

SUPPORTING INFO

Metal-assisted exfoliation of few-layer black phosphorus with high yield

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Experimental Section

Bulk BP: The bulk BP was grown by the chemical vapor transportation. Red phosphorus (Aladdin, 99.999% metal basis), tin (Aldrich, powder, 99.99% trace metal basis), and iodine (Aldrich, 99.995% trace metal basis) were used as source materials and sealed in silica glass ampule at a certain proportion. The silica glass ampule was loaded in a tube furnace and slowly heated to 863 K from room temperature and kept for 2h. Then the temperature was decreased to 758 K and kept for 2 h and followed decreased to 393 K slowly. After the silica glass ampule cooled down to room temperature, bulk BP was moved out and cleaned in ethyl alcohol by ultrasonic and stored in a glove box.

Metal layer etching process: The substrate or tape with metal layer was soaked in Gold Etch-type TFA (KI: I₂: DI water= 4g/1g/40mL) for 5mins to remove the metal layer. Then the substrate or tape was rinsed in DI water to remove the residual TFA solution. Finally, the substrate or tape was blow-dried by a N₂ gas gun.

OM and Raman spectroscopy: After Au or Ag layer was etched, few-layer BP (FLBPs) were initially observed by optical microscopy (OLYMPUS BX51M), and the lateral size of FLBPs was measured. Raman spectra of the exfoliated FLBPs were obtained using a micro-Raman setup (ZTJD6-13471HK) with a laser wavelength of 532nm, spot size of $\sim 0.5\mu\text{m}$ and a micro-Raman setup (LabRAM HR Evolution) with a laser wavelength of 532nm, spot size of $\sim 1\mu\text{m}$ to measure the properties of exfoliated FLBPs.

Comparison of the lateral areas of the exfoliated FLBPs: Five samples were prepared

by the metal-assisted and the normal “scotch tape method”, respectively, using the same size substrates (1 cm × 1cm) and same bulk BP crystal. The magnification of OM images was X200. The statistical regions were 760×580μm.

AFM and TEM: Atomic force microscopy (VEECO NanoScope 3D) was used to measure the thickness and roughness of FLBPs. TEM images of FLBP were obtained using a JEM-2010(HR) TEM and aTecnai G2 F20 S-TWINTeM. A holey support grid was covered on the SiO₂(300nm)/Si substrate with FLBPs. Then a drop of isopropanol was dropped on the holey support grid and evaporated to improve the contact between FLBPs and holey support grid. SiO₂layer was etched by hydrofluoric acid and FLBPs were transferred onto the holey support grid. Finally, the grid was rinsed in deionized water and ethyl alcohol for TEM observation.

FET fabrication and test: The 300 nm SiO₂/Si wafer was chosen as the substrate to fabricate devices. After Au or Ag etched, photo lithography was applied to fabricate electrode pattern and Ti/Au(10nm/50nm) electrodes were sputtered on the FLBP by magnetron sputtering method, and Al was sputtered on the back of 300 nm SiO₂/Si wafer as the gate electrode. The electronic properties of BP FETs were tested in a scanning electron microscope chamber to exclude the influence of air and degeneration of BP. Keithley 6487 and 2400 ammeters were used as the voltage sources to measure the $I_{ds} - V_{ds}$ and $I_{ds} - V_g$ curves.

Raman spectra analysis: The intensity of No.1 in figure S2 was multiplied by five. It is reported that Raman peaks red-shift with the increase of BP thickness.¹ In addition, the intensity ratio between A_g^1 and Si peaks can be used to estimate the thickness of FLBP.² However, the results in figure S2 are not consistent well with the refs. We think it is difficult to accurately identify the thickness by the position and intensity of the Raman peaks in our cases.

References:

- 1 Z. Guo, et al., *Advanced Functional Materials*, 2015, **25(45)**, 6996-7002.
- 2 Z. Cui, et al., *Advanced Materials Interfaces*, 2017 (accepted manuscript).

