Research article

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Room temperature wideband tunable photoluminescence of pulsed thermally annealed layered black phosphorus

https://doi.org/10.1515/nanoph-2020-0244 Received April 20, 2020; accepted July 23, 2020; published online August 24, 2020

Abstract: Newly explored two-dimensional (2D) materials have shown promising optical properties, owning to the tunable band gap of the layered material with its thickness. A widely used method to achieve tunable light emission (or photoluminescence) is through thickness modulation, but this can only cover specific wavelengths. This approach limits the development of tunable optical devices with high spectral resolution over a wide range of wavelengths. Here, we report wideband tunable light emission of exfoliated black phosphorus nanosheets via a pulsed thermal annealing process in ambient conditions. Tunable anisotropic emission was observed between wavelengths of 590 and 720 nm with a spectral resolution of 5 nm. This emission can be maintained for at least 11 days when proper passivation coupled with adequate storage is applied. Using hyperspectral imaging X-ray photoelectron spectroscopy (*i*-XPS), this tunable emission is found to be strongly

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dependent on the level of oxidation. We finally discuss the underlying mechanism responsible for the observed tunable emission and show that tunable emission is only observed in nanosheets with thicknesses of (70–125 nm) \pm 10 nm with the maximum range achieved for nanosheets with thicknesses of 125 ± 10 nm. Our results shed some light on an emerging class of 2D oxides with potential in optoelectronic applications.

Keywords: black phosphorus; black phosphorus oxide; photoluminescence; tunable band gap; tunable light emission; two-dimensional materials.

1 Introduction

New emerging two-dimensional (2D) materials have attracted significant attention in recent years due to their extraordinary mechanical, electrical, and optical properties at the nanoscale [1–5]. Among these materials, layered black phosphorus has played a key role in several applications. Phosphorene exhibits a layer-dependent band gap ranging from 0.3 to 1.7 eV for bulk to monolayer, respectively [6]. Moreover, phosphorene is desirable for light emission applications since the band gap depends only on the number of layers. Also, phosphorene has demonstrated high carrier mobility [7, 8], layer-dependent photoluminescence (PL) [6, 9], and anisotropic thermoelectric behavior [10]. In fact, electronic and optoelectronic devices with remarkable performance have been confirmed to employ black phosphorus [11, 12]. However, phosphorene still suffers from major obstacles including long-term stability in ambient conditions [13-16], which can be overcome by layer passivation or layer functionalization [17, 18].

In contrast, oxidized black phosphorus has remained a largely unexplored material. Black phosphorus oxide can be produced with different black phosphorus to oxygen contents $(P_x O_y)$. Theoretical calculations predict that black phosphorus oxide exhibits a wide band gap range which depends on the oxygen concentration [19]. Lu et al. [20] first പ്പ

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showed photoluminescence emission of laser-induced oxide on black phosphorus nanosheets and measured an emission of approximately 600 nm. The measured emission after laser oxidation was attributed to band gap emission of oxidized black phosphorus. Another group showed tunable PL from electrochemically oxidized black phosphorus crystals which showed a tunability range that did not exceed 50 nm, with a very broad emission linewidth [21]. More recently, Zhao et al. [22] observed PL emission at 600 nm after controllably oxidizing black phosphorus in the furnace. Although no tunability was observed, the method used several hours of annealing in order to oxidize black phosphorus [22].

Here, we report a wideband tunable PL emission over a broad range (up to 100 nm) by means of a pulsed thermal annealing method. We show that this emission can be finetuned with annealing time to achieve high spectral resolution. Lastly, we discuss the origins of this emission which holds potential in optoelectronic devices.

2 Results

Figure 1a illustrates the pulsed thermal annealing experiment. In this process, a heating pulse is applied to the substrate using an in-house hot plate setup for a short time interval (3 s interval). The heating temperature for the pulse was maintained at 360 ± 10 °C. Annealing time was controlled manually. The substrate was left at room temperature after annealing to cool down. Figure 1b shows the measured PL spectra (normalized) after applying pulsed thermal annealing for different cycles. Before annealing, no PL emission was observed. After the first cycle of pulsed thermal annealing, PL emission was observed at 720 nm. This PL peak downshifts and broadens at each sequential pulsed thermal annealing cycle, reaching 590 nm. In Figure S1a-c, measured PL emission spectra at different annealing times are illustrated in one plot along with additional samples exhibiting the same emission pattern.

