Defining the role of humidity in the ambient degradation of few-layer black phosphorus

Walia, Sumeet; Sabri, Ylias; Ahmed, Taimur; Field, Matthew; Ramanathan, Rajesh; Arash, Aram; Bhargava, Suresh

https://researchrepository.rmit.edu.au/esploro/outputs/9921860050101341/filesAndLinks?institution=61RMIT_INST&index=null

Walia, S., Sabri, Y., Ahmed, T., Field, M., Ramanathan, R., Arash, A., Bhargava, S., Sriram, S., Bhaskaran, M., Bansal, V., & Balendhran, S. (2016). Defining the role of humidity in the ambient degradation of few-layer black phosphorus. *2D Materials*, 4(1), 1–8. <https://doi.org/10.1088/2053-1583/4/1/015025>

Document Version: Accepted Manuscript

Published Version: <https://doi.org/10.1088/2053-1583/4/1/015025>

Repository homepage: <https://researchrepository.rmit.edu.au>

© 2016 IOP Publishing Ltd

Downloaded On 2023/04/26 19:27:30 +1000

Thank you for downloading this document from the RMIT Research Repository.

The RMIT Research Repository is an open access database showcasing the research outputs of RMIT University researchers.

RMIT Research Repository: <http://researchbank.rmit.edu.au/>

Citation:

Walia, S, Sabri, Y, Ahmed, T, Field, M, Ramanathan, R, Arash, A, Bhargava, S, Sriram, S, Bhaskaran, M, Bansal, V and Balendhran, S 2016, 'Defining the role of humidity in the ambient degradation of few-layer black phosphorus', 2D Materials, vol. 4, no. 1, 015025, pp. 1-8.

See this record in the RMIT Research Repository at:

<https://researchbank.rmit.edu.au/view/rmit:38939>

Version: Accepted Manuscript

Copyright Statement:

© 2016 IOP Publishing Ltd

Link to Published Version:

<https://dx.doi.org/10.1088/2053-1583/4/1/015025>

Defining the role of humidity in the ambient degradation of few-layer black phosphorus

Sumeet Walia,^{1*} Ylias Sabri,² Taimur Ahmed,¹ Matthew R. Field,³ Rajesh Ramanathan,⁴ Aram Arash,¹ Suresh K. Bhargava,² Sharath Sriram,¹ Madhu Bhaskaran,¹ Vipul Bansal,^{4*} and Sivacarendran Balendhran^{1*}

E-mail: sumeet.walia@rmit.edu.au, vipul.bansal@rmit.edu.au, shiva.balendhran@rmit.edu.au

¹Functional Materials and Microsystems Research Group, School of Engineering, RMIT University, Melbourne VIC 3001, Australia

²Centre for Advanced Materials and Industrial Chemistry, School of Science, RMIT University, Melbourne VIC 3001, Australia

³RMIT Microscopy and Microanalysis Facility, School of Science, RMIT University, Melbourne VIC 3001, Australia

⁴Ian Potter NanoBioSensing Facility, NanoBiotechnology Research Laboratory, School of Science, RMIT University, Melbourne VIC 3001, Australia

Keywords: phosphorene, black phosphorus, two-dimensional materials, humidity sensing, photo-oxidation

Abstract

Few-layer black phosphorus (BP) is an emerging material of interest for applications in electronics. However, lack of ambient stability is hampering its incorporation in practical devices as it demands for an inert operating environment. Here, we study the individual effects of key environmental factors, such as temperature, light and humidity on the deterioration of BP. It is shown that humidity on its own does not cause material degradation. In fact, few-layer BP is employed as a recoverable humidity sensor. This study eliminates humidity as an active parameter in BP degradation. Hence, by simply isolating BP from light, its lifetime can be prolonged even in the presence of O₂. As such, this study opens the pathway for devising new strategies for the practical implementation of BP.

