Supporting Information

Fundamental Insights into the Degradation and Stabilization of Thin Layer Black Phosphorus

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Experimental Information

Materials and exfoliation process:

Throughout all experiments, BP with purity higher than 99.999% (Smart Elements) was used. BP nanosheets were produced by mechanical exfoliation with a commercially available Scotch Tape (3M). Afterwards, the FL-BP flakes were transferred onto Si/SiO$_2$ substrates (300 nm oxide layer). The exfoliation was performed in an argon filled LABmasterpro sp glove box (MBraun) equipped with a gas purifier and solvent vapor removal unit (oxygen and water content lower than 0.1 ppm).

Solvent purification:

Anhydrous, 99,9% purity solvents (THF, NMP and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF$_4$)) were purchased from Sigma-Aldrich. The BMIM-BF$_4$ was degassed under vacuum during 3 days prior to the experiments. THF and NMP were first dried over molecular sieve (3 Å) for at least 3 days to remove dissolved water. The water content was determined by using the “Karl Fischer” method, obtaining values lower than 5 ppm. Additionally, both solvents were degassed by iterative pump freezing (a minimum of 7 cycles) in liquid nitrogen to remove oxygen, before introducing them into the glove box.

Characterization:

Immediately after the removal from the inert atmosphere, images of FL-BP flakes were recorded under an optical microscope (Zeiss Axio Imager M1m), using different objectives enabling their re-localization in Raman and AFM measurements.

Raman spectra were acquired on a LabRam HR Evolution confocal Raman microscope (Horiba) equipped with an automated XYZ table using 0.80 NA objectives. All measurements were conducted using an excitation wavelength of 532 nm, with an acquisition time of 2 s and a grating of 1800 grooves/mm. To minimize the photo-induced laser oxidation of the samples, the laser intensity was kept at 5 % (0.88 mW). For the wavelength-dependent experiments, laser excitations of 457 nm, 473 nm, 532 nm, and 633 nm were used. The step sizes in the Raman mappings were in the 0.2–1 µm range depending on the experiments. Data processing was performed using Lab Spec 5 as evaluation software. When extracting mean intensities of individual BP Raman modes, it is
important to keep each spectral range constant, e.g. from 355–370 cm\(^{-1}\) and from 460–475 cm\(^{-1}\) because otherwise the resulting value of the \(A^1_g/A^2_g\)-ratio can be slightly influenced.

 AFM tapping mode images were obtained using a Solver Pro scanning probe microscope (NT-MDT) equipped with a Sony Exwave HAD camera with optical zoom. Etalon polysilicon high-resolution tips with a diameter of approximately 10 nm were used to obtain images resolved by 512x512 or 1024x1024 pixels.

 Scanning transmission electron microscopy (STEM) observations were carried out in a JEOL ARM200cF operated at 80 kV and equipped with a spherical aberration corrector and a Gatan Quantum electron energy-loss spectrometer (EELS).
SI 1: Raman scattering of two dimensional BP:

The point group of AA- and AB-stacked BP is independent of the layer number $D_{2h}$. $D_{2h}$ has the uncommon property that it has three different orthogonal rotation axis all showing exactly the same symmetric properties. As a consequence, there are always six possible ways to define the unit cell of the BP. As a result, the representations of the phonon modes also depend on the chosen orientation of the unit cell. It is therefore extremely important for the determination of the Raman scattering selection rules, that the Raman scattering geometry and the unit cell of the BP use the same coordinate system, as otherwise false predictions would be made. Historically, the z-axis is often chosen to be parallel to the BP planes, as we did in the main text to achieve better comparability with the available literature. However, considering the recent popularity of van-der-Waals heterostructures, we strongly suggest for future reports to choose an orientation in which the normal of the BP planes is parallel to the z-axis, to achieve compatibility with other 2D materials such as graphene or MoS$_2$. This has been done, e.g. in Ref. 1, where the armchair direction of the BP points toward the x-axis, the zig-zag direction along the y-axis, and the normal of the BP planes parallel to the z-axis.

In $D_{2h}$ all phonons that are even under inversion symmetry are Raman active, i.e. $A_g$, $B_{1g}$, $B_{2g}$, and $B_{3g}$. Analyzing the corresponding Raman tensors shows that only phonons with two of those symmetries can be expected to be observable in backscattering geometry with the incoming light propagating perpendicular to the BP planes. These symmetries are the $A_g$ symmetry and one of the three B symmetries, depending on the orientation of the unit cell. For the orientation we have chosen, this symmetry is $B_{2g}$. In the case of other orientations of the x-, y- and z-axes are chosen, the assignment of the symmetries will change accordingly in such a way that the Raman selection rules remain completely unchanged.

