Electronic Supporting Information

Work Functions and band alignment of Few-Layer Violet Phosphorene

Bo Zhang, [a] *Zhenyu Wang,* [a] *Hongyang Huang,*[a] *Lihui Zhang,* [a] *Mengyue Gu,* [a] *Yonghong Cheng,* [a] *Kai Wu,* [a] *Jun Zhou,* [a] *Jinying Zhang*[a]*

[a]State Key Laboratory of Electrical Insulation and Power Equipment, Center of Nanomaterials for Renewable Energy (CNRE), School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Address correspondence to jinying.zhang@mail.xjtu.edu.cn

KPFM measurements of violet phosphorene

The topography and surface potential map of violet phosphorus were characterized simultaneous by using KPFM (Bruker Dimension Icon). The schematic diagram of the KPFM system is shown in Figure S1. Surface potential measurement was employing a Pt-Ir coated Si probes (SCM-PIT) with force constant of 3 N/m and a typical tip radius about 20 nm. KPFM images were acquired at a probe scan rate of 0.5 Hz. The KPFM measurements were used to record images of violet phosphorene nanoflakes surface topography and contact potential difference (CPD) between the conducting Pt-Ir tip and violet phosphorus surface. Two-pass technique (lift-mode) was applied in KPFM experiments.

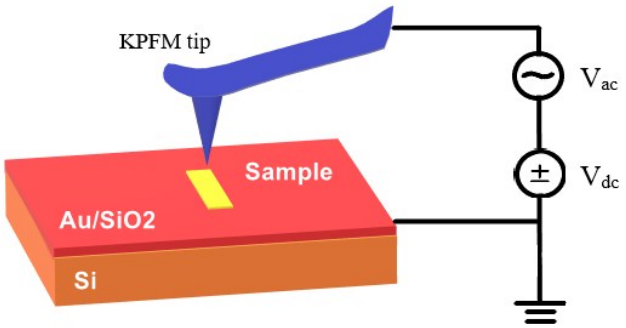

Fig. S1 The schematic diagram of the KPFM system

The topographies and surface potentials were measured by KPFM based on dynamic force microscopy principles to give work functions of the few-layer violet phosphorene. The work function ϕ_{sample} was further calculated from the surface potential according to equation S (1):

$$\phi_{Sample} = \phi_{Tip} + qV_{CPD} \quad (1)$$

However, in the actual measurement, it is necessary to measure the boundary region of the sample with the substrate as the reference value. Therefore, the surface potential of violet phosphorene on Au/silicon oxides was calculated according to equation S (2):

$$\Delta V_{CPD} = V_{CPD-sample} - V_{CPD-substrate} \quad (2)$$

The work function of sample can be obtained by the establishment of the equation S (1) and S (2).

$$\phi_{sample} = \phi_{substrate} + q\Delta V_{CPD} \quad (3)$$

Where $V_{CPD\text{-}sample}$, $V_{CPD\text{-}substrate}$ are the contact potential difference of sample and substrate measured by KPFM in volts, ϕ_{tip}, ϕ_{sample} and $\phi_{substrate}$ are the work functions of tip, sample and substrate in eV, respectively and q is the electronic charge. The work functions of tip can be calculated by measuring gold samples by KPFM.

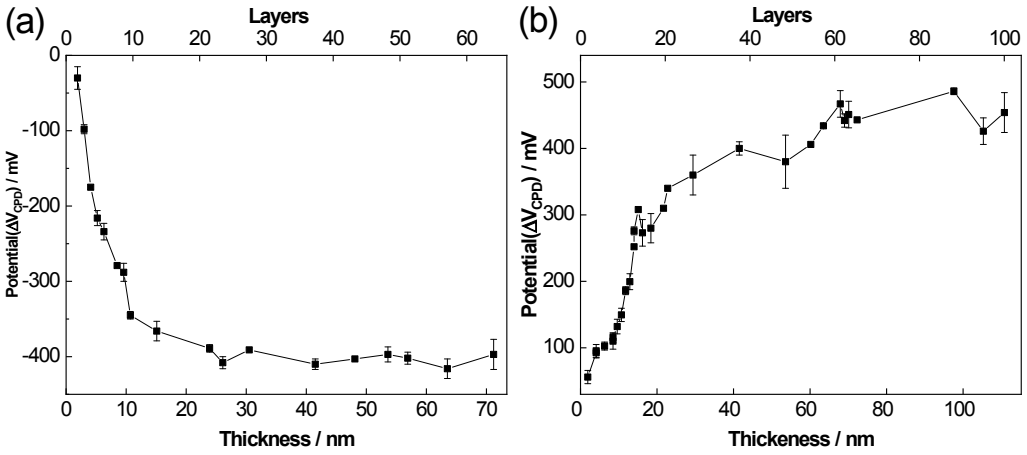

Fig. S2 The variation of surface potential according to the thickness (layers) of violet phosphorene on (a) gold and (b) SiO_2/Si substrate.

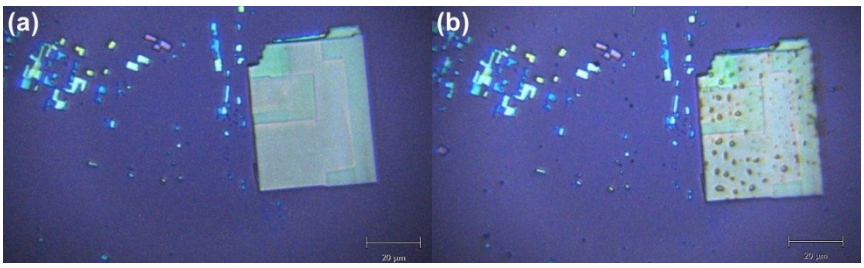

Fig. S3 Optical images of violet phosphorene.(a) freshly prepared sample,(b)after exposure to air for 7days.