1 **Introduction**

2 Two-dimensional (2D) materials have been garnering attention in the field of nanoelectronics,
3 with the promise of delivering alternative solutions for high speed electronics and digital
4 processing. Their exotic properties at atomically thin dimensions arise from their planar
5 nature and the consequent quantum confinement of charge carriers.[1,2] Whilst graphene has
6 been the most popularly researched 2D material, the lack of an intrinsic energy gap has led to
7 the pursuit of alternative 2D semiconductors.[3,4] Typical 2D semiconductors include
8 transition metal dichalcogenides/oxides (TMDO) and Group IV elemental sheets.[3] However,
9 TMDOs have not yet been demonstrated to be able to match the exceptional carrier transport
10 performances seen in graphene, which is attributed to graphene's planar elemental nature. On
11 the other hand, even though theorized to be excellent alternatives, the progress on Group IV
12 elemental sheets for nanoelectronics has been minimal due to their relatively unstable nature
13 and the lack of facile synthesis approaches.[5] Recently, a layered crystal phase of phosphorus
14 (black phosphorus: BP) that had been overlooked for so long, has risen as a potential
15 candidate for 2D electronics.[6,7]

16 A single-layer of BP (phosphorene) occurs in a puckered honeycomb structure (Figure 1a),
17 which encapsulates the advantages of an elemental 2D material, while possessing an intrinsic
18 bandgap close to that of silicon.[7,8] Although desirable for electronics, the ambient
19 instability of BP remains the weakest link in its research progress, as it has to be stored and
20 handled in inert environments, rendering it to be unfavorable for practical implementation.[9-
21 12] Within a span of a few days, the material develops large droplet like surface protrusions
22 and eventually decomposes completely.[13] The reason for this degradation is still a topic of
23 debate. Initial reports suggest that humidity adsorption on the BP surface results in a layer by
24 layer decomposition, while some recent studies indicate the role of photo-oxidation.[14] To
25 date, the solution to avoid degradation has been capping BP to minimize its interaction with

1 the ambient environment.[15-19] Such preservation methodologies are complex and may
2 result in altering its intrinsic properties.

3 Here, we individually study the effect of key environmental factors (temperature, humidity
4 and light) in order to understand how they influence the generally observed ambient
5 degradation of BP. A thorough spectroscopic investigation into the origin of degradation right
6 from the point of exfoliation reveals that humidity on its own does not cause any degradation.

7 Based on these observations, we show that it is possible to preserve BP for over a week
8 without using any surface passivation techniques. To further elucidate this finding, we report
9 the recoverable humidity sensing capabilities of pristine BP. Although, humidity sensing
10 capabilities of chemically passivated, re-stacked BP thin films have been reported, our work
11 represents the humidity response from mechanically exfoliated pristine BP flakes.[20-22]

12 without any surface passivation. Therefore, the response and the recoverability can be solely
13 attributed to the intrinsic properties of pristine BP. As such, this study has important
14 implications for prolonging the lifetime of BP in ambient conditions, without the requirement
15 of an inert environment; thereby opening an opportunity towards BP based practical
16 nanoelectronic, chemical/sensing and energy storage applications.

Figure 1. Crystal Structure of black phosphorus. (a) Illustration of the monolayer BP crystal adopting a puckered honeycomb structure. The purple spheres represent covalently bonded phosphorus atoms. (b) TEM image of a mechanically exfoliated, multilayer BP crystal. Insets show the SAED patterns and a HRTEM image of the highlighted phosphorene layer, indicating the presence of crystalline BP.

Results and Discussion

The layered nature of BP can be seen in the transmission electron microscopy (TEM) image of a mechanically exfoliated flake under ambient conditions (Figure 1b). The inset (on the right) illustrates a magnified high resolution TEM (HRTEM) scan of the highlighted monolayer area of the BP flake. The lattice fringes seen here correlate well with those reported in literature, indicating the presence of monolayer BP.[23,24] The inset to the left shows the selective area electron diffraction (SAED) pattern of the highlighted area, which further signifies the occurrence of perfectly crystalline phosphorene. These results show that the crystallinity of the material remains intact after being subjected to mechanical exfoliation process, under ambient environment.

