Supporting Information for

Atomic Scale Study for Black Phosphorus Degradation

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Experimental Methods

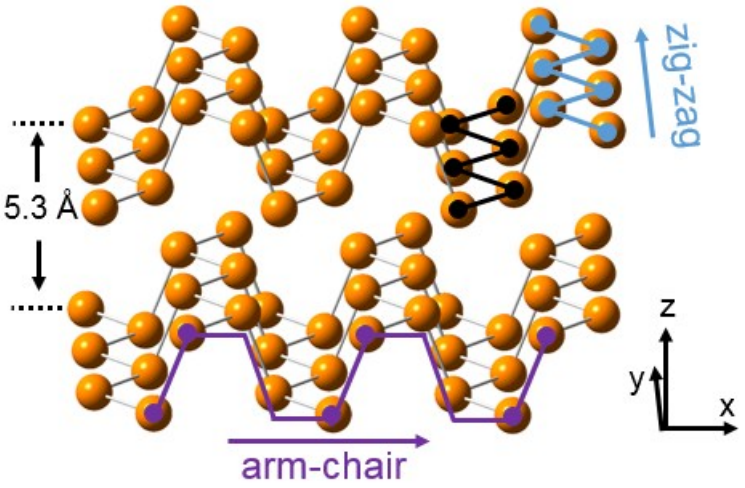

Figure S1. Oblique view of the puckered layered crystal structure of black phosphorus.

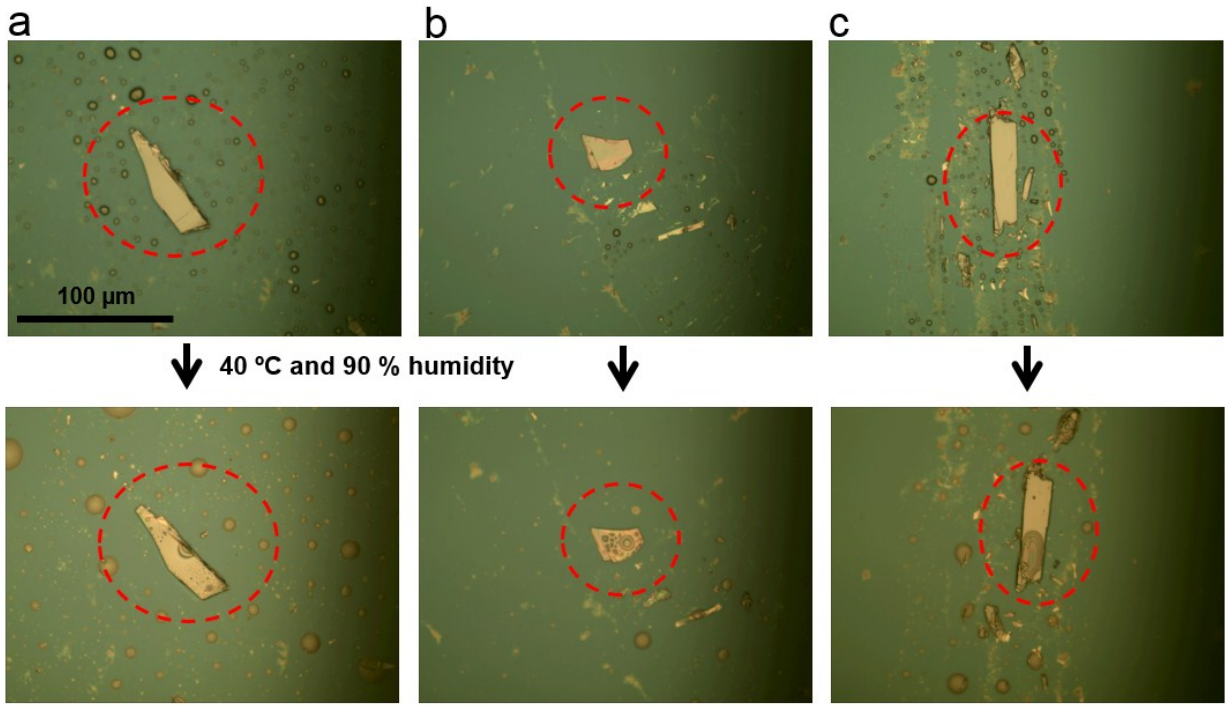

Figure S2. Optical microscopy images before and after storing black phosphorus flakes for 40 h at 40°C and 90% relative humidity.

