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Degradation of Black Phosphorus: The Role of Oxygen and Water
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Abstract

Black phosphorus has attracted significant attention due to its exceptional electronic and optoelectronic properties, but its poor stability under ambient conditions limits its use in applications. Despite several previous studies, the degradation mechanism and especially the role of the different reactive species present in air (oxygen, water vapor) still remains unclear. Here, we systematically studied the degradation process of black phosphorus in different environments (air; water with dissolved O2; and deaerated water) by optical microscopy, analytical transmission electron microscopy, field-effect transistor (FET) device characteristics, and electrochemical characterization. Whereas the materials and devices exposed to air and oxygen-saturated water showed signs of rapid degradation, immersion in deaerated water maintained relatively stable morphologies and device characteristics. This enabled the use of water as a solution top gate in FETs, which substantially enhanced the charge carrier mobility from 230 cm2/V·s (back-gated in air) to 1260 cm2/V·s. Our results, which show that oxygen plays the dominant role in the chemical conversion of black phosphorus and that the material is stable in oxygen-free water pave the way for its use in aqueous solutions (e.g., in photo-catalysis or electrochemistry) and can guide future efforts to identify suitable encapsulation strategies for black phosphorus for potential applications in air.

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Black phosphorus (BP) stands out among the other known elemental layered materials, such as graphene or silicene,\(^1\),\(^2\) due to several of its unique properties. In contrast to the semimetallic graphene, black phosphorus is a semiconductor with a sizable bandgap.\(^3\),\(^4\) Compared to silicene, which is unstable in air,\(^5\) black phosphorus has lower reactivity and can be handled under ambient conditions, at least for limited time periods.\(^6\) By simple mechanical exfoliation, black phosphorus can be exfoliated down to monolayer thickness\(^7\) due a weak interlayer interaction, similar to graphite, MoS\(_2\), and other layered crystals.\(^8\),\(^9\) In contrast to layered metal dichalcogenides, many of which are n-type indirect gap semiconductors at finite thickness and switch to a direct bandgap only in monolayer form,\(^10\)\textsuperscript{-}\textsuperscript{12} black phosphorus shows p-type doping and has a direct bandgap for all thicknesses,\(^11\) which varies from 0.3 eV in the bulk to 2 eV for a single layer.\(^3\),\(^13\) Due to its unique crystal structure, black phosphorus shows highly anisotropic electric transport\(^14\),\(^15\) and optical properties.\(^16\),\(^17\) Exfoliated black phosphorus flakes show carrier mobilities of ~100 – 1000 cm\(^2\)/V\cdot s and current modulation of ~10\(^5\), which makes this material suitable for digital logic as well as optoelectronic devices.\(^16\),\(^18\)\textsuperscript{-}\textsuperscript{21}\) In addition, black phosphorus based heterojunction devices are showing promise for electronics and optoelectronics applications due to the high hole mobility and thickness-dependent direct band gap of this material.\(^20\),\(^22\),\(^23\)

Though the properties of black phosphorus are promising, degradation under ambient conditions appears to be a serious issue. Recently, a number of studies have addressed this limited stability. Castellanos-Gomez \textit{et al.} studied the environmental stability of black phosphorus flakes, and they concluded that their surface is hydrophilic and long-term exposure to air and moisture can completely etch away the material.\(^6\) In later work the same
group found that thinner flakes absorb water faster than thicker ones, and that the flakes can be etched layer-by-layer under ambient conditions. Boron nitride used for top-side encapsulation was shown to be insufficient for passivating black phosphorus FET devices, presumably due to water and oxygen entering along interfaces and leading to eventual breakdown. Recent DFT calculations by Ziletti et al. suggested that oxygen could be responsible for black phosphorus’ degradation and that dangling oxygen atoms could increase the hydrophilicity of its surface. However, the DFT results on the hydrophilicity of black phosphorus are contradictory: Du et al. and Castellanos-Gomez et al. suggested that the surface of black phosphorus is intrinsically hydrophilic, while Ziletti et al. suggested that the surface becomes hydrophilic after oxidation. Many observations by AFM and optical imaging found droplet-like structures on surfaces exposed to air. These structures are believed to be water, but no direct evidence has been given. Recently, Favron et al. suggested that three major environmental parameters are simultaneously required for the degradation of black phosphorus: water, oxygen and visible light, but they did not point out the specific role of water. Yasaei et al. reported the performance of humidity sensors fabricated from black phosphorus nanoflakes, showing that the sensors could be stable for more than 3 months. Characterizing the degradation of their devices, they found that it proceeds fastest in humid air, in agreement with several previous reports. Although these results point to a consensus in the literature, the degradation mechanism of black phosphorus in ambient conditions is far from clear and more experiments are needed to uncover the chemistry involved in the breakdown of the material so that suitable encapsulation strategies for devices can be identified. The interaction of black phosphorus with water in particular is important in
situations beyond (opto-) electronics. The electrochemical properties of black phosphorus, for example, remain largely unexplored, primarily due to the assumption that the material would not be stable in aqueous solution. If that assumption proved to be wrong, new applications such as electro- or photocatalysis could open up for black phosphorus.

