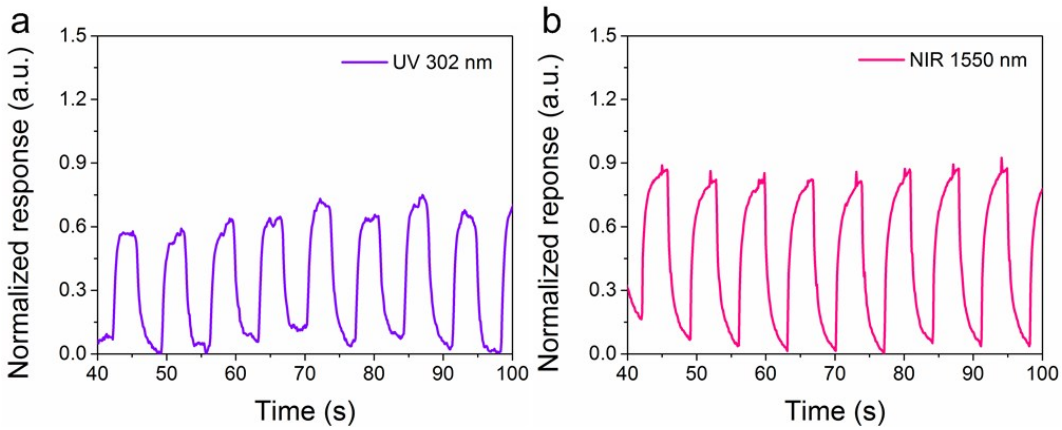

Fig S13. Normalized on/off photo-response of the phosphorene photodetector under irradiation with a) 302 nm UV lamp and b) 1550 nm NIR laser.

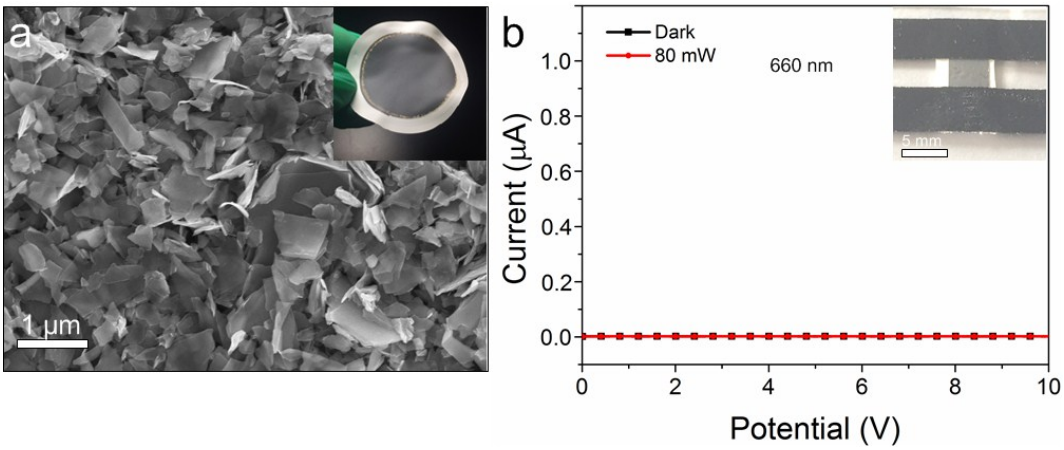

Fig S14. a) SEM image with inset photograph of the film of ultrasonically exfoliated phosphorene; b) I–V characteristics of the photodetector fabricated with the phosphorene film.

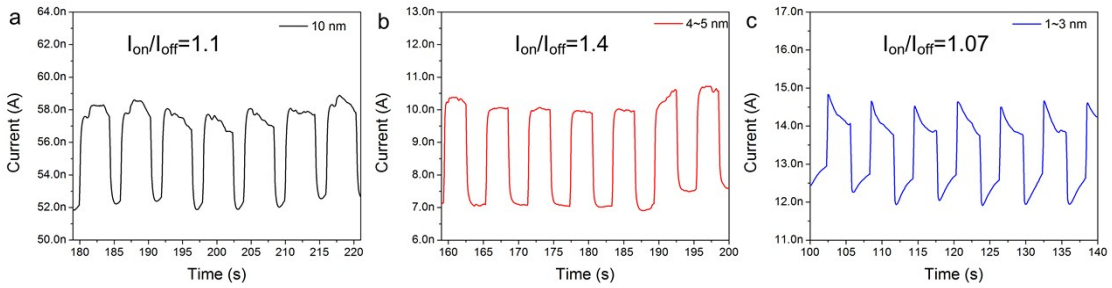

Fig S15 On/off photo-response of the photodetectors consist of different thickness phosphorene under irradiation with 660 nm laser.

Reference

1 D. Mariotti, V. Svrcek, J. W. J. Hamilton, M. Schmidt, M. Kondo, *Adv. Funct. Mater.* 2012, **22**, 954-964.