In Figure 1c, fits for the wavelength, emission peak intensity, and emission linewidth are plotted for different pulsed thermal annealing times. These fits were obtained via Gaussian fitting of each PL spectrum (see Figure S2). From our fits, the emission peak starts to change in profile after an annealing time of 130 s. We notice from our fits that a secondary broad peak starts to emerge at 651 nm. This additional peak wavelength is relatively insensitive to the pulsed thermal annealing time as shown in Figure 1c. The origin of this additional peak stems from arbitrary oxidation states with different energies due to the formation of amorphous black phosphorus oxide, as discussed later. In contrast, the prominent peak shows a significant downshift to 590 nm with increasing pulsed thermal annealing time, while the intensity increases by $11.5\times$ as illustrated in Figure 1c. The secondary peak intensity, however, is relatively invariant to pulsed thermal annealing cycles.

In Figure 1d, we show two different spectra measured at different angles with respect to the laser polarization for a pulsed thermally annealed black phosphorus nanosheet. We see a $2.5 \times$ increase in the intensity when PL measurements are taken at a 90° angle. This change in the PL intensity suggests anisotropic behavior in pulsed thermally treated black phosphorus nanosheets, as further verified in Figure 1e. The origin of the observed anisotropic behavior in the black phosphorus oxide could be attributed to the anisotropy of pristine black phosphorus, where the atomic structure exhibits a puckered shape with an armchair direction and a zigzag direction.

In Figure 2a–e, spatial PL maps for different pulsed thermally annealed black phosphorus nanosheets are shown. Uniform emission along the surface of the nanosheets was observed, with wavelengths of 700, 670, 640, 613, and 595 nm. The low intensity spots in Figure 2b and e are artificial and were generated by longer laser exposures during single spot measurements. To demonstrate the fine tunability of the PL, a nanosheet was pulsed thermally annealed at 5 s intervals, as demonstrated by the spectra in Figure S3a–f. Indeed, the spectral resolution of the treated black phosphorus nanosheet can be tuned within a 5 nm peak difference covering a broad wavelength range between 600 and 713.5 nm. The PL emission was also confirmed using a different laser line (514 nm) as shown in Figure S4.

Raman intensity maps of the A_g^1 , B_{2g} , and A_g^2 modes have been implemented to study surface oxidation of pulsed thermally annealed black phosphorus. Previous work demonstrated that the intensity of these Raman modes can be significantly modulated with further oxidation in ambient conditions, which leads to nonuniform etching on the surface of the nanosheet [14]. Accordingly, the Raman mode intensity modulation technique can be a good indicator to measure any structural changes on the surface of pulsed thermally annealed black phosphorus nanosheets. In Figure 3a-c, Raman intensity maps of a pulsed thermally annealed black phosphorus nanosheet are shown before and after different annealing cycles. Figure S5 shows all Raman maps along with the corresponding PL at each pulsed thermal annealing cycle. Before annealing (Figure 3a), all Raman modes show relatively uniform intensities. Remarkably, after the pulsed



Figure 1: (a) Schematic diagram showing the pulsed thermal annealing process of exfoliated black phosphorus after exfoliation with no light emission, after cycle one of treatment and emitting at wavelength (ω_1), and after cycle two of treatment and emitting at wavelength (ω_2). (b) Photoluminescence (PL) intensity versus wavelength (λ) at different treatment times for a 120 nm thick exfoliated black phosphorus nanosheet. The treatment time shown for each cycle is cumulative. Arrow indicates the direction of increasing treatment cycles. (c) PL wavelength, intensity, and linewidth of unnormalized data sets. (d) PL spectra of another pulsed thermally annealed black phosphorus nanosheet at a 90° angle difference. (e) PL intensity versus angle showing anisotropic behavior.

thermal annealing cycles (Figure 3b and c), the Raman modes preserve intensity uniformity for each pulsed thermal annealing cycle, which indicates a uniform surface thinning as will be explained later.