To address the need for a deeper understanding of the interaction of black phosphorus with water, we carried out a systematic experimental study in which exfoliated black phosphorus flakes were exposed to different conditions, including ambient air and de-ionized (DI) water.

Figure 1 – Optical and AFM images of an exfoliated black phosphorus flake supported by SiO$_2$/Si. a. Optical image of the freshly exfoliated, pristine black phosphorus flake. b. AFM image within the flake, obtained in the area outlined by a dashed square in a. c. AFM image of the surface of the monolayer black phosphorus flake (ML$^{\text{BP}}$, marked by a dashed circle in a). d. Optical image after exposing the sample to air for 1 day. Note the buildup of a chain of islands/droplets along the flake edge (e.g., dashed line), and the disappearance of an entire monolayer black phosphorus segment (marked ML$^{\text{BP}}$ in a, and outlined with a dashed circle). e. AFM image within the flake (dashed square). f. AFM image at the former location of the monolayer black phosphorus flake, showing increased corrugation in the form of large islands/droplets.

To independently verify the environmental stability of black phosphorus, we prepared flakes of different thickness (bulk, few-layer, and monolayer) on SiO$_2$/Si supports by using the
modified exfoliation method, and followed their evolution in air by optical microscopy and tapping-mode atomic force microscopy (AFM). Figure 1 shows optical and AFM images of a pristine black phosphorus flake, and of the same flake after exposure to air for 1 day. Within 1 hour after exfoliation, the surface of the flake appeared optically flat and the surrounding SiO$_2$ was featureless in optical microscopy (Figure 1a). At this stage, AFM showed arrays of small clusters decorating the black phosphorus surface (Figure 1b), which were previously suggested to be water droplets. The same droplet morphology was found on the surface of thick, bulk-like (Figure 1b) and monolayer flakes (Figure 1c). After ambient exposure for 1 day, several changes are observed. Optical microscopy detects relatively minor changes to thick black phosphorus flakes. However, their outline now appears more rounded, and the surrounding SiO$_2$ support shows large, drop-like features in the vicinity of all flakes (Figure 1d). The surface of bulk-like flakes is no longer flat, but now appears rough. The well-defined small droplets seen shortly after exfoliation are no longer clearly observable (Figure 1e), but seem to have coalesced to a thin film after the small clusters grew larger. The thinnest portions (e.g., the monolayer segment, ML$^\text{BP}$ marked by a circle in Figure 1a) are completely decomposed and only large drops remain in their place on the substrate (Figure 1f). These findings are consistent with previous reports of the morphology change of black phosphorus in air.

Focusing on the specific role of water in the chemical reactivity of black phosphorus, we immersed exfoliated flakes supported on SiO$_2$ for different time periods in DI water, ultimately followed by exposure to air (Figure 2). Figure 2a shows an optical micrograph of a freshly exfoliated black phosphorus flake. Subsequently, the sample was immersed in DI
water. As shown in Figure 2b, after one week in DI water the morphology of the flake did not show any obvious changes, and no droplets (as seen after 1 hour air exposure, Figure 1d) were observed in its vicinity. After 2 weeks in water, the optical contrast of the flake had evidently changed (Figure 2c), in a way that suggests that the thickness was modified across the entire flake, but still no droplets were found in the vicinity. The thickness change after 2 weeks in DI water implies a measurable etching of the black phosphorus flake under these conditions. As we will show below, oxygen dissolved in water is responsible for this etching. The lack of observable features in the vicinity of the flake suggests that the drop-like features observed after air exposure are soluble in or react with water and have been eliminated during immersion in water, thus supporting the assumption of previous reports that these drops may consist of aqueous decomposition products of black phosphorus. On the other hand, this also suggests that the surface of black phosphorus may be not intrinsically hydrophilic, as reported.