(a–c) Optical microscopy images of BP before (top images) and after (bottom images) storing BP flakes for 40 h at 40°C and 90% relative humidity. The image size is about 190 × 252 µm^2. The BP degraded during storage.

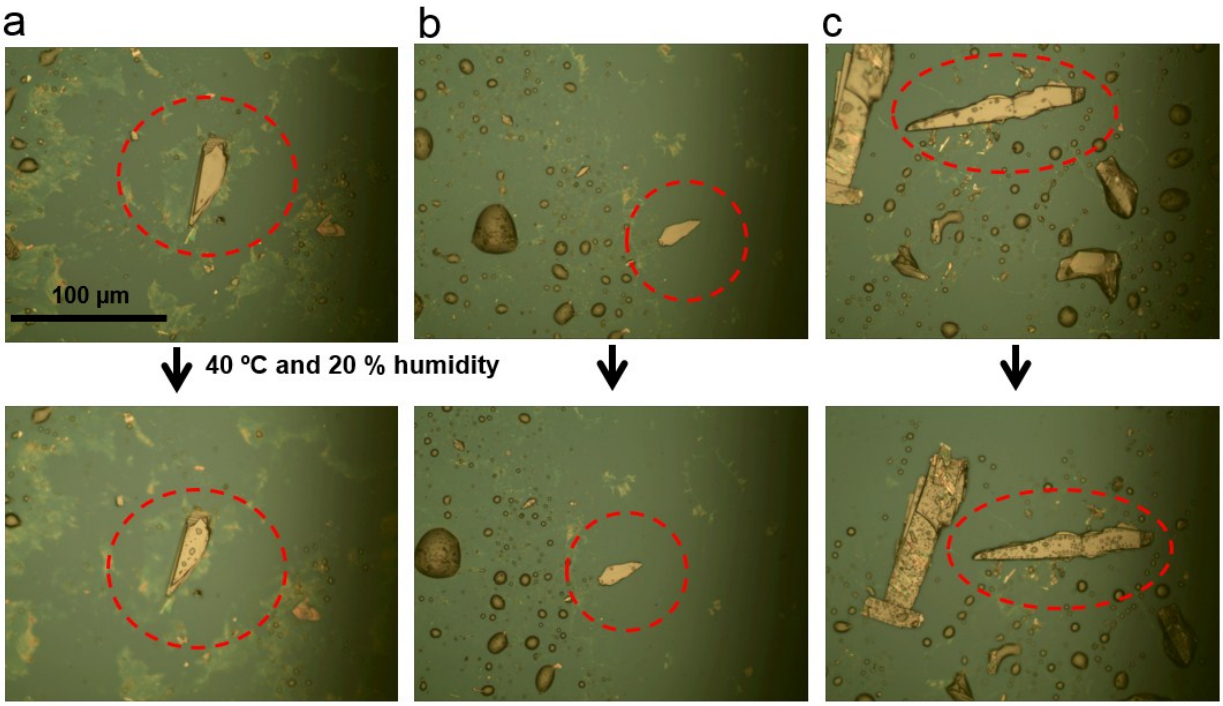

Figure S3. Optical microscopy images before and after storing black phosphorus flakes for 40 h at 40°C and 20% relative humidity.

(a–c) Optical microscopy images of BP before (top images) and after (bottom images) placing BP flakes for 40 h at 40°C and 20% relative humidity. The image size is about 190 × 252 μm^2. The BP flakes had degraded during storage.