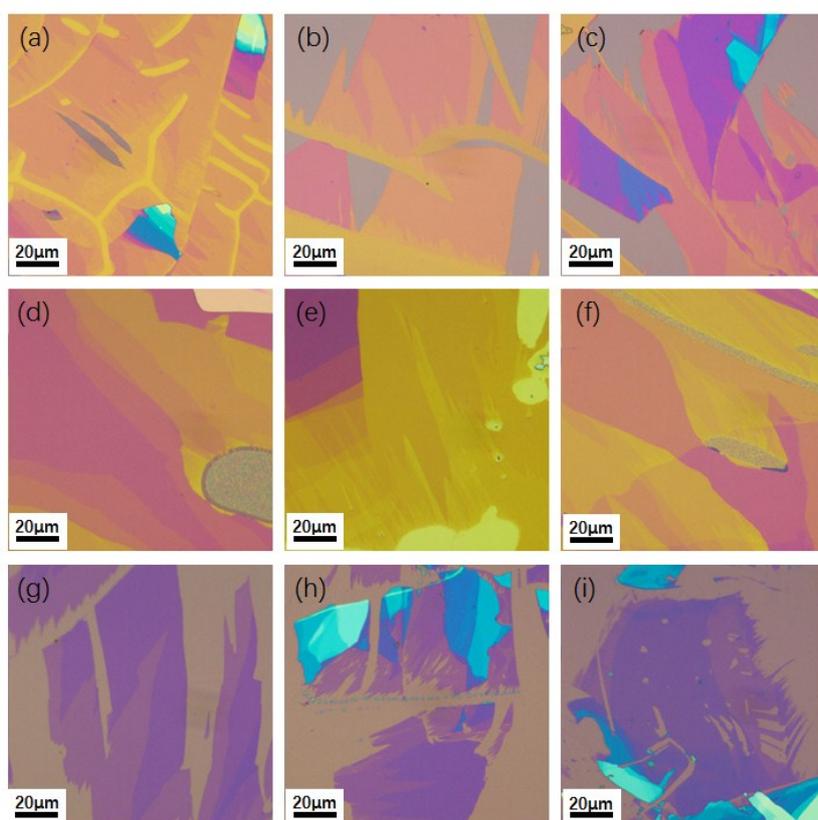


Figure S1. The optical photos of FLBPs exfoliated by metal-assisted method. (a), (b) and (c) are FLBP on Au layer/SiO₂/Si. (d), (e) and (f) are FLBPs on Ag layer/SiO₂/Si. (g) is FLBPs on SiO₂/Si, the Au layer has been etched. (h) and (i) are FLBPs on SiO₂/Si, the Ag layer has been etched.

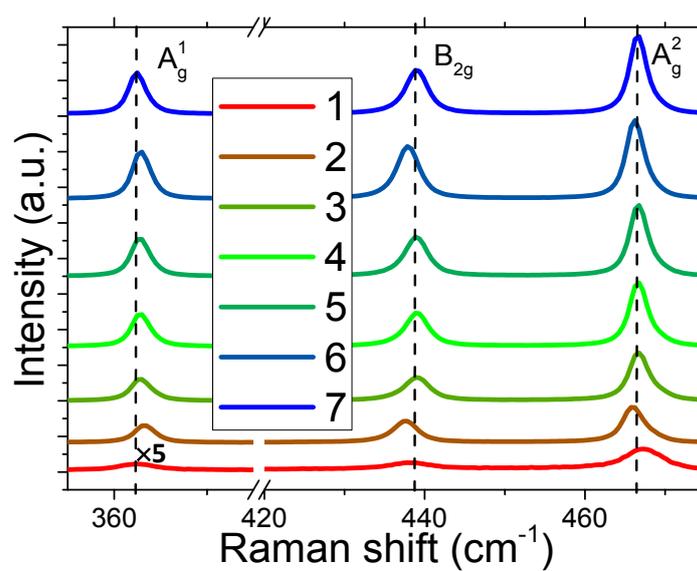
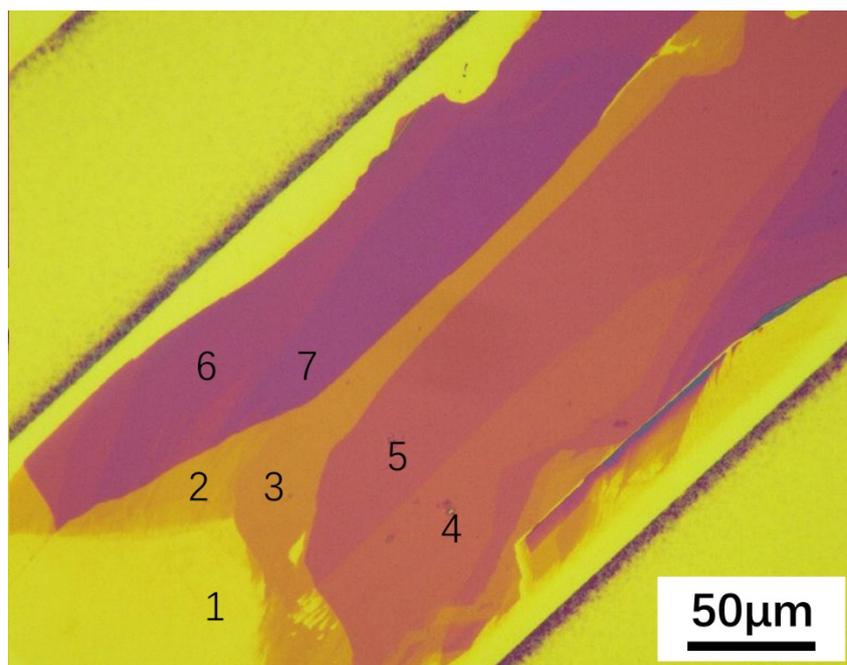