Figure 2 – Morphology change of an exfoliated black phosphorus flake on SiO$_2$/Si after exposure to water and air. a. Optical images of a freshly exfoliated black phosphorus flake. b. Same flake after being submerged in DI water for 1 week. c. Same flake after a total of 2 weeks exposure to water. d. Image after removal of the flake from DI water and exposure to air for 1 week, showing the complete dissolution of the flake and droplet-like residues within its footprint. e. Same sample after annealing at 120 °C for 2 hours in ultrahigh vacuum (10$^{-9}$ Torr). f. After additional annealing at 250 °C for 2 hours in ultrahigh vacuum.
by Du et al. and Castellanos-Gomez et al., because no droplets were observed even after the black phosphorus was taken out of DI water. After the prolonged immersion in water, the same sample was exposed to air for 1 week. As seen in Figure 2d, the flake decomposed completely, leaving behind a number of drop-shaped residues of different size within its previous outline. This indicates that the decomposition in air is much faster than in DI water. The sample was subsequently loaded into ultrahigh vacuum (UHV, 10\textsuperscript{-9} Torr) for several hours, but the droplet-like morphology did not show any change. The sample was then annealed in UHV at 120 °C for 2 hours (Figure 2e), which led to a slight decrease in the density of droplets compared to that in Figure 2d, but the larger droplets still remained. Only after annealing at a higher temperature (250 °C for 2 hours, Figure 2f), also the large droplets were replaced by drying patterns within their original footprint. These observations suggest that the droplet-like objects do not consist of water, but are accumulations of species with lower vapor pressure, such as phosphorus oxides (P\textsubscript{x}O\textsubscript{y}); thus the degradation mechanism may not be as previously reported\textsuperscript{6,28}. Phosphorus trioxide (P\textsubscript{2}O\textsubscript{3}) and pentoxide (P\textsubscript{2}O\textsubscript{5}) are both solids near room temperature (P\textsubscript{2}O\textsubscript{5} sublimes; P\textsubscript{2}O\textsubscript{3} melts at 23.8°C). P\textsubscript{2}O\textsubscript{3} has high vapor pressure (7.5 Torr at 47°C; 75 Torr at 100°C), whereas P\textsubscript{2}O\textsubscript{5} is far less volatile (vapor pressure 7.5\cdot10\textsuperscript{-3} Torr at 285°C).\textsuperscript{33} Hence, our experiments involving vacuum annealing of air-exposed black phosphorus are consistent with a reaction of black phosphorus with oxygen in air to form a phosphorus oxide with composition close to P\textsubscript{2}O\textsubscript{5}.

In order to better understand the decomposition pathway, we compared the degradation process under well-defined conditions: in air and DI water (Figure 3 a,b and Figure 3 c,d, respectively); and in oxygen-depleted (i.e., deaerated) and oxygen-enriched DI water (Figure
4 b,c and Figure 4 d,e, respectively).

The first set of images (Figure 3 a, c; Figure 4 b, d) are optical images of pristine BP flakes, captured within 5 min after exfoliation onto a SiO$_2$/Si substrate. The second set of images shows the same sample areas after 2 days of exposure to the different environments. After 2 days of exposure to air, thin flakes (Figure 3b, arrows) were completely etched away. 2 days of immersion in DI water completely removed monolayer flakes, whereas bilayer areas were transformed into monolayer (Figure 3d). The comparison with the sample exposed to air shows that decomposition of black phosphorus is substantially slower in DI water, but some residual reactivity remained. It is well know that molecular oxygen can be dissolved in water. At 25 °C, the equilibrium solubility of O$_2$ in water is 8.27 mg/L (1.26 mM), but by deaeration the concentration of O$_2$ can be reduced by 3-4 orders of magnitude (to $\sim$10$^{-7}$ M). To control the oxygen concentration in water, we used a setup in which different gases could be controllably bubbled through the DI water reservoir in which the black phosphorus sample