Figure 4a-f show the morphology of two pulsed thermally annealed nanosheets measured using atomic force microscopy (AFM) at different annealing intervals. Before

annealing, the black phosphorus nanosheets show a smooth surface. However, with increasing pulsed thermal annealing, we observe surface thinning occurs after different pulsed thermal annealing cycles. Figure 4g-i illustrate this thinning behavior. We also observe an increase in surface roughness when layered black phosphorus reaches thicknesses of 20 nm. This increase in



Intensity (a.u.)

Figure 2: Spatial photoemission maps of different black phosphorus nanosheets showing the maximum light emission occurring at (a) 700 nm, (b) 670 nm, (c) 640 nm, (d) 613 nm, and (e) 595 nm. Each black phosphorus nanosheet is deposited on a different substrate and is treated at different treatment time intervals.

surface roughness is attributed to an increase in oxidation rate, which occurs at thicknesses smaller than 30 nm [22]. This enhanced oxidation is caused by a thickness dependent oxidation mechanism, where few-layer black phosphorus exhibits a larger oxidation probability than thicker black phosphorus (>30 nm). Moreover, as will be discussed later in Figure 6a, we plot the measured thickness ($D_{\rm BP}$) of the pulsed thermally annealed nanosheet after each cycle. A linear decrease in layer thickness is observed with uniform etching up until about 10 ± 10 nm. At this thickness threshold, we see an exponential decrease in nanosheet thickness, which indicates an increase in the oxidation rate.

Raman spectra support the observed AFM black phosphorus thinning. We show in Figure S6 Raman

intensity modulation for the A_g^1 , B_{2g} , and A_g^2 modes at different annealing times using the 532 nm laser. As expected, all Raman modes exhibit a nonmonotonic trend. This behavior can be explained by considering the effect of Raman light interference with the incident laser beam, which can be influenced by the thickness of the nanosheet for a given laser excitation wavelength [14, 23]. This phenomenon was previously observed in graphene nanosheets, where the intensity of the *G* and *D* bands change dramatically with graphene thickness [24, 25].

It is important to distinguish between PL emission due to degraded black phosphorus and PL emission due to pulsed thermal annealing black phosphorus. We test the PL emission of a degraded black phosphorus nanosheet, as shown in Figure S7. After exposure to ambient conditions



Figure 3: Photoluminescence (PL) and Raman intensity maps of the A_g^1 , B_{2g} , and A_g^2 modes for a pulsed thermally annealed black phosphorus nanosheet at (a) 0 s, (b) 50 s, and (c) 80 s.

for 16 days, the nanosheet starts to exhibit a very broad PL emission peak centered at 587 nm, indicating amorphous black phosphorus oxide. With increasing degradation time, the intensity of this broad emission peak increases to reach its maximum at 31 days, which is after the nanosheet has completely degraded. Unlike pulsed thermally



Figure 4: Atomic force microscopy (AFM) topographic maps showing the morphology of a pulsed thermally annealed (a–c) 135 nm nanosheet and (d–f) 120 nm nanosheet. (g–i) AFM cross-sectional data as a function of treatment time.

annealed black phosphorus nanosheets, PL emission from degraded black phosphorus does not exhibit any tunability.

To assess changes to the oxidation state of the phosphorus from pulsed thermally annealing, nanosheets were examined *ex situ* using imaging X-ray photoelectron spectroscopy (*i*-XPS). Specifically, four different exfoliated black phosphorus nanosheets were characterized, where one nanosheet was never treated and the other three nanosheets were treated differently to obtain emissions at 721, 691, and 607 nm, as shown in Figure 5a–d, respectively. Samples were examined after transport under vacuum to the spectrometer. Due to the relatively small size of the exfoliated nanosheets (lateral dimensions as small as 10 μ m), *i*-XPS is achieved by employing X-ray photoelectron spectroscopy (XPS) in parallel imaging mode for

improved spatial resolution. Due to the low cross-section for photoemission attributed to the P (2p) photoelectrons, high pass energy was utilized to maximize collected photoelectrons at the expense of spectral resolution. While hyperspectral imaging stacks were acquired for P (2p), Si (2p), and Au (4f) as shown in Figure S8, only the P (2p) data are represented in Figure 5. It is also important to note that each value is the result of a single measured sample.