As BP degradation is considered to be an oxidative process,[18] the effect of temperature under ambient conditions was investigated using Raman spectroscopy. For this purpose, mechanically exfoliated BP crystals were heated up to 100 °C and cooled down, while acquiring Raman spectra *in situ*, at step-sizes of 25 °C. Figure 2a shows the Raman spectra of a thin (<5 nm) BP flake and the observed peak shifts with respect to temperature. At room temperature, the A_g^1 , B_g^2 and A_g^2 modes were observed at 360.5, 438.4, and 465.7 cm^{-1} , respectively. A maximum redshift of 2.4 cm^{-1} was observed at 100 °C. As the temperature was ramped back down to room temperature, the peaks reverted back to their respective initial positions. Figure 2b illustrates the Raman peak shifts observed on BP crystallites of three thickness (t) ranges. It should be noted that the peak shift seen during the heating and cooling cycles follow the same trend (Figure 2b), resulting in the overlap of some data points on the graph. In line with previous studies,[6] the initial peak position of the thinner crystallite was observed to be shifted. The temperature-induced peak shift was fully recoverable in all the cases. This observation was consistent on several exfoliated BP crystallites of varying thicknesses (refer to Supporting Information Figure S1 for the full temperature-dependent Raman spectra acquired on multiple flakes). Characteristically in BP, a drastic change in the full width at half maximum (FWHM) values of the Raman peaks is known to occur with reducing thickness.[18] Figure 2c illustrates the variation in FWHM values (obtained through a linear extrapolation) of all three Raman modes for multiple BP crystallites, with respect to temperature. As expected, a larger FWHM value was observed in thinner crystallites ($t < 5$ nm). As a layer-by-layer etching phenomenon is observed during BP degradation, a change in FWHM values is expected with the progression of degradation. However, for all three thicknesses, a variation of only 0.2 cm^{-1} is observed in the FWHM values upon recovery from the temperature treatment, which is less than the resolution of the Raman spectrometer (1 cm^{-1}) and can therefore be ignored. Such a recovering shift indicates a reversible thermal expansion in the crystal lattice caused by an increase in temperature. This suggests a minimal

influence of temperature towards degradation of BP. It must be noted that BP has been shown to decompose at temperatures in excess of 400 °C in vacuum.[25] Nearly identical thermally-induced Raman shifts in inert environments have also been reported.[26] However, based on our experimental observations, it is inferred that no indications of degradation or oxidation occurs at typical operating temperatures for electronic devices (<120 °C) in ambient conditions (see Supporting Information Figure S2).

Figure 2. Temperature dependent Raman analysis. a) Raman spectra of a few-layer BP crystal (thickness $t < 5$ nm) with varying temperature, under ambient environment. b) Raman peak shift with respect to temperature, observed in multiple flakes of varying thicknesses. c) Variation in the full width at half-maximum (FWHM) values of the three BP Raman peaks with respect to temperature.

To investigate the individual effects of humidity (RH) and light, the following experimental scheme was implemented. Four samples of mechanically exfoliated BP crystals under

ambient conditions were stored separately in the following ways: (Sample 1) control sample stored on a standard lab storage shelf, exposed to air (humidity) and ambient light (+RH+L); (Sample 2) stored in an opaque container, exposed to air (humidity) in the absence of light (+RH-L); (Sample 3) stored in a desiccator chamber to avoid humidity but exposed to light (-RH+L); (Sample 4) stored in an opaque container inside a desiccator, in the absence of light and humidity (-RH-L). Multiple BP crystallites of 5-10 nm thickness were identified using their optical contrast (refer to Supporting Information Figure S3 for representative AFM images) from each sample were marked and subjected to spatial Raman mapping every alternate day. The A_g^1 Raman mode is considered for the mapping as it remains constant when normalized to the Si transverse optical mode and hence provides a good reference for comparison.[27] Figure 3 illustrates the normalized Raman peak intensity (A_g^1) maps acquired from BP crystals stored under the various conditions outlined above. BP crystallites from Sample 1, (Figure 3a) went through rapid degradation and within 8 days the chosen crystallites completely deteriorated. This observation is in line with several reports.[18,28] A detailed set of corresponding Raman maps between Days 1 and 8 can be seen in Supporting Information (Figure S2).