As a result, three Raman lines can be expected (and measured) for monolayer BP. Two from two phonons with $A_g$ symmetry denoted $A_g^1$ (353 cm$^{-1}$) and $A_g^2$ (462 cm$^{-1}$) and one from phonons with $B_{2g}$ (434 cm$^{-1}$) symmetry. As the frequencies were calculated, see SI 2, experimental values might slightly differ.

Additionally, two-dimensional materials with few layers can show Raman active modes not present for the monolayer or the bulk. This is also the case for BP. The number of the
atoms in the unit cell and therefore the number of phonon modes scales with the number of layers $N$ linearly for few-layer BP. However, it is not necessary to examine every possible layer number independently, as it was shown using group theory that each normal mode of the single layer will lead to $N$ normal modes of the few-layer with comparable frequencies that will belong to two different representations with opposite behavior under inversion symmetry.\textsuperscript{2}

Using the method described in Ref. 2, we thus derived the representations of the $\Gamma$-point phonon modes of AA- and AB-stacked BP depending on the layer number and the orientation of the BP unit cell, see Table 1. Aside the low-frequency shear and breathing like modes, multilayer BP shows, compared to single-layer BP, additional Raman active modes at \(~172\;\text{cm}^{-1}\), \(~427\;\text{cm}^{-1}\), and \(~476\;\text{cm}^{-1}\), with the latter two being in principle observable in backscattering geometries with the incoming light propagating perpendicular to the BP planes. As we show for the bulk structure, the stacking order can have a significant effect on the vibrational frequencies, e.g. for the $A_g^1$ mode, where the difference is 20 cm$^{-1}$. This might be used to distinguish between different stacking orders in experimental samples.
Table S1. Number of Γ-point phonon modes and their representation of the point group of single-, few-layer, and bulk AA- and AB-stacked BP. Since the representations of the phonon modes depend on the orientation of the BP in the unit cell, we specify the orientation by a vector. Here, A stands for armchair direction, Z for zig-zag representation and N for the normal of the BP planes, e.g. (A,Z,N) means that the armchair direction of the BP points toward the x-axis, the zigzag direction along the y-axis, and the normal of the BP planes parallel to the z-axis. Bold letters denote the symmetries of Raman-active phonons, which are allowed in backscattering geometry with the incoming light propagating perpendicular to the BP planes. The asterisk (*) denotes Raman active modes only present in multilayer structures. [ ] and ⌈ ⌉ are the ceiling and floor functions, respectively.