Figure 5: Imaging X-ray photoelectron spectroscopy (*i*-XPS) measurements for (a) a nontreated black phosphorus nanosheet and (b–d) several treated black phosphorus nanosheets with light emission at 721, 691, and 607 nm, respectively.

For each different emission wavelength, there is a corresponding P (2p) processed image representative of the black phosphorus feature centered at ≈129 eV (center column). A set of masks was created in a manner consistent with previous work [5] to define the edge of each nanosheet as illustrated in Figure S9, and spectra associated with pixels inside these regions of interest were assembled from the raw image stack, as shown in the right column. We observe from the extracted P (2p) spectrum that the native black phosphorus (P_{BP}) was characterized by a broad feature at ≈ 129 eV for the $2p^{3/2}$ component, consisting of >97% of the total phosphorus species on the surface. The remainder was composed of some small contributions from an oxidized phosphorous component (Pox) between 132 and 135 eV. With the pulsed thermal annealing of the black phosphorus nanosheet and the development of PL, the contributions from the $P_x O_y$ component significantly increased at a peak location of \approx 133.7 eV for the 2p^{3/2} component. The relative ratio of Pox:PBP increased as the PL wavelength decreased after pulsed thermal annealing, specifically to 0.22, 0.33, and 0.38 for emission wavelength of 721, 691, and 607 nm, respectively (see Figure S9 for fitted spectra). This is perhaps better illustrated in Figure 6b, which demonstrates a clear correlation between the oxidized black phosphorus:native black phosphorus ratio and PL wavelength and, more generally, between the surface oxidation and energy of emitted light.

Previous work on black phosphorus nanosheet degradation has illustrated that poly(methyl methacrylate) (PMMA) passivation and storage in a dark vacuum environment should preserve the nanosheet for a longer period of time [14]. In addition to this passivation method, oxidized black phosphorus can act as a protective layer to the underlying phosphorene layers [26, 27]. Accordingly, a pulsed thermally annealed nanosheet was passivated with PMMA and stored in a dark vacuum environment in order to assess the stability of the PL emission. Figure S10a and b illustrate the Raman and PL emission measurements at 0 days (immediately after PMMA deposition) and after 11 days in a dark vacuum environment. After 11 days, the measured Raman modes do not exhibit any noticeable changes, suggesting preserved nanosheet properties. This is further confirmed by the PL measurements which demonstrate no observable change in PL emission wavelength and only a minimal change in the intensity.

3 Discussion

The tunable emission of pulsed thermally annealed black phosphorus nanosheets can be explained by examining black phosphorus oxide properties. Phosphorene oxide exhibits two forms, stoichiometric and nonstoichiometric, depending on how oxygen atoms bond to phosphorus atoms [28]. While the band gap for each of these forms is



Figure 6: (a) Atomic force microscopy (AFM) measurements after each pulsed thermal annealing cycle for a nanosheet with an initial thickness of 120 nm. The inset shows $dD_{\rm BP}/dt$ versus annealing time with an exponential decrease for the last few cycles. (b) The ratio of black phosphorus oxide to black phosphorus measured using imaging X-ray photoelectron spectroscopy (i-XPS) for differently treated samples. The ratio is increasing with increasing treatment time, indicative of higher black phosphorus oxide compared to black phosphorus on the surface of the nanosheet. (c) Schematic diagram showing how oxygen atoms (red) bond with black phosphorus at the sublimation temperature.

different, it has been found that the band gap solely increases from 1.62 to 8 eV with increasing oxygen concentration [19, 20, 28, 29].

First, we confirm that the observed PL emission is due to oxidation by annealing black phosphorus nanosheets in the furnace and in different environments. Figure S11 illustrates this behavior. Two sets of exfoliated black phosphorus samples are annealed in oxygen and in nitrogen environments. Each set is annealed at different temperatures for 1 min. Freshly exfoliated samples used in this experiment do not exhibit any PL emission prior to thermal annealing. After annealing, a broad PL peak is observed at around 600 nm for all oxygen annealed samples. In contrast, samples annealed in the nitrogen environment did not show any PL emission post annealing, which is further evidence that the main contributing factor in the observed PL emission is oxygen reaction with black phosphorus nanosheets.