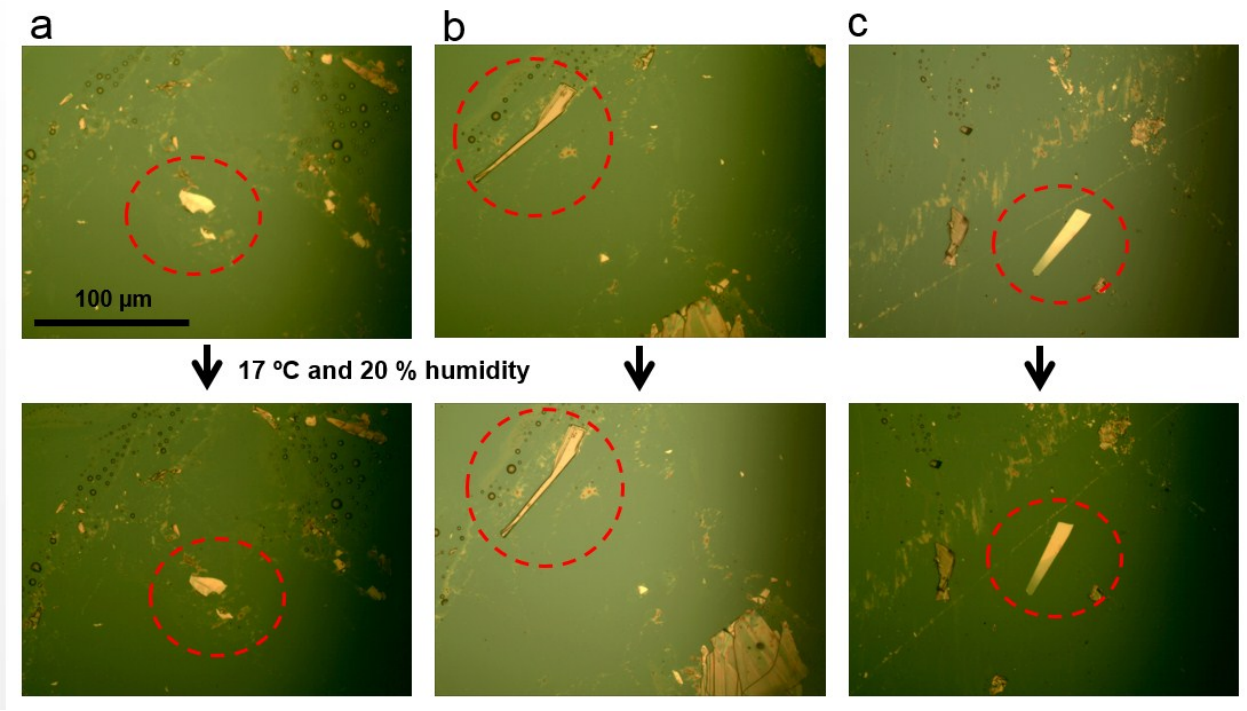

Figure S4. Optical microscopy images before and after storing black phosphorus flakes for 40 h at 17°C and 20% relative humidity.

(a–c) Optical microscopy images of BP before (top images) and after (bottom images) storing BP flakes for 40 h at 17°C and 20% relative humidity. The image size is about 190 × 252 µm^2. The BP did not degrade during storage under these conditions.