![Image](image_url)

**Figure 3 – Effects of air exposure and water immersion on exfoliated black phosphorus flakes.**

- **a.** Optical micrograph of freshly exfoliated black phosphorus flakes supported on SiO$_2$/Si.
- **b.** Same sample region after exposure to air for 2 days.
- **c.** Freshly exfoliated black phosphorus flakes.
- **d.** Same sample region after immersion in DI water for 2 days.
was held (Figure 4a). To lower the concentration of dissolved O$_2$, nitrogen gas was bubbled continuously through the DI water. A sample containing flakes with both monolayer and bilayer black phosphorus was exposed to these conditions for 2 days, after which the flake remained almost completely unchanged (Figure 4c). Notably, the monolayer and bilayer areas are still observable, *i.e.*, have not been affected as in the case of neat DI water with a higher (equilibrium) concentration of dissolved O$_2$. Some groups claimed that thinner flakes show accelerated decomposition,$^{24, 28}$ yet under oxygen-depleted conditions we did not see any change down to monolayer thickness. This suggests that black phosphorus is unable to activate and react with H$_2$O itself and that the primary reaction pathway requires O$_2$, either present in air or dissolved in water. To demonstrate the key role of O$_2$, we performed a control experiment in which the water was enriched in dissolved oxygen by bubbling O$_2$.

**Figure 4** – Effects of immersion in oxygen-depleted and oxygen-enriched DI water on exfoliated black phosphorus flakes. **a.** Schematic diagram of the setup used to remove dissolved O$_2$ from DI water (by bubbling N$_2$) and enriching water with O$_2$ (by bubbling O$_2$). **b.** Optical micrograph of freshly exfoliated black phosphorus flakes supported on SiO$_2$/Si. Based on their optical contrast, the deep blue segments are identified as monolayer and bilayer black phosphorus. **c.** Same sample region after immersion in oxygen-depleted water (N$_2$ bubbling) for 2 days. **d.** Freshly exfoliated black phosphorus flakes. **e.** Same sample region after immersion in oxygen-enriched DI water (O$_2$ bubbling) for 2 days.
instead of N$_2$. As can be seen by comparing Figures 4d and e, even few-layer flakes are completely etched away under these conditions.

To obtain nanoscale structural and chemical information, we performed analytical (scanning) transmission electron microscopy ((S)TEM) using a JEOL 2100F TEM operated at 200 kV. Multilayer black phosphorus flakes were exfoliated and immediately transferred onto a copper grid for TEM observation. Figure 5a shows a high-angle annular dark-field STEM (HAADF-STEM) image of the pristine (freshly exfoliated) black phosphorus flakes on amorphous carbon support. Uniform contrast within the flakes indicates a relatively

**Figure 5 – (S)TEM and EELS characterization of a multilayer black phosphorus flake before and after air exposure.** a. HAADF-STEM image at 200 kV of a flake immediately after exfoliation and transfer onto a TEM grid. b. High-resolution plan-view TEM image of a black phosphorus flake. c. Cross-sectional TEM image of a folded section of the flake. The basal plane is along the [110] axis. The interlayer spacing is ~5.4 Å. d. Enlarged STEM image within the rectangular area marked in a, and corresponding 2D STEM-EELS map of the black phosphorus flake immediately after exfoliation. e. STEM image and 2D STEM-EELS map after exposure to air for 1 day. P is shown in green, and O in red. f. Representative EELS spectra of pristine and oxidized (1 day air exposure) black phosphorus samples.
constant thickness. High-resolution TEM (HRTEM) imaging reveals the atomic structure of a black phosphorus flake in plan-view (along the [110] axis, Figure 5b) and cross-sectional directions (Figure 5c), illustrating that the flake is single-crystalline with interlayer spacing of ~5.4 Å. In order to monitor structural and chemical changes due to ambient exposure, we performed electron energy loss spectroscopy in STEM (STEM-EELS) within the same region (red rectangle in Figure 5a) before and after exposing the sample to air for 1 day. Comparing the HAADF-STEM images in Figure 5d (pristine) and Figure 5e (after 1 day in air), we find darker contrast near the edge of sample after ambient exposure, implying that the thickness was reduced.

