

Supporting Information

Control of Surface and Edge Oxidation on Phosphorene

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1. Materials and general handling

The chemicals used in this work include red phosphorus ($\geq 99.999\%$, Sigma Aldrich), *N*-methyl-2-pyrrolidone (anhydrous, 99.5%, Acros Organics), 2-propanol (certified ACS plus, FisherSci), acetone (ACS grade, FisherSci), Sn (Alfa Aesar), SnI₄ (Alfa Aesar), and P₂O₅ (reagent grade, $\geq 97\%$, Sigma Aldrich). The gasses used for sample exposure include research grade oxygen gas (99.999%, Air Gas), nitrogen gas (high purity 4.8 grade, Air Gas), and distilled water (17.2 M Ω ·cm).

The solvents—NMP, IPA and acetone—were degassed with nitrogen and dried by molecular sieves, then stored in a glovebox. Water was degassed by either oxygen or nitrogen and then heated to 100°C to create water vapor for use in the oxidation studies.

All black phosphorus samples were prepared and handled under a nitrogen-filled glovebox (O₂ < 1.00 ppm, H₂O < 0.10ppm). Samples removed from the glovebox were sealed in screw-cap vials and further sealed with parafilm for liquid exfoliation. TEM grids with black phosphorus samples were removed from the glovebox, sealed in 2 polypropylene bags. Thin films of black phosphorus were sealed in an air-tight glass tube.

2. Synthesis of bulk black phosphorus

Chemical vapor transport of red phosphorus with Sn and SnI₄ yielded bulk black phosphorus crystals, by the procedure, modified from Nilges,¹ used in previous literature.^{2,3}

3. Method of liquid exfoliation

Liquid exfoliation of black phosphorus was performed in anhydrous, degassed NMP under inert atmosphere with an initial concentration of 0.5 mg/mL, similar to a published method.² After sonication for 8 cycles of 99 minutes, the suspensions were transferred to Nalgene Oak Ridge FEP 50-ml centrifugation tubes. The suspensions were centrifuged at 10,000 revolutions per minute (rpm) for 45 minutes using a Sorvall RC-5B super speed refrigerated centrifuge with a rotor radius of 14.56 cm. The resulting supernatant from the first centrifugation cycle was collected and centrifuged a second time under identical conditions. To transfer the resulting 2D material into IPA, ~10% of the supernatant was removed and IPA was added. The suspension was mixed and centrifuged at 20,000 rpm for 60 minutes. Then ~50% of the supernatant is removed and replaced with IPA. The suspension was mixed and centrifuged again at 20,000 rpm for 60 minutes. Finally, the supernatant was removed and the sediment of 2D material was re-

dispersed in IPA. The distribution of 1-7 layers of 2D flakes are used in thin film assembly and individual flake studies.

4. Thin film substrates and assembly

Conductive substrates were produced to eliminate charging issues associated with photoemission spectroscopy for thin film characterization. We deposited 5 nm of titanium followed by 50 nm of gold onto silicon wafers with a 300nm thermal silicon oxide by an Thermionics VE-100 electron beam evaporator, shown in Fig. 1a. We prepared the metal-plated silicon wafers as substrates for thin film assembly of 2D black phosphorus by rinsing with acetone and isopropanol. To ensure the surface was hydrophilic, we cleaned the surface by UV-ozone at 150°C for 300 seconds. We immediately brought the clean substrate into the glovebox for film assembly.

Re-concentrated suspensions of 2D black in isopropanol were used to create thin films of the material by the doctor blade technique. The substrate was immobilized, by adhering it to a surface. In this work, Scotch[®] transparent tape was used to tape two opposite edges of the wafer to a stable surface, each covering the edge of the substrate by approximately 1-2 mm. Then, 3 μ L aliquots of the 2D suspension were placed on the gold surface near an edge not adjacent to the tape. A hydrophilic glass microscope slide is slide across the surface, spreading the 2D material across the substrate. This was repeated \sim 400 times; it became apparent that the 2D suspension was sufficiently concentrated if a visible color change of the substrate occurred at \sim 30 swipes.