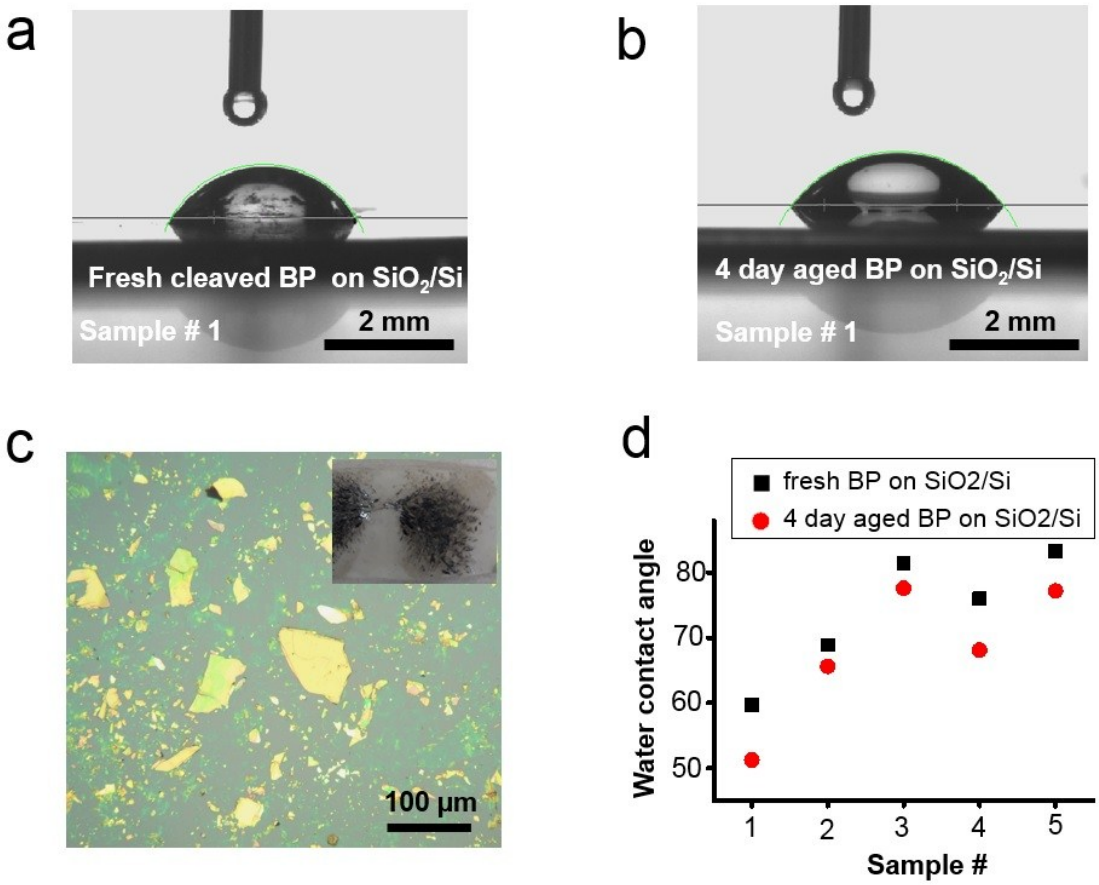

Figure S5. Water contact angle measurement of BP on SiO2/Si substrate.

(a-b) Sessile drop contact angle measurement of fresh cleaved BP (a) and BP exposed to ambient conditions for 4 days (b). (c) Optical image of a fresh cleaved BP flakes. Inset: photo of BP flakes on an adhesive tape before transferring onto a substrate. (d) Water contact angle measurement of 5 samples when freshly cleaved and when 4 days after cleaving.