Crystallites from Sample 2 (Figure 3b) show only a marginal loss in Raman peak intensity even after 8 days. This suggests that degradation slows down tremendously when samples are stored in the absence of light, even though they are exposed to ambient humidity. The slight loss in intensity can be attributed to the laser induced deterioration during Raman measurements.

Flakes from Sample 3 (stored in the absence of humidity and presence of light) show a slight loss in peak intensity. However, a reduction in the lateral dimensions from the edges of the crystallites is observed (Figure 3c). This suggests that solely in the presence of light, degradation originates at the crystal edges rather than the surface. This is in line with previously reported theoretical predictions, which suggests that oxidation at the edges is more

likely to occur than at the basal plane.[29] As such, in the absence of humidity, edge degradation leaves the basal plane largely intact and should not influence the properties of BP other than reduced lateral dimensions as observed in Sample 3.

Sample 4, which was isolated from both humidity and light, does not reveal any considerable loss in peak intensity or a reduction in lateral dimensions (Figure 3d) in 8 days. We further observed that the BP crystallite is predominantly intact even after 16 days (Supporting Information Figure S5). It should be noted that signs of degradation start emerging by day 16, which can be attributed to regular exposure of high intensity Raman laser, which induces photo-oxidation. Based on these set of experimental observations over a number of days on multiple BP crystallites, it can be inferred that photo-oxidation is the dominant degradation phenomenon originating at the edges of the BP crystals. We have also observed that the presence of humidity hyper-activates the photo-oxidation process by facilitating surface deterioration along the basal plane. Humidity on its own does not result in BP degradation against the popular notion. Consequently, it is evident that by protecting the material from light (for instance by simply storing it in an opaque container), BP degradation can be significantly delayed and its lifetime prolonged in ambient environment.

Figure 3. Influence of humidity and light on the A_g^1 Raman mode. Spatial maps of A_g^1 peak intensity acquired on BP crystals (values normalized to Day 1), stored under various environmental conditions: a) ambient environment (+RH+L), b) absence of light (+RH–L), c) absence of humidity (–RH+L), d) absence of humidity and light (–RH–L). Scale bar corresponds to 2 μ m. Extended set of spatial maps can be found in Supporting Information Figure S2.

To further quantify the observations, average peak intensities acquired on multiple crystallites from each of the samples were analysed. Figure 4 presents the trends of the average peak intensities (normalised to the respective Day 1 values) over the course of eight days. It should be noted that this method of analysis represents for the surface deterioration and does not accurately depict the degradation in the case of Sample 1, as it does not account for the severe reduction in lateral dimensions that occurs due to rapid ambient degradation. Nonetheless, all three Raman modes show an average reduction of up to 70% in Sample 1, which is an under estimation, considering the lateral size reduction. In the case of Samples 2 and 3, an average reduction of approximately 20% in 8 days is seen. In Sample 4, the intensity average remains well above all other cases, at an average intensity drop of between 5-10% over 8 days. The marginal loss observed in the case of Sample 4 can be attributed to laser induced degradation

that occurs during the Raman measurements. The error bars in Figure 4 represent a confidence interval of 95%. The average trend observed in multiple BP crystallites coupled with the spatial Raman analysis presented in Figure 3, further strengthens the proposed mechanism against the ambient degradation of BP.

Figure 4. Trend analysis of the Raman peak intensity. The average Raman peak intensity (normalized to Day 1) obtained from the spatial Raman maps of multiple BP crystals, stored under various environmental conditions. Legend: ambient environment (+RH+L), absence of light (+RH-L), absence of humidity (-RH+L), absence of humidity and light (-RH-L). The error bars are at a confidence interval (CI) of 95%.