5. Oxidant exposure procedure

Thin films of 2D assemblies or TEM grids with flakes of 2D black phosphorus underwent the same exposure procedures. The sample was placed in an air-tight glass tube inside the glovebox and wrapped in aluminum foil. Then, we removed the sample from the glovebox. The glass tube, shown in Fig. 1b, was specifically designed for this study; it was equipped with an air-tight screw cap and a Teflon-sealing valve adjacent to a hose connection. For each oxidation environment, the sample was exposed in the dark to a flow of the oxidant gas(es) by opening the Teflon valve and screw cap for 5 minutes. The screw cap was then closed, followed immediately by the Teflon valve. The aluminum foil was removed and the sample was illuminated with a 460 nm LED with a specific power of 0.6 mW/cm² for 1, 6, or 18 hours. The 460 nm light source was selected to ensure all material—monolayers to bulk—was photo-excited during oxidation. At the end of the exposure, thin film samples were brought into the glovebox with a minor opening in the Teflon valve to evacuate the oxidants. For flakes on TEM grids, N₂ was used to purge the glass tube, sealed, and then taken into the glovebox.

To create the O₂ environment, P₂O₅ desiccant (\sim 0.2 g) was placed upstream of the sample, ensuring the environment was devoid of H₂O before reaching the sample. Then, research grade O₂ (99.999%) was flowed over the dessicant and the sample. To create the H₂O/N₂ environment, N₂ gas was bubbled through distilled water for 30-60 minutes and heated to 100°C. The H₂O vapor with N₂ as a carrier gas were used in the sample exposure. To create a H₂O/O₂ environment, O₂ was bubbled through distilled water for 30-60 minutes and heated to 100°C. Then, the sample was exposed to H₂O vapor with O₂ as a carrier gas. For ambient exposures, the samples were exposed to ambient conditions (ca. 50% humidity) for 5 minutes and then sealed.

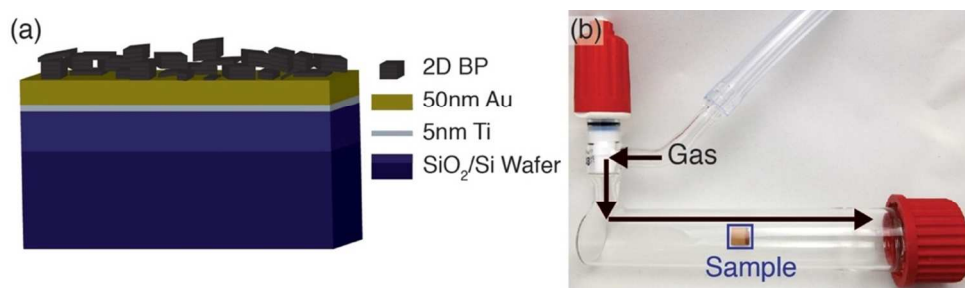


Figure S1. Oxidation of thin films of 2D black phosphorus. (a) Thin film of 2D black phosphorus assembled on a conductive, metal-plated silicon wafer. (b) Basic setup for oxidant exposure of 2D black phosphorus samples, showing the glass tube with an air-tight screwcap and a Teflon valve adjacent to a hose connection. The arrows indicate the direction of oxidant gas flow.

6. Transmission electron microscopy

A JEOL 100CX II TEM with an accelerating voltage of 80 kV and a resolution of 2 Å (lattice) and 3 Å (point to point) was used to characterize 2D black phosphorus flakes before and after oxidant exposures. Samples were prepared for TEM imaging by drop-casting 6 μL aliquots of 2D black phosphorus suspended in IPA onto 300-mesh copper TEM grids a lacey carbon film (Ted Pella) in the glovebox. Each grid was allowed to dry for a minimum of 45 minutes. Each grid was sealed and transported in polypropylene bags, then loaded and unloaded at the TEM under N₂ in dim light conditions. After characterizing unoxidized flakes, samples underwent oxidant exposure. After 1, 6, and 18 hours of exposure, the samples were purged with N₂, and then stored in the glovebox for TEM imaging. At each time interval, all previous flakes were re-imaged to provide information about physical degradation. Additionally, two new flakes were imaged at each time step. Imaging new flakes allowed for physical changes to be observed and for the possibility of knock-on damage to be addressed. Previously imaged flakes did not show any distinguishable differences from flakes characterized at later time steps indicating that knock-on damage did not significantly contribute to the observed physical changes of flakes, in agreement with previous work using the same accelerating voltage.⁴