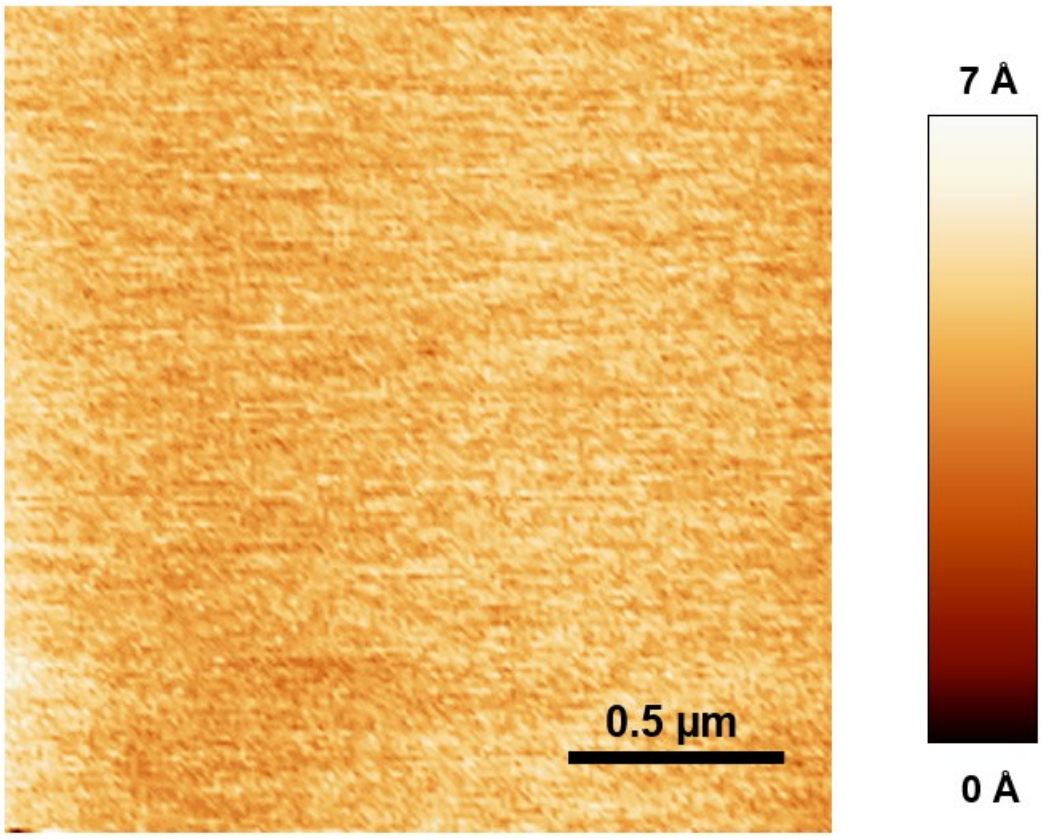

Figure S6. Atomic force microscopy image of black phosphorus surface at 300 mV tip-sample bias

Topographic AFM image of the BP surface when the surface was scanned at 0.3 V bias voltage. The BP had a relatively uniform surface at the start of scanning.

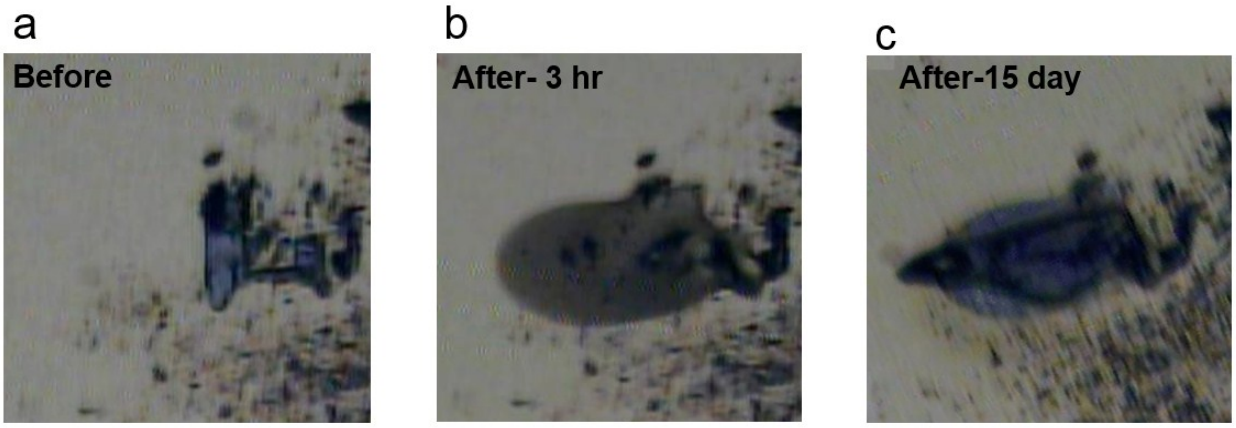

Figure S7. Optical images of black phosphorus before and after voltage-assisted tip etching.

Optical microscopy images of BP (a) before, (b) 3 h after and (c) 15 days after the BP was scanned at a bias voltage of 4 V by conductive AFM. Figure S6a and S6c correspond to Figure 4a and 4b in the main text, respectively.