Second, the observed tunable PL can be explained by considering the Marcus–Gerischer theory (MGT) model which is given as follows:

$$\frac{d([BP]_{ox})}{dt} = -\frac{d([BP])}{dt}$$
$$= b(A\sigma_{abs}\rho_A\tau_n nk_o J_{ph}) \cdot [BP] \cdot [O_2] \cdot$$
$$exp\left(-\frac{\left(\frac{|E_{g,n}|}{2} + E_i - E_{OX} - \lambda\right)^2}{4k_{BT}T\lambda}\right), \quad (1)$$

where *b* is a constant that includes different factors (the molecular geometry of the system and normalization parameter), *A* is the exposure unit area, σ_{abs} is the absorption cross-section per atom, ρ_A is the phosphorus surface density, τ_n is the effective carrier lifetime, *n* is the number of layers, k_0 is the reaction rate constant, and J_{ph} is the photon flux. [BP] and [O₂] are the black phosphorus coverage and oxygen concentration, respectively. $E_{g,n}$ is the band gap for *n* number of layers, E_i is the intrinsic Fermi level potential, E_{OX} is the unoccupied energy state of oxygen acceptor, and λ is the renormalization energy of oxygen. It should be mentioned that for thin nanosheets, surface oxidation is the dominant oxidation mechanism. Therefore, the term [BP] is only affected by surface changes and hence can be observed in the AFM thickness measurements.

In this model, the oxidation rate depends linearly on the oxygen concentration and the number of layers. For few-layer nanosheets, the oxidation rate depends exponentially on the square of $E_{g,n}$. This means the oxidation rate is significantly higher in few layered black phosphorus nanosheets compared to multilayer nanosheets. Indeed, by looking at the AFM measurements in Figure 6a, we observe an initial linear decrease in thickness at each different thermal cycle and then an exponential decrease when the nanosheet reaches 10 ± 10 nm. We also plot $dD_{\rm BP}/dt$ from the measurements and fit it to an exponential function. Remarkably, the exponential fit follows the same trend as the MGT model above.

We now discuss the mechanism of which this surface oxidation occurs. At temperatures close to 375 ± 20 °C, black phosphorus sublimation occurs [30], where black phosphorus atoms migrate and cause unbound black phosphorus (BP) atoms at the surface. This process makes the surface of black phosphorus vulnerable to oxidation, where vacancies are created in each thermal annealing cycle. These vacancies exhibit low energy barriers, which allows them to diffuse into black phosphorus layers at a rate higher than other van der Waals semiconductors [22]. These surface vacancies make it easier for oxygen to bond with phosphorus since the energy required to create this bond decreases to 0.59 eV at the vacancy. Accordingly, the likelihood of creating an O–P bond at the vacancy is three orders of magnitude higher than areas with a P-P bond [31]. Increasing the number of pulsed thermal cycles will increase the likelihood of oxygen atoms bonding to random black phosphorus atoms and hence increase oxygen concentration per atom. Figure 6c shows a simplified schematic illustrating the process of black phosphorus oxidation with the help of sublimation. In this schematic, edge oxidation has been ignored for simplicity.

According to Born-Oppenheimer molecular dynamics (BOMD) simulations on temperature annealed black phosphorus nanosheets, black phosphorus oxide with different compositions of $P_x O_y$ can form different P–O bonding with increasing annealing time at a given temperature [29]. Formed bonds can be a mixture of dangling bonds and bridging bonds. Although black phosphorus oxide should exhibit a band gap between 1 and 8 eV, BOMD simulations show that amorphous black phosphorus oxide with varying oxygen concentrations exhibits a significant band gap reduction up to 5.5 eV, resulting in a band gap range between 1 and 2.5 eV. This band gap reduction is caused by in-gap states due to P-rich bonds on the nanosheet. Our findings here are aligned with BOMD simulated amorphous black phosphorus oxide with varying oxygen concentration. Accordingly, the observed tunable PL emission is caused by varying oxygen concentration in the amorphous $P_x O_v$ composition. Nonetheless, investigating the dynamics of how oxygen atoms bond with black phosphorus atoms after pulsed thermal annealing to create P_xO_y with varying y is beyond the scope of this work and should be studied in more detail in the future.