After ascertaining that humidity is not the main governing factor of BP degradation, we implemented a set of freshly exfoliated BP crystallites for humidity sensing. The sensitivity of BP towards humidity was assessed using a quartz crystal microbalance (QCM), which is a mass-based transducer, commonly used to quantify solid-vapour interactions with the highest precision.[30,31] These measurements were conducted in the absence of light. Figure 5a illustrates the mechanism adopted by a QCM based approach in quantifying vapour adsorption/desorption on the transducer surface. This method utilizes the linear relationship between the change in the natural frequency (Δf) of a quartz crystal and the variation in its mass (Δm), induced by the adsorption/desorption of the exposed vapour:[30]

$$\Delta f = f_0 - f = -\frac{2f_0^2}{A\sqrt{\mu_q\rho_q}}\Delta m \quad (1)$$

where f_0 is the natural frequency, f is resonant frequency after adsorption, A is the active surface area of the QCM electrode, μ_q is the shear modulus ($2.947 \times 10^{11} \text{ g.cm}^{-1}.\text{s}^{-1}$) and ρ_q is the density (2.648 g.cm^{-3}) of the quartz crystal.[30] Based on this technique, the affinity of BP towards humidity was determined.

The QCM transducers with exfoliated BP flakes were subjected to sequential cycles of relative humidity and dry N_2 , and the corresponding shift in resonant frequency was measured. A well accepted method of quantifying the repeatability of each sensor is by first calculating the coefficient of variance for five humidity pulses.[30,31] Figure 5b shows the dynamic response of frequency magnitudes of two QCM transducers: 1. Control gold (Au) transducer 2. Au transducer with mechanically exfoliated BP crystals, subjected to multiple cycles of dry N_2 and 50% RH (at 30 °C). It was found that the control transducer had a repeatability of up to 80% which was lower than the obtained 95% for the transducer containing the BP crystals. Figure 5c shows the obtained normalized (by material mass) frequency response magnitude of the QCM containing BP crystals, towards increasing levels of RH. The response magnitudes of the BP crystals at 12.5 and 90% RH were ~ 2.0 and 82.7 Hz/pg. Such a large frequency shift generated at a scale of picograms demonstrates the substantial affinity of BP towards humidity. The corresponding dynamic response can be seen in Supporting Information Figure S3. Based on the results, QCM sensors with BP can achieve a detection limit as low as 10% RH with a broad dynamic range of 10-90% RH (30 °C). Considering the observed response, a further improved humidity sensing performance can be achieved, through an effective choice of transducer design (such as resistive sensors with hydrophobic electrodes) and operating conditions. The BP crystallites demonstrate very high recovery rates on exposure to dry N_2 (even at 90% RH), which not only highlights their capability as a viable

1 humidity sensing platform, but also re-affirm the previously stated observations that humidity
2 is not the main contributor towards BP deterioration.

3 To assess their selectivity towards humidity, BP flakes were subjected to multiple classes of
4 interferent gas species. Figure 5d shows the response magnitude of the QCM transducers
5 towards various interfering gas species, with and without the presence of 50% RH at 30 °C.
6 The response magnitude of each QCM was normalized to their response toward 50% RH
7 without the presence of any interfering gas species. The results illustrate that BP crystals show
8 better selectivity toward humidity and the introduction of multiple gas species had little
9 influence on this selectivity. It should be noted that the control Au thin-film based QCM
10 produces a false negative humidity level in the presence of ammonia and ethylmercaptan (due
11 to well-known high affinity of gold towards amines and thiols). Given that BP is highly inert
12 towards other gas species, while having a remarkably high affinity/response towards
13 humidity; it has the potential of being employed as a selective and sensitive layer in high
14 precision humidity sensing applications.

Figure 5. Selective humidity sensing capability of BP. a) Illustration of the QCM based response output mechanism in quantifying the humidity adsorption on the BP crystals. b) Normalized (by mass) QCM dynamic response towards multiple cycles of RH (50% at 30 °C) showcasing the repeatable recovery of BP. c) Normalized (by mass) QCM dynamic response of BP crystals, when subjected to increasing levels of RH. d) Percentage sensor response magnitude towards various interferent gases, with and without the presence of humidity. The results highlight the particular selectivity of BP towards humidity.

Conclusion

In summary, it is shown that humidity adsorption on BP does not cause degradation. We have investigated the individual roles of three key environmental factors (temperature, light and humidity) to conclude that humidity merely facilitates photo-oxidation. As further evidence, we demonstrate the recoverable humidity sensing capabilities of BP, with detection levels down to 10% RH, which can be further extended with smarter device designs and BP deposition techniques to achieve a sensitive layer with full coverage. This finding has important implications for designing methodologies to render BP stable in ambient conditions.