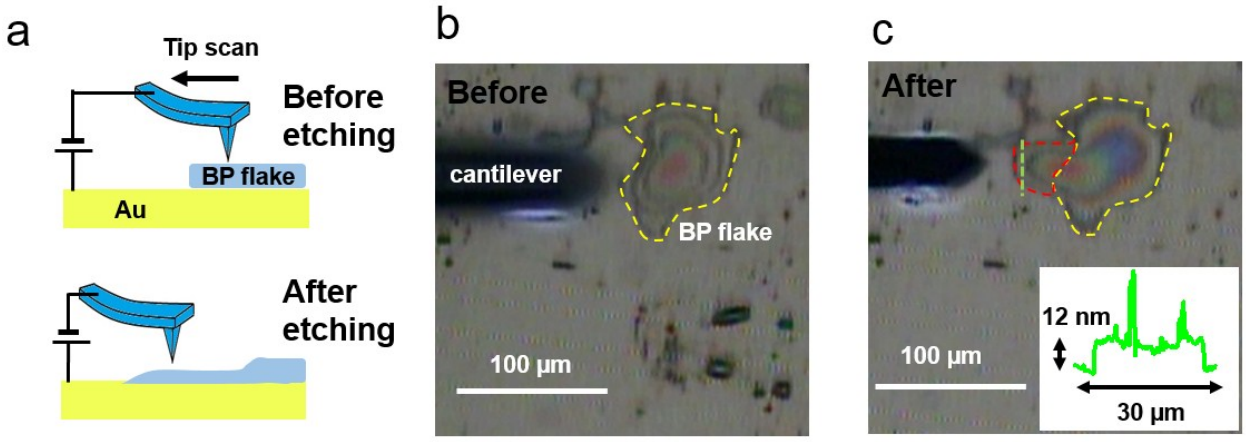

Figure S8. Optical images of black phosphorus before and after voltage-assisted tip etching.

(a) Schematic diagrams of the BP surface before (top) and after (bottom) etching. (b, c) Optical microscopy images of BP before (b) and after (c) applying 4V bias voltage. The area of BP expanded after voltage-assisted etching; the height of the expanded region in the inset of (c) is 12 nm.

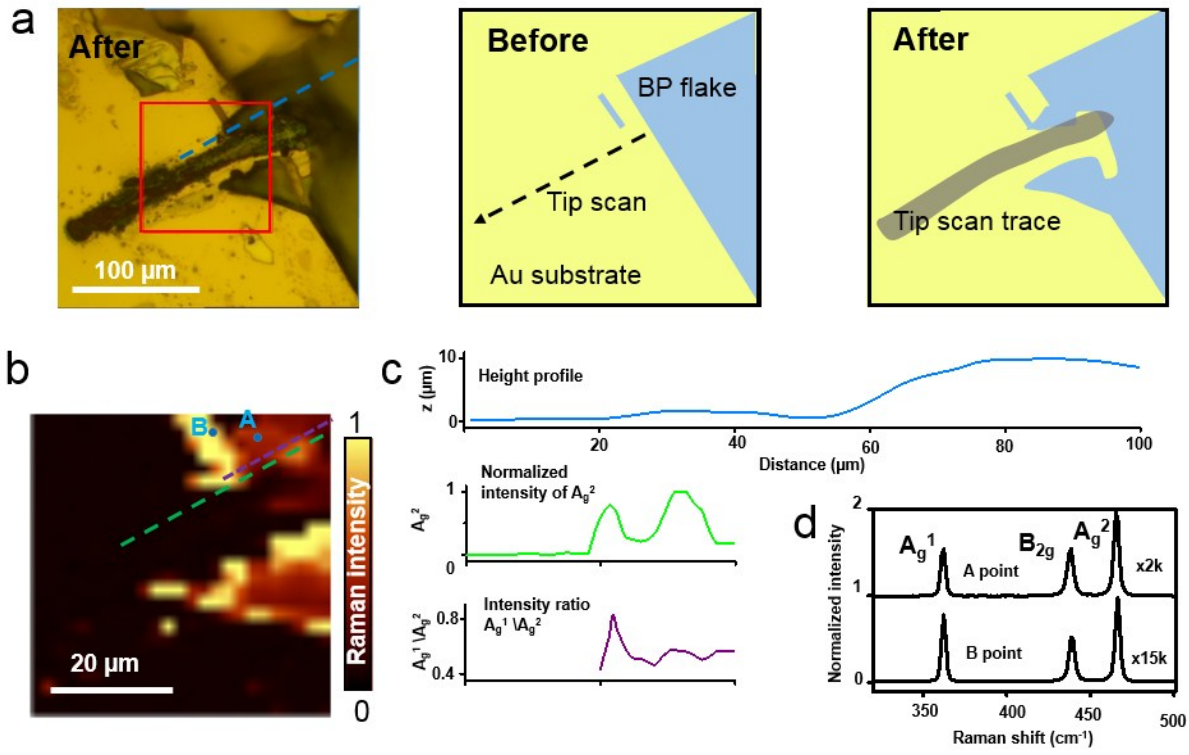

Figure S9. Voltage-assisted etching in vacuum.