6.1 Image processing

Images were acquired and further processed using Gatan Digital Micrograph. Due to inherent noise present imaging process and the specific 2K X 2K Gatan CCD camera used, a background subtraction was performed post-imaging to reduce the camera detector noise in the image. This image processing technique is demonstrated in Fig. S2. For each image of a flake, a minimum of two additional images were collected at the same condenser settings with higher magnifications in an area adjacent to the flake, without any portion of the TEM grid present. These higher magnification images were then averaged—herein referred to as the background image—to obtain a representation of the noise inherent to the image acquisition process. Finally, the background image was subtracted from the original image to reduce the detector noise.

In each of the images in Fig. S2, an increased presence of white pixels is evident on the right side of each of the images, implying the noise is inherent to the image acquisition process. An image of a flake was acquired at 72X magnification at an accelerating voltage of 80 kV (Fig. S2a). Twelve additional

images adjacent to the flake were taken at 100X (Fig. S2b) and 140X at the same condenser setting. The average of these higher magnification images is shown in Fig. S2c. Finally, the average background is subtracted from the original image, depicted in Fig. S2d. The images shown in Fig. S2a,d are at the same brightness, contrast, and gamma values in Gatan Digital Micrograph; the standard deviation in the Fig. S2a is reduced from 72.68 to 58.32 in Fig. S2d.

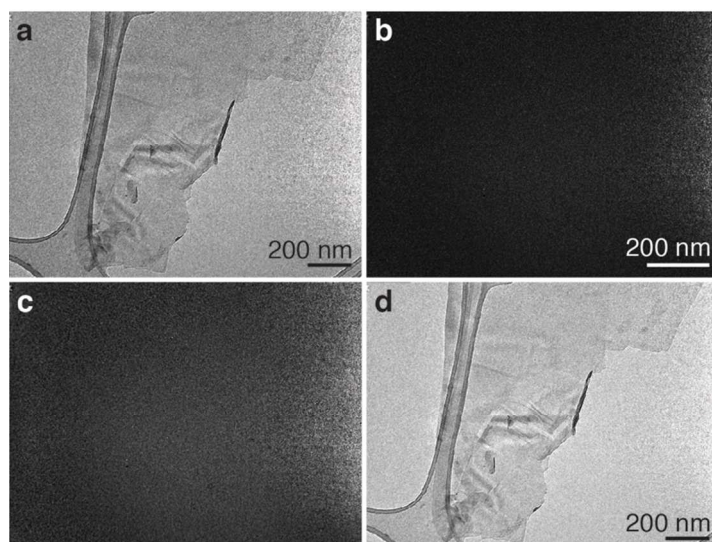


Figure S2. Processing of TEM images to reduce camera noise. (a) Image of a 2D black phosphorus flake acquired at 72X magnification at an accelerating voltage of 80 kV. (b) To visualize the pixel noise resulting from the TEM instrument and CCD camera, a 100X image was acquired adjacent to the flake at the same condenser settings. (c) The average background image is an average of the images collected adjacent to the flake at 100X and 140X magnifications. (d) The processed TEM image of a 2D black phosphorus flake after the average background image (c) was subtracted from the original image (a).

6.2 Diffraction patterns

During the time-lapsed TEM study of individual flakes of 2D black phosphorus with exposure to oxidants for up to 18 hours, a selected area diffraction pattern of each flake was acquired at each time interval. The orthorhombic crystal structure of 2D black phosphorus is observed after exposure to oxidants O_2 (Fig. S3a), H_2O/N_2 (Fig. S3b), and ambient conditions of H_2O and O_2 (Fig. S3c) for 18 hours. This further verifies that not all 2D black phosphorus is oxidized.