Figure S2. The optical photo of the exfoliated FLBPs and the corresponding Raman spectra.

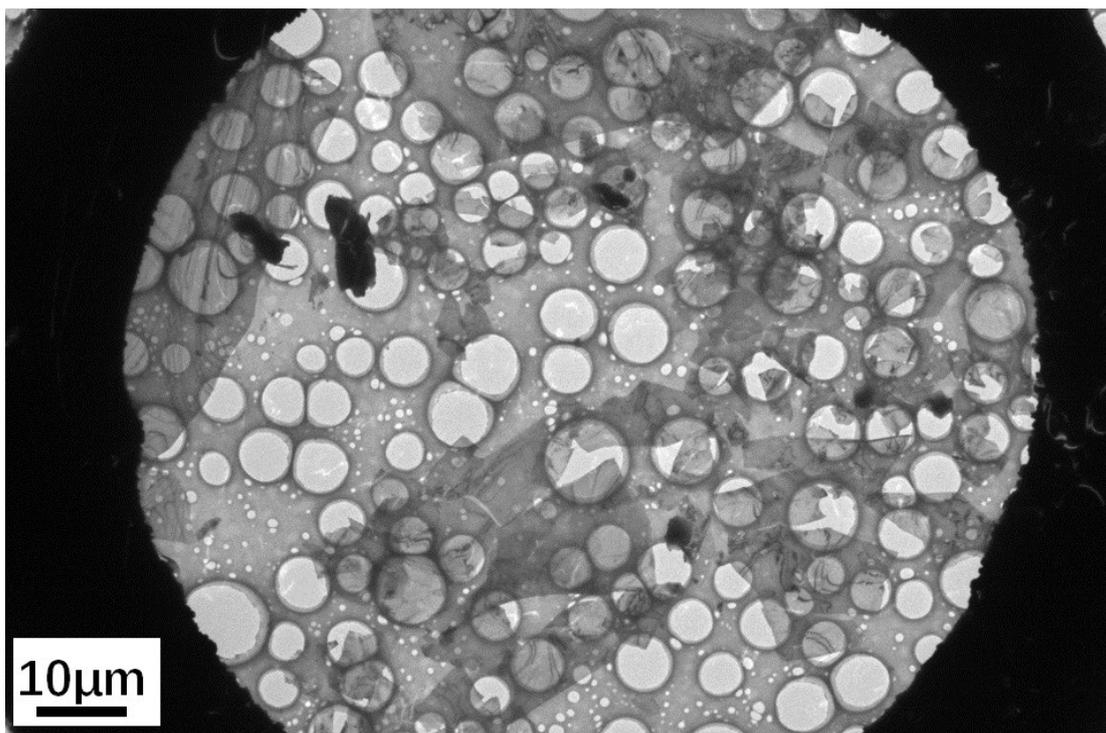


Figure S3. A typical TEM image of exfoliated FLBPs on a holey support grid.