One can interpret the absence of tunability for thick nanosheets in Figure S12, where we show a broad PL emission with no tunability. This broad PL emission can be understood based on different defect emissions (black phosphorus oxide) created after pulsed thermal cycling. The shape and linewidth of this broad peak change with repeated pulsed thermal annealing. This is expected by considering Equation (1) and a thick nanosheet. Due to the larger coverage of thick black phosphorus nanosheets ([BP]), the oxidation rate is faster than that of thinner nanosheets under the same pulsed thermal annealing conditions $d([BP]_{ox})/dt|_{d=800 \text{ nm}} \gg d([BP]_{ox})/dt|_{d=100 \text{ nm}},$ which readily leads to uncontrolled PL emission tunability. Besides, the oxidation mechanism for these thick nanosheets is different than that for thinner nanosheets. Figure S13 demonstrates this behavior with optical images at different pulsed thermal annealing cycles. A decrease in lateral and vertical directions of the nanosheet is observed, which is attributed to surface and edge oxidation. For thinner nanosheets, surface oxidation is the dominant mechanism which affects the vertical size only (see Figure S14). This decrease in both directions for thick nanosheets contributes to the accelerated oxidation (compared to thinner nanosheets) and can give rise to the observed multiple PL peak energies where oxygen concertation is varied at different sites on the nanosheet due to surface and edge oxidation.

Based on our results and the discussion above, the tunable PL feature is only observed for black phosphorus nanosheets with thicknesses between $(70-125 \text{ nm}) \pm 10 \text{ nm}$, with the highest tunability bandwidth being achieved for nanosheets with thicknesses around $125 \pm 10 \text{ nm}$. Beyond this thickness threshold, edge oxidation starts to compete with surface oxidation, causing an accelerated oxidation rate and hence the observed broad PL emission. For few-layer nanosheets, the oxidation rate is higher due to alignment of the black phosphorus band gap with oxygen acceptors causing charge transfer and hence faster oxidation.

4 Conclusions

In summary, black phosphorus nanosheets were treated using cyclic pulsed thermal annealing at high temperature and for short time intervals. The nanosheets exhibited wideband tunable PL between 590 and 720 nm with a broad linewidth. The intensity of this emission increased dramatically with increasing pulsed thermal annealing

time. The spectral resolution obtained was 5 nm. By preserving the treated black phosphorus in a dark vacuum environment after PMMA capping, the treated black phosphorus can be stable for at least 11 days. The wideband tunable PL emission can be attributed to controlled oxidation of exfoliated black phosphorus nanosheets. i-XPS measurements show the formation of oxidized black phosphorus with different levels of oxidation. We show that the PL emission is due to the formation of black phosphorus oxide, while tunable PL is caused by varying oxygen concentration of the formed black phosphorus oxide with pulsed thermal annealing time. This PL tunability feature is only observed in nanosheets with thicknesses between $(70-125 \text{ nm}) \pm 10 \text{ nm}$ with the maximum tunable PL range achieved for nanosheets with a thickness of 125 ± 10 nm. This tunability feature disappears for few-layer nanosheets and bulk nanosheets (>150 nm) due to increased oxidation. Our work demonstrates a promising technique to produce nanoscale tunable PL emission in the optical range with a ≈ 5 nm spectral resolution and hence unlocks doors to future optoelectronic devices based on 2D oxidized black phosphorus.

5 Experimental methods

5.1 Nanosheet fabrication

Mechanically exfoliated black phosphorus nanosheets were deposited onto Si/SiO₂ substrates. Optical microscopy was used to pick uniform black phosphorus nanosheets. The thicknesses were estimated using the ratio of the intensity of the A_g^1 Raman mode $(I_{A_g^1})$ to the intensity of the silicon peak (I_{Si}) [18, 32]. This ratio is obtained from AFM and Raman measurements. Data are fitted to a linear relation as shown in Figure S15.