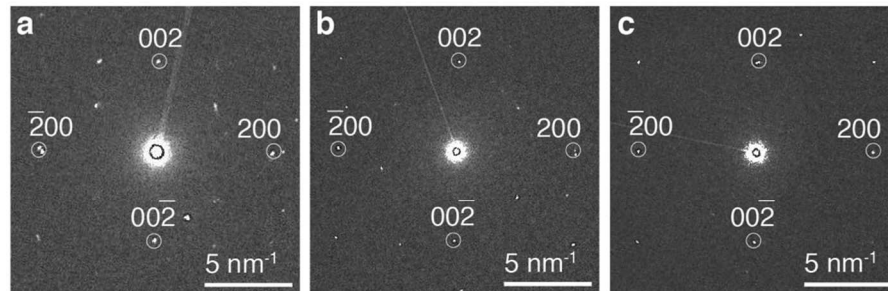


Figure S3. Diffraction patterns of 2D black phosphorus after 18 hours of oxidant exposure: (a) O₂ (99.999%), (b) H₂O/N₂ (99.998%), and (c) ambient conditions (humidity ca. 50%).

7. Raman Spectroscopy

Raman spectra of thin films of 2D black phosphorus were attained using a Reinschaw inVia Raman Microscope with an excitation wavelength of 633 nm, a 1200 l/mm grating, and 50X objective. The samples were sealed under N₂ between a glass microscope slide and cover slip, which were sealed with a two-part epoxy (Loctite[®] Hysol[®] 1C[™]) which cured at room temperature in a glovebox for a minimum of 36 hours.

The Raman active modes of the unoxidized 2D black phosphorus thin films, shown in Fig. S4 were observed at 360.82cm⁻¹, 438.08cm⁻¹, and 465.74cm⁻¹ for the A_g¹, B_{2g}, and A_g² modes, respectively, in good agreement with previous literature.⁴⁻⁶ While the intensity ratio of the active modes is dependent on sample thickness and orientation due to its anisotropic crystal structure,⁷ the ratio of the integrated intensity of the A_g¹ to A_g² peak was previously observed to be sensitive to the degree of oxidation.⁴ A ratio greater than 0.2 indicates low degrees of material oxidation.⁴ Unoxidized thin films of 2D black phosphorus had an average A_g¹ to A_g² integrated intensity ratio of 0.71 for 35 spectra acquired from different flakes, further validating the pristine quality of 2D black phosphorus. For a thin film exposed to H₂O/O₂ for 18 hours, the A_g¹, B_{2g}, and A_g² modes were located at 360.82cm⁻¹, 466.57cm⁻¹, and 438.09cm⁻¹. The intensity ratio of the A_g¹ to A_g² peaks was 0.63. Thin films of the material exposed to H₂O for 18 hours had A_g¹, B_{2g}, and A_g² modes located at 361.01cm⁻¹, 438.08cm⁻¹, and 465.92cm⁻¹; furthermore, these films had an average integrated intensity ratio of the A_g¹ to A_g² peaks of 0.52. This indicates that the degree of oxidation (1) after short-term exposures to ambient conditions and (2) after exposure to a single oxidant cannot be adequately probed by Raman spectroscopy. In previous literature, it was noted that exposure to O₂ or H₂O individually does not exhibit evidence of degradation in Raman spectroscopy,⁴ and the results presented here provide evidence that Raman spectroscopy is not a good means of detecting early stages of oxidation, especially for single-oxidant environments. Therefore, we did not rely on Raman spectroscopy as strong evidence for degradation, but utilized it for confirmation that the sample still retained 2D black phosphorus after oxidation.