1 **Methods**

2 *Sample Fabrication and Characterization:* For all the experiments conducted in this work,
3 few-layered black phosphorus crystals were obtained *via* poly-dimethyl-siloxane (PDMS)
4 assisted micromechanical exfoliation of commercial bulk black phosphorus crystals (Smart
5 Elements). Transmission electron microscopy (TEM) images of exfoliated specimens were
6 acquired using a JEOL. Atomic force microscopy (AFM) was employed to validate the
7 thickness of the optically identified BP crystallites. AFM imaging was conducted on a
8 Dimension Icon AFM in Scan Assist mode. Temperature-dependent micro-Raman
9 spectroscopy was performed on a Renishaw InVia system in a backscattering configuration
10 excited with a visible laser light ($\lambda = 532$ nm). Spectra were collected through a 50 $\times$ objective
11 and recorded with 1800 lines mm⁻¹ grating that provided a spectral resolution of ~ 1 cm⁻¹.
12 The *in situ* heating experiments were conducted on a modified Linkam DSC600 chamber with
13 precise temperature control, at a heating and cooling rate of 5 °C.min⁻¹. Spatial Raman peak
14 intensity mapping was conducted on a Horiba LabRam evolution micro Raman system
15 equipped with 532 nm laser (0.5 μ m lateral resolution, 0.25 s exposure) and a 50 $\times$ objective.
16 *QCM Transducer Fabrication and Characterization :* The quartz crystal microbalance (QCM)
17 transducers were fabricated by employing optically polished AT-cut quartz substrates with a
18 diameter of 7.5 mm and undergoing metal electrode (diameter of 4.5 mm) depositions on each
19 side of the substrate through electronbeam evaporation (Balzers, BAK 600). The two metal
20 electrodes were each made up of a 10 nm Ti adhesion layer under a 150 nm Au layer. This
21 ensured they have QCM quality factors (Qfactors >3,000). The Q factor is an indication of the
22 sensor performance as it represents the stored to dissipated energy ratio. The QCMs tested in
23 this study had Q factors well above 8,000 and their sensitivities were calculated to be
24 4.39 ng.cm⁻².Hz⁻¹ (specific to 10MHz crystals with 4.5 mm electrodes employed in this
25 study).[30,31] These were determined using an Agilent E5100A network analyzer in order to
26 assess their suitability for being employed as a gas sensor. The center frequency changes of

the QCMs were monitored throughout the tests using research quartz crystal microbalance (RQCM, Maxtek) units which have a frequency resolution of ± 0.03 Hz. The mass of material deposited on the QCM transducers was determined using the frequency shift (difference in center frequency before and after deposition) and applying Sauerbrey's equation. The amount of phosphorene deposited on the QCMs was approximately $4,016 \text{ ng.cm}^{-2}$. The QCM response magnitudes were normalized using the mass deposition data in order to obtain a better understanding of the affinity (based on mass) of each material towards humidity.

Humidity Uptake Measurements : The humidity uptake measurements were performed in a custom-built gas chamber, which housed the QCM transducers while maintaining a constant operating temperature (at 30°C) as well as the overall gas flow rate. The QCMs were exposed to a gas stream containing a mixture of dry N_2 gas and a known concentration of humidity (with or without interferent gases) for 5 min. Thereafter, the sensors were allowed to recover by subjecting the transducers to dry N_2 flow for 5 min. In order to assess the selectivity of BP towards humidity, additional interferent gases were introduced with and without the presence of humidity. Throughout the experiments, the total gas flow rate was kept constant at 200 sccm using a multi-channel gas delivery system, employing mass flow controllers (MKS Instruments, Inc. USA). The humidity levels (12.5% to 90.0% relative humidity at 30°C) were generated using a relative humidity generator (V-Gen from InstruQuest).