The EELS spectrum taken from this dark region is compared to that of a pristine sample in Figure 5f. The characteristic energy-loss edges, the L$_{2,3}$-edge of P and the K-edge of O, can be used to identify the chemical valance states. Our data clearly show that the phosphorus L$_{2,3}$-edge shifts from 130 eV to 136 eV and the oxygen K-edge at 532 eV appears after exposure to air, both indicating the oxidation of P to form P$_x$O$_y$. The elemental distribution of P and O in the observed region can be revealed by false-color two-dimensional (2D) STEM-EELS maps (Figure 5d,e). Combining the STEM and EELS results, we can correlate the morphology change (thickness reduction) with the local chemical change (oxidation), and further confirm that air exposure causes oxidation accompanied by thickness reduction.

A similar comparative characterization was performed on a similar black phosphorus flake before and after immersion in water for 1 day (Figure 6). HAADF-STEM images obtained before (Figure 6a) and after (Figure 6b) exposure to H$_2$O do not show any obvious changes in morphology, such as the thinning observed after exposure to air. EELS line-scans
were measured at the same sample position before and after exposure to water (indicated by red and blue arrows, respectively, in Figures 6a, b). The corresponding energy-loss profiles are displayed in Figure 6c. The spectra do not show any significant chemical shift, but show phosphorus remaining mostly in elemental (zero-valent, P$^0$) state. There is a small, but detectable increase in intensity at $\sim$138 eV, indicating the formation of traces of P$_x$O$_y$ likely by reaction with oxygen dissolved in the DI water (which was not deaerated by bubbling with N$_2$) and during the sample transfer and loading process. Comparing the results after air and water exposure, we find ratios of P L$_{2,3}$-edge intensities of P$^0$:P$_x$O$_y$ of 0.24 (1 day in air) and 2.3 (1 day in DI water). The large difference in intensity ratios indicates that water does not play an effective role in the oxidation of black phosphorus, but that oxygen-free water instead protects it from decomposition. This strongly suggests that crystalline black phosphorus is unable to oxidize via dissociation of water, e.g., via reactions such as

$$x \text{P} + y \text{H}_2\text{O} \rightarrow \text{P}_x\text{O}_y + n \text{H}_2 \quad \text{or}$$

$$\text{P} + 4 \text{H}_2\text{O} \rightarrow (\text{PO}_4^{3-})_{\text{aq}} + 4 \text{H}_2, \text{etc.,}$$

but instead is oxidized exclusively by reaction with O$_2$, either present in air or dissolved in water. This means even though bulk red phosphorus and white phosphorus compounds can react with water to form phosphine,\textsuperscript{34-37} crystalline black phosphorus is evidently more stable against reaction with water than these other phosphorus allotropes.
Figure 6 – STEM-EELS on black phosphorus before and after water exposure. a. HAADF-STEM image of a freshly exfoliated black phosphorus flake. b. Same flake after submersion in DI water for 1 day. c. EELS line scan profiles along the arrows in a and b, showing the phosphorus L-edge without any detectable oxidization.