(a) Optical microscopy images of BP after applying a 5 V bias voltage (left) and a schematic view before (middle) and after (right) tip etching. The original BP pieces are colored blue, and the Au substrate is colored yellow in the schematic view. (b) Intensity of the Raman Ag2 mode measured in the red rectangular region in (a). (c) The height profile measured by a surface profiler along the blue dashed line in (a) is shown at the top of (c). The normalized intensity of the Ag2 mode along the green dashed line in (b) is shown at the middle of (c). The green dashed line in (b) is a part of the blue dashed line in (a). The ratio A_g^1/A_g^2 along the purple dashed line in (b) is shown at the bottom of (c). (d) Raman spectra at locations A and B in (b). The spectra are normalized to the A_g^2 peak and scaling factors are shown at the right side. Comparing the Raman spectra of (d) at locations A and B indicates that BP was crystalline at A, while a small amount of pristine BP remained at B.

Experimental Methods

Atomic Force Microscopy (AFM). AFM head and body are custom-machined to get high resolution data while customizing a tip holder and a sample holder for any specific experiment in our laboratory. A super luminescent diode laser (Hamamatsu Photonics, Japan) is used to illuminate cantilever to reduce laser-related noise. The XYZ Piezo tube-scanner is custom-made (EBL Products Inc., USA). The range of XYZ scanner is ~3 µm x 3 µm x 0.5 µm. The resolution of the XYZ scanner is ~1 Å x 1 Å x 0.2 Å. The AFM controller and operating software are custom built (NanoFocus Inc., Korea). The AFM images are obtained in contact mode in air. The AFM body is on an anti-vibration table to reduce vibration noise. The AFM body and the anti-vibration tables are enclosed by an acoustic chamber (1.1 m x 1.1 m x 1.7 m) to reduce noise caused by sounds. The acoustic chamber is inside a basement room (~5 m x 4 m x 3 m), and the temperature and humidity of the room is controlled by an air handling unit (cooling capacity of 13 kW, heating capacity of 6 kW, and humidity capacity of 0.001 kg/s).

AFM Tip. High resolution topographies are obtained by PNP-TR-20 cantilevers (Nanoworld). The cantilever has a triangular shaped silicon nitride cantilever with 0.32 N/m spring constant , 70 nm thick gold layer coating on its detector side, and >10 nm tip radius. Current mode AFM images are obtained by SHR150 probe (BudgetSensors). Both side of its cantilever are coated with 70 nm thick gold. Its spring constant and tip radius are 5 N/m and > 1 nm, respectively. For voltage-assisted etching in air, we use PPP-MFMR cantilevers (NANOSENSORS). The cantilever's detector side is coated with Aluminum, and the tip side is coated with CoCr. The spring constant and tip radius is 2.8 N/m and < 30 nm, respectively.

Raman Spectroscopy. The Raman is obtained using an Alpha300S (WITec, Germany) in air. The power of 520 nm excitation laser is maintained about 1mW.

Temperature- and humidity- controlled cabinet. The experiment of supplementary Fig. S2-S4 is carried out in a temperature and humidity controlled cabinet (CTHC-65P, SORITECH Co., Korea).

Voltage-assisted etching in vacuum. The voltage-assisted etching in vacuum is carried out in a vacuum probe station (CG-196, MODUSYS Inc., Korea) at room temperature. The Raman spectroscopy is measured ex-situ in air.

Contact angle measurement. After putting bulk BP crystals on an adhesive tape, the tape is folded and unfolded more than 10 times to increase the BP covered area, then BP on the tape was transferred to the surface of a 300nm SiO_2/Si substrate by standard method. Water contact angle measurement is carried out in air using DSA10-Mk2 (KRUSS, Germany).