Acknowledgements

The authors acknowledge support from the Australian Research Council (ARC) with project support through DE150100909 (S.B.) and DP140100170 (M.B.), and equipment funding through LE110100223 and LE150100001. The authors also acknowledge the facilities and technical assistance of the MicroNano Research Facility.

References

1. Novoselov, K. S. *et al.* Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**, 197–200 (2005).
2. Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
3. Balendhran, S. *et al.* Two-dimensional molybdenum trioxide and dichalcogenides. *Adv. Funct. Mater.* **23**, 3952–3970 (2013).
4. Wang, Q. H., Kalantar-zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **7**, 699–712 (2012).
5. Balendhran, S., Walia, S., Nili, H., Sriram, S. & Bhaskaran, M. Elemental Analogues of Graphene: Silicene, Germanene, Stanene, and Phosphorene. *Small* **11**, 640–652 (2015).
6. Liu, H. *et al.* Phosphorene: An unexplored 2D semiconductor with a high hole mobility. *ACS Nano* **8**, 4033–4041 (2014).
7. Li, L. *et al.* Black phosphorus field-effect transistors. *Nat. Nanotechnol.* **9**, 372–377 (2014).
8. Kim, J. *et al.* Observation of tunable band gap and anisotropic Dirac semimetal state in black phosphorus. *Science* **349**, 723–726 (2015).
9. Deng, Y. *et al.* Black Phosphorus–Monolayer MoS₂ van der Waals Heterojunction p–n Diode. *ACS Nano* **8**, 8292–8299 (2014).
10. Qiao, J., Kong, X., Hu, Z.-X., Yang, F. & Ji, W. High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. *Nat. Commun.* **5**, 4475 (2014).
11. Xia, F., Wang, H. & Jia, Y. Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics. *Nat. Commun.* **5**, 5458 (2014).
12. Wang, X. *et al.* Highly anisotropic and robust excitons in monolayer black phosphorus. *Nat. Nanotechnol.* **10**, 517–521 (2015).

- 1 13. Castellanos-Gomez, A. *et al.* Isolation and characterization of few-layer black
2 phosphorus. *2D Mater.* **1**, 025001 (2014).
- 3 14. Favron, A. *et al.* Photooxidation and quantum confinement effects in exfoliated black
4 phosphorus. *Nat. Mater.* **14**, 826–832 (2015).
- 5 15. Avsar, A. *et al.* Air-stable transport in graphene-contacted, fully encapsulated ultrathin
6 black phosphorus-based field-effect transistors. *ACS Nano* **9**, 4138–4145 (2015).
- 7 16. Doganov, R. A. *et al.* Transport properties of pristine few-layer black phosphorus by
8 van der Waals passivation in an inert atmosphere. *Nat. Commun.* **6**, 6647 (2015).
- 9 17. Liu, H., Neal, A. T., Si, M., Du, Y. & Ye, P. D. The effect of dielectric capping on few-
10 layer phosphorene transistors: Tuning the schottky barrier heights. *IEEE Electron*
11 *Device Lett.* **35**, 795–797 (2014).
- 12 18. Ryder, C. R. *et al.* Covalent functionalization and passivation of exfoliated black
13 phosphorus via aryl diazonium chemistry. *Nat. Chem.* **8**, 597–602 (2016).
- 14 19. Chen, X. *et al.* High-quality sandwiched black phosphorus heterostructure and its
15 quantum oscillations. *Nat. Commun.* **6**, 7315 (2015).
- 16 20. Erande, M. B., Pawar, M. S., Late, D. J., Humidity sensing and photodetection
17 behavior of electrochemically exfoliated atomically thin-layered black phosphorus
18 nanosheets. *ACS Appl. Mater. Interf.* **2016**, 8, 11548– 11556.
- 19 21. Late, D. J. *et al.* Liquid exfoliation of black phosphorus nanosheets and its application
20 as humidity sensor. *Micropor. Mesopor Mater.* **2016**, 225, 494–503.
- 21 22 Yasaei, P. *et al.* Stable and selective humidity sensing using stacked black phosphorus
22 flakes. *ACS Nano* **2015**, 9, 9898–9905.
- 23 23. Du, Y., Ouyang, C., Shi, S. & Lei, M. Ab initio studies on atomic and electronic
24 structures of black phosphorus. *J. Appl. Phys.* **107**, 093718 (2010).