To determine the effects of air and water on black phosphorus devices, we fabricated field-effect-transistors (FETs) from exfoliated black phosphorus flakes (Figure 7). Figure 7a shows the overall configuration of our devices (channel thickness: ~15 nm), which were fabricated on SiO$_2$/Si substrates with Ti (5 nm)/Au (50 nm) as source and drain contact electrodes. Figure 7b,c summarize measurements on a representative device, performed using three-terminal DC field-effect transistor characteristics with back gating via the SiO$_2$ dielectric at room temperature in ambient air. At low source-drain voltage ($V_{SD}$ from 0 - 0.5 V), the current-voltage ($I_{SD}$ - $V_{SD}$) characteristics are linear over the entire range of back-gate voltages from -30 to +30 V, which indicates ideal ohmic contacts between the Ti/Au electrodes and the black phosphorus channel. As the back-gate voltage $V_G$ is changed from -30 V to +30 V, the drain current, $I_{SD}$, first decreases and then increases again, confirming the ambipolar transfer characteristics shown in previous reports.$^{19}$ This ambipolar behavior is also clearly seen in Figure 7c, which shows $I_{SD}$-$V_G$ characteristics for $V_G$ from -40 V to +40
V, with source-drain voltage varying from 0.5 to 2.5 V in steps of 0.5 V. The field effect mobility extracted from these characteristics is \( \sim 230 \text{ cm}^2/\text{V} \cdot \text{s} \) for holes and \( \sim 30 \text{ cm}^2/\text{V} \cdot \text{s} \) for electrons, respectively, consistent with mobility values observed previously.\(^1\) We then tested the stability of the device in air. The results are summarized by plotting values of \( I_{SD} \) at constant conditions \( (V_{SD} = 200 \text{ mV}; V_G = +20 \text{ V}) \) as a function of air exposure time (Figure 7d). The conductance of the device initially increases, as shown by an increase of \( I_{SD} \) from 14 \( \mu \text{A} \) to 17 \( \mu \text{A} \) in the first 5 hours. A saturation of \( I_{SD} \) is followed by a continuous decrease to \( \sim 4 \mu \text{A} \) over the next 60 hours. The initial rise in conductance may be explained by an effect of current annealing,\(^3\) which could lower the contact resistance between the black phosphorus channel and the source- and drain metal electrodes. After long time exposure to air, our results discussed previously suggest that the black phosphorus flake becomes oxidized, which we see here as a decrease in the channel conductance. This effect of degradation of our black phosphorus FET device is similar to that reported previously for unencapsulated devices, which also showed an initial increase in \( I_{SD} \) followed by a decrease of the channel current, ultimately leading to the complete breakdown of the device after \( \sim 56 \) hours in air.\(^3\)

Previous experiments on MoS\(_2\) and SnS\(_2\) transistors have shown that top gating by high-k dielectrics, such as HfO\(_2\), DI-H\(_2\)O and others can effectively screen scattering centers, and thus lead to increased carrier mobility while maintaining high on-off ratios.\(^3\) Within the present study, the use of DI water as an electrolytic top gate can serve two purposes: i) identification if screening by a high-k dielectric (here H\(_2\)O, with \( \varepsilon \sim 80 \varepsilon_0 \)) can lead to
increased carrier mobilities, as in layered metal dichalcogenides; and ii) exploration of the electrical behavior of black phosphorus FETs in contact with water. For these experiments, we first fabricated conventional (back-gated) FET devices on 300 nm SiO$_2$/Si substrates, and then patterned PMMA windows using electron beam lithography. The latter provide a defined contact area between the DI water gate and the device channel, while preventing its contact with the metallic source- and drain electrodes. A schematic of the device layout and an optical micrograph of an actual device are shown in Figure 8a. Figure 8b compares $I_{SD}$-$V_{SD}$ characteristics before and after introduction of the water drop used for top gating; the data were measured for zero back-gate and top-gate voltages. Bringing the device channel in contact with DI water substantially increased the conductance. The drain current, $I_{SD}$, at $V_{SD} = 0.2$ V, for instance, increased from 9 $\mu$A (dry) to 41 $\mu$A after applying a drop of DI water (Figure 8b). This implies that even for zero top-gate voltage the DI water either induced a
doping of additional charge carriers in the black phosphorus channel or resulted in a reduced

impurity scattering because of screening due to the altered dielectric environment. Indeed, by analyzing the transfer curves with DI water top gate we find dramatic mobility enhancements to $\sim 1260 \text{ cm}^2/\text{V} \cdot \text{s}$ in solution-gated black phosphorus devices using a DI water drop as gate dielectric. This finding indicates that the conductance increase upon surrounding of the device channel by water is primarily due to an increased charge carrier mobility due to effective dielectric screening.