5.2 Pulsed thermal annealing

Pulsed thermal annealing was achieved using a lab hot plate. First, the hot plate is set at 360 ± 10 °C and is left to reach this target temperature. Once a steady target temperature is reached, the substrate is placed in the middle of the hot plate for the specified treatment time. The substrate is immediately lifted after the treatment time is lapsed and is placed on a room temperature surface to cool down. Further characterization measurements are carried out after the cool down.

5.3 Photoluminescence and Raman measurements

Each sample is characterized using confocal Raman spectroscopy (Renishaw) with a charge-coupled device detector and 1800 lines/mm grating. The 532 nm laser line is used as an excitation source for all measurements with 0.93 mW laser power and spot size of $\approx 1 \,\mu\text{m}$, unless otherwise noted. The laser power used in the measurements was minimized to prevent damage to the nanosheets. We used a 100× objective lens for all samples to ensure nanosheet emission. PL maps were recorded with a 0.3 μm step size. All emission spectra were fitted according to a Gaussian fit as shown in Figure S2.

5.4 *i*-XPS measurements

Samples were prepared by deposition of exfoliated nanosheets onto a single silicon wafer with gold fiducial markers which were utilized to find the specified nanosheets for photoemission after pulsed thermal annealing. A second wafer was prepared in the same way without pulsed thermal annealing as the control. The samples were promptly packaged under vacuum prior to shipping for XPS analysis at the National Institute of Standards and Technology (NIST). Samples were pumped down immediately upon opening the package. Total time from sample preparation to pump down to Ultra High Vacuum (UHV) conditions was less than 2 weeks. Prior testing of this vacuum storage method for shipping showed vacuum integrity held from 2 to 3 weeks.

i-XPS analysis was carried out using an Axis Ultra DLD spectrometer from Kratos Analytical (Chestnut Ridge, NY). *i*-XPS imaging was conducted using Field of View 3/High Resolution (FoV3/HR) lens and aperture settings, respectively, with a lateral resolution estimated to be between 3 and 10 µm, based on manufacturer's specification and internal checks. Imaging was conducted using Mg K α X-rays at 225-300 W with photoelectrons collected for 300-900 s/image, both conditions varying with the size of the feature. Images were collected for the P (2p) region, the Si (2p) region, and the O (1s) region at 0.25 eV intervals across a defined energy range. Image processing was carried out using Mathematica to correct for stage drift. Creation of masks and spectral processing was conducted using CasaXPS (Teignmouth, UK) with the former being previously described [5]. Extracted spectra were energy referenced based on adjusting the fitted Si region to 103.5 eV for the $2p^{3/2}$ functionality for SiO₂, the median value based on SRD 20 [33]. For the P (2p) region, extracted spectra had X-ray satellites subtracted and were fit with a

Shirley background prior to fitting. Two sets of doublets were employed to fit the P (2p) region, the first for native black phosphorus and the second for oxidized black phosphorus, which were only constrained in the following ways: the doublets, $2p^{3/2}$: $2p^{1/2}$, had a peak area ratio of 2:1 for a given chemistry, full width at half maximum was equal for a given chemistry, and the peak-to-peak separation was 0.87 eV for a given chemistry. Reported ratio values are reflective of the sum of the P_{ox} area divided by the sum of the P_{BP} area for each sample.

Acknowledgments: This research was financially sponsored in part by King Abdulaziz City for Science and Technology (KACST) through the Center of Excellence for Green Nanotechnologies (CEGN), part of the technical leaders program. J. M. Gorham and F. W. DelRio acknowledge support from the National Institute of Standards and Technology. Certain commercial equipment, instruments, or materials are identified to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the NIST nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This research was financially sponsored in part by King Abdulaziz City for Science and Technology (KACST) through the Center of Excellence for Green Nanotechnologies (CEGN), part of the technical leaders program. J. M. Gorham and F. W. DelRio acknowledge support from the National Institute of Standards and Technology.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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Supplementary Material: The online version of this article offers supplementary material (https://doi.org/10.1515/nanoph-2020-0244).