24. Appalakondaiah, S., Vaitheeswaran, G., Lebègue, S., Christensen, N. E. & Svane, A. Effect of van der Waals interactions on the structural and elastic properties of black phosphorus. *Phys. Rev. B* **86**, 035105 (2012).
25. Liu, X., Wood, J. D., Chen, K.-S., Cho, E. & Hersam, M. C. In situ thermal decomposition of exfoliated two-dimensional black phosphorus. *J. Phys. Chem. Lett.* **6**, 773–778 (2015).
26. Luo, Z. *et al.* Anisotropic in-plane thermal conductivity observed in few-layer black phosphorus. *Nat. Commun.* **6**, 9572 (2015).
27. Zhang, S. *et al.* Extraordinary photoluminescence and strong temperature/angle-dependent Raman responses in few-layer phosphorene. *ACS Nano* **8**, 9590–9596 (2014).
28. Joshua, O. I., Gary, A. S., Herre, S. J. v. d. Z. & Andres, C.-G. Environmental instability of few-layer black phosphorus. *2D Mater.* **2**, 011002 (2015).
29. Hanlon, D. *et al.* Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics. *Nat. Commun.* **6**, 9563 (2015).
30. Sabri, Y. M. *et al.* Gold nanospikes based microsensor as a highly accurate mercury emission monitoring system. *Sci. Rep.* **4**, 6741 (2014).
31. Sabri, Y. M., Kandjani, A. E., Ippolito, S. J. & Bhargava, S. K. Ordered monolayer gold nano-urchin structures and their size induced control for high gas sensing performance. *Sci. Rep.* **6**, 24625 (2016).

Supporting Information

Defining the role of humidity in the ambient degradation of few-layer black phosphorus

Sumeet Walia,* Ylias Sabri, Taimur Ahmed, Matthew R. Field, Rajesh Ramanathan, Aram Arash, Suresh K. Bhargava, Sharath Sriram, Madhu Bhaskaran, Vipul Bansal,* and Sivacarendran Balendhran*

Figure S1. Temperature dependent Raman spectra of BP crystallites. Raman spectra of few-layer BP crystals with varying thicknesses (t), under ambient conditions. The results indicate a recovering thermal expansion regardless of crystal thickness.

Figure S2. Topographic AFM images of an exfoliated BP crystal, before and after heating at 100 °C for 5 mins, in ambient environment. The crystal surface roughness before and after heat treatment was measured to be ~ 0.34 nm, which suggests that there is no significant morphological changes at the material surface.

Figure S2 shows an AFM image of a BP crystallite before and after heating. The heating process was conducted in a dark environment to eliminate the possibility of photo-oxidation induced degradation. The BP flake was heated in sequential steps of 5 °C/min, whereby the temperature was increased to a peak value of 100 °C. The sample was subsequently allowed to cool down to room temperature. The AFM image was obtained at room temperature following the heat treatment step. It can be seen from Figure S2 that the flake does not show any morphological signs of degradation which typically include the formation of bubble like features on the surface.

Figure S3. AFM images of representative BP flakes identified using optical contrast, along with their corresponding thickness profiles. This is to illustrate the typical thicknesses of the BP flakes used for spatial Raman mapping.

Figure S4. Extended set of spatial Raman maps. Values normalized to Day 1 of the respective BP crystals, stored under various environmental conditions: a) ambient environment (+RH+L), b) absence of light (+RH-L), c) absence of humidity (-RH+L), d) absence of humidity and light (-RH-L). Scale bar corresponds to 2 μm.

Figure S5. Spatial Raman maps of the A_g^1 peak intensity obtained over a period of 16 days. Signs of degradation start to emerge by day 16 mainly due to the Raman laser induced photo-oxidation. The scale bar denotes 2 μm .

Figure S6. Dynamic response of BP towards humidity. Real time frequency response of BP (normalized by mass) towards increasing levels of relative humidity. Results show a recovery rate of up to 95% (except for an aberration seen at 60% RH).