The stability of the device in contact with water was monitored initially over a period of 1 hour, as shown in Figure 8c. The $I_{SD}-V_{SD}$ curves were linear and symmetric for all times,
and even though the conductance decreased minimally over 1 hour the performance of the device remained nearly unchanged. This result based on field-effect device characteristics confirms our previous conclusions from exposure to different ambients, namely that black phosphorus shows minimal degradation when in contact with DI water. Device measurements also confirm the crucial importance of oxygen in the degradation chemistry. Fig. 8d shows a comparison of the evolution of $I_{SD}$ with time for devices kept in water with equilibrium oxygen concentration at room temperature, compared with storage in water that was maintained in a deaerated state by bubbling $N_2$ gas. Whereas $I_{SD}$ for the device held in water with dissolved $O_2$ dropped to near-zero over the course of ~2 hours, the device held in deaerated water showed an initial drop in $I_{SD}$ to about 60% of its original value within ~20 hours, but then maintained a stable conductance with negligible further decrease in $I_{SD}$ for the entire duration of the experiment (~100 hours). Strikingly, the degradation in $O_2$ containing water was even faster than in air. From the absence of significant changes in deaerated water, we conclude that the degradation of black phosphorus is dependent on its exposure to oxygen ($i.e.$, the reaction of $P \rightarrow P_xO_y$). However, in our experiments with oxygen-containing solutions, water appears to play an important secondary role: it enables the subsequent reaction of $P_xO_y$ to the final products, $e.g.$, (PO$_4^{3-}$) ions that dissolve into the solution and form phosphoric acid (H$_3$PO$_4$). This process ensures the removal of $P_xO_y$ and continued exposure of fresh $P^0$ at the surface and in this way contributes to fast overall reaction rates, hence the faster degradation in oxygen-containing water than in air.

To obtain further confirmation of the proposed reaction sequence of the degradation of black phosphorus, we performed electrochemical experiments in which redox reactions were
driven by electrochemical bias. Representative cyclic voltammograms (CVs) of a BP electrode measured in oxygen saturated and deaerated 0.1 M HClO₄ solutions are compared in Fig. 9. A broad oxidation peak at $\sim +0.4$ V is observed at similar position and intensity in both cases, i.e., it obviously does not depend on the concentration of dissolved oxygen in the electrolyte. This peak corresponds to the electrochemical oxidation of elemental phosphorus ($P^0$) to a higher oxidation state.

This suggests that a $P_2O_y$ film is formed on the surface of the black phosphorus in this potential range. At more positive potentials (higher than +0.5 V), the phosphorus is further oxidizing to $P^{5+}$, forming $(PO_4^{3-})$ ions that dissolve into the solution and form the end product, phosphoric acid ($H_3PO_4$). These observations are consistent with our EELS results, as well as recently reported results by Wang et al. The oxidation peak at +0.4 V is not observed in CV curves measured in deaerated solution (shown in blue in Fig. 9), in which the reverse potential sweep is stopped before reaching the threshold for the hydrogen evolution reaction.

Figure 9 – Cyclic voltammograms (CVs) measured on a black phosphorus working electrode in 0.1M perchloric acid (HClO₄) solution (Ag/AgCl reference electrode). Comparison of CVs obtained in oxygen saturated (red curve) and $N_2$ deaerated solutions (black, blue curves). In the blue curve, the potential, $V$, was restricted to small negative potentials below the threshold for the hydrogen evolution reaction. Scan rate: 100 mV/s. Area of the black phosphorus sample: 50 mm².
(HER, -0.9 V). This indicates that hydrogen gas generated at potentials more negative than -1.0 V chemically reduces the P$_x$O$_y$ on the electrode surface to elemental phosphorus.\textsuperscript{41} Thus, when the potential is swept in the anodic direction, the bare phosphorus surface (not covered with an oxide) is oxidized, and the peak at +0.4 V is observed. Finally, we also observe a cathodic peak at -0.2 V, which appears only in the CV curve measured in oxygen-saturated solution. We attribute this peak to the oxygen reduction reaction (ORR) taking place on the black phosphorus electrode surface in this potential range.

In summary, the degradation of black phosphorus under different conditions was systematically characterized structurally and spectroscopically. By comparing exposures to air, water with dissolved oxygen, and properly deaerated water, we find that the degradation of black phosphorus in ambient requires to the contact with oxygen, and that water does not play a primary role in the reaction, in contrast to previous conclusions. However, black phosphorus devices immersed in oxygen-saturated water degrade faster than those exposed to air, which suggests that water (or humidity) plays an important secondary role in removing the P$_x$O$_y$ from the surface and exposing P$^0$ for continued reaction. Exposure to water alone, however, does not decompose black phosphorus, as is shown by much slower degradation rates in deaerated water compared to the process in air. Our findings have implications for the identification of suitable encapsulation strategies for black phosphorus, e.g., in device applications, by suggesting that the most important role of an encapsulation material is to prevent the contact of black phosphorus with oxygen, either directly or via diffusion.

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