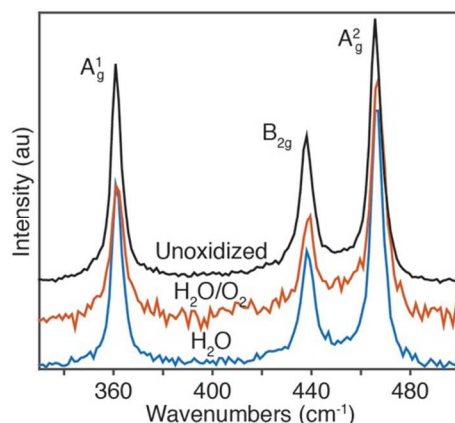


Figure S4. Raman spectra of 2D black phosphorus thin films for unoxidized material (black) and after 18 hours of exposure to H₂O/O₂ (orange) or H₂O (blue) oxidants.

8. Extent of Oxidation

Using XPS spectra of the phosphorus 2p core electron peaks, the phosphorus oxide on the surface of the 2D material can be quantified. The area of the phosphorus oxide peaks were compared to the area of the unoxidized 2p_{3/2} and 2p_{1/2} peaks, centered at 130.1 eV and 131.0 eV, respectively. The ratio of areas allows for quantification of the percent of oxide on the surface of the 2D material, summarized in Table S1.

Table S1. Percent of phosphorus oxides on thin films of 2D black phosphorus.

| Time (hrs.) | O ₂ (99.999%) | H ₂ O/N ₂ (99.998%) | H ₂ O/O ₂ |
|-------------|--------------------------|---|---------------------------------|
| 1 | 10.7 % | 8.3% | 20.7 % |
| 6 | 23.1 % | 17.8% | — |
| 1* | 20.5 % | 22.1 % | — |
| 18 | 33.0 % | 26.3 % | 52.3 % |

The percent of oxides present on the surface of the material are large enough to be observable in contrast variations in TEM imaging. For exposure to H₂O, the 2D black phosphorus showed evidence of step and edge oxidation as early as one hour. For exposure to O₂, the 2D material did not show changes in TEM. This further supports the theory that oxidation by O₂ primarily leads to basal surface oxidation, while H₂O leads to the oxidation of highly defect sites, such as edges and steps.

9. Supporting references

- (1) Köpf, M.; Eckstein, N.; Pfister, D.; Grotz, C.; Krüger, I.; Greiwe, M.; Hansen, T.; Kohlmann, H.; Nilges, T. Access and in Situ Growth of Phosphorene-Precursor Black Phosphorus. *J. Cryst. Growth* **2014**, *405*, 6–10.
- (2) Woomer, A. H.; Farnsworth, T. W.; Hu, J.; Wells, R. A.; Donley, C. L.; Warren, S. C.

- Phosphorene: Synthesis, Scale-Up, and Quantitative Optical Spectroscopy. *ACS Nano* **2015**, *9*, 8869–8884.
- (3) Hu, J.; Guo, Z.; McWilliams, P. E.; Darges, J. E.; Druffel, D. L.; Moran, A. M.; Warren, S. C. Band Gap Engineering in a 2D Material for Solar-to-Chemical Energy Conversion. *Nano Lett.* **2015**, *16*, 74–79.
 - (4) Favron, A.; Gaufres, E.; Fossard, F.; Phaneuf-L'Heureux, A.-L.; Tang, N. Y.-W.; Lévesque, P. L.; Loiseau, A.; Leonelli, R.; Francoeur, S.; Martel, R. Photooxidation and Quantum Confinement Effects in Exfoliated Black Phosphorus. *Nat. Mater.* **2015**, *14*, 826–832.
 - (5) Sugai, S.; Ueda, T.; Murase, K. Pressure Dependence of the Lattice Vibration in the Orthorhombic and Rhombohedral Structures of Black Phosphorus. *J. Phys. Soc. Jpn.* **1981**, *50*, 3356–3361.
 - (6) Sugai, S.; Shirovani, I. Raman and Infrared Reflection Spectroscopy in Black Phosphorus. *Solid State Commun.* **1985**, *53*, 753–755.
 - (7) Xia, F.; Wang, H.; Jia, Y. Rediscovering Black Phosphorus as an Anisotropic Layered Material for Optoelectronics and Electronics. *Nat. Commun.* **2014**, *5*, 4458.