| Number | Frequency | Symmetry |
|--------|-----------|----------|
|        | 1L       | 2L       | bulk | (A,Z,N) | (Z,A,N) | (N,A,Z) | (A,N,Z) | (Z,N,A) | (N,Z,A) |
| [ N/2 ] | 0        | 0.0      | 0    | 0       | B_{3u}  | B_{2u}  | B_{1u}  | B_{3u}  | B_{2u}  | B_{1u}  |
| [ N/2 ] | -        | 16.2     | -    | -       | B_{2g}  | B_{3g}  | B_{3g}  | B_{1g}  | B_{1g}  | B_{2g}  |
| [ N/2 ] | 0        | 0.0      | 0    | 0       | B_{2u}  | B_{3u}  | B_{3u}  | B_{1u}  | B_{1u}  | B_{2u}  |
| [ N/2 ] | -        | 41.7     | -    | -       | B_{3g}  | B_{2g}  | B_{1g}  | B_{3g}  | B_{2g}  | B_{1g}  |
| [ N/2 ] | 0        | 0.0      | 0    | 0       | B_{1u}  | B_{1u}  | B_{2u}  | B_{2u}  | B_{3u}  | B_{3u}  |
| [ N/2 ] | -        | 71.5     | -    | -       | A_g    | A_g    | A_g    | A_g    | A_g    | A_g    |
| [ N/2 ] | 154.2    | 151.0    | 142.4 | 149.8   | B_{3u}  | B_{2u}  | B_{1u}  | B_{3u}  | B_{2u}  | B_{1u}  |
| [ N/2 ] | -        | 171.8    | -    | -       | B_{2g}  | B_{3g}  | B_{3g}  | B_{1g}  | B_{1g}  | B_{2g}  |
| [ N/2 ] | 198.7    | 197.9    | 197.1 | 196.5   | B_{3g}  | B_{2g}  | B_{1g}  | B_{3g}  | B_{2g}  | B_{1g}  |
| [ N/2 ] | -        | 196.7    | -    | -       | B_{2u}  | B_{3u}  | B_{3u}  | B_{1u}  | B_{1u}  | B_{2u}  |
| [ N/2 ] | 238.2    | 236.7    | 229.5 | 235.0   | B_{2g}  | B_{3g}  | B_{3g}  | B_{1g}  | B_{1g}  | B_{2g}  |
| [ N/2 ] | -        | 231.6    | -    | -       | B_{3u}  | B_{2u}  | B_{1u}  | B_{3u}  | B_{2u}  | B_{1u}  |
| [ N/2 ] | 352.8    | 352.9    | 335.8 | 355.0   | A_g    | A_g    | A_g    | A_g    | A_g    | A_g    |
| [ N/2 ] | -        | 352.6    | -    | -       | B_{1u}  | B_{1u}  | B_{2u}  | B_{2u}  | B_{3u}  | B_{3u}  |
| [ N/2 ] | 429.3    | 419.7    | 428.0 | 426.1   | A_u    | A_u    | A_u    | A_u    | A_u    | A_u    |
| [ N/2 ] | -        | 426.6    | -    | -       | B_{1g}  | B_{1g}  | B_{2g}  | B_{2g}  | B_{3g}  | B_{3g}  |
| [ N/2 ] | 430.1    | 430.4    | 419.9 | 423.2   | B_{2g}  | B_{3g}  | B_{3g}  | B_{1g}  | B_{1g}  | B_{2g}  |
| [ N/2 ] | -        | 427.7    | -    | -       | B_{3u}  | B_{2u}  | B_{1u}  | B_{3u}  | B_{2u}  | B_{1u}  |
| [ N/2 ] | 434.5    | 433.5    | 432.1 | 434.9   | B_{1g}  | B_{1g}  | B_{2g}  | B_{2g}  | B_{3g}  | B_{3g}  |
| [ N/2 ] | -        | 435.1    | -    | -       | A_u    | A_u    | A_u    | A_u    | A_u    |
| [ N/2 ] | 462.4    | 459.9    | 455.1 | 459.8   | A_g    | A_g    | A_g    | A_g    | A_g    | A_g    |
| [ N/2 ] | -        | 460.5    | -    | -       | B_{1u}  | B_{1u}  | B_{2u}  | B_{2u}  | B_{3u}  | B_{3u}  |
| [ N/2 ] | 475.3    | 474.9    | 472.4 | 472.6   | B_{1u}  | B_{1u}  | B_{2u}  | B_{2u}  | B_{3u}  | B_{3u}  |
| [ N/2 ] | -        | 475.5    | -    | -       | A_g    | A_g    | A_g    | A_g    | A_g    | A_g    |
SI 2: DFT calculations

The frequencies in Tab. 1 and the corresponding atomic displacement patterns of the phonon modes of monolayer, bilayer, and bulk AB-stacked BP were computed within the framework of density functional perturbation theory (DFPT) as implemented in the Quantum Espresso code. Both atomic positions and cell parameters were optimized to obtain the ground state geometries of the studied systems. We sampled the Brillouin zone of the few-layer (bulk) materials by grids of 12x12x1 (12x12x10) k-points. The valence electrons of the system were described by normconserving pseudopotentials and an energy cutoff of 80 Ry. We used the PBE approximation to the exchange-correlation interaction, where we added semi-empiric dispersion corrections from the DFT-D2³ scheme in both optimization and DFPT steps.
SI 3: Scanning Raman microscopy (SRM) setup:

Considering that photo-oxidation of BP nanosheets could be induced by permanent laser irradiation, low excitation energies (5%) as well as relatively short acquisition times (2 s) were used during Raman measurements. Normally, we decided to set a step size of 1 µm in SRM as a sufficient resolution is still guaranteed, and applicable mappings could be obtained relatively fast. Nevertheless, it is worth mentioning that with our local setup it is possible to highly resolve BP flakes located closely next to each other by reducing the step size to 0.2 µm (Fig. SI 1).

**Figure SI 1:** Raman mappings displaying the $A_{1g}^1/A_{2g}^2$ ratio comparing different step sizes. By reducing the step size to 0.2 µm the resolution of the morphology of the flakes becomes more accurate. However, the downside is that the mapping presented on the right took more than 20 h of measuring time.
SI 4: Polarization dependence of Raman modes for BP flakes below 10 nm:

Figure SI 2: Polar plots of the angle-dependent Raman intensities of $A_{1g}$, $B_{2g}$, and $A_{2g}$ modes, as well as $A_{1g}/A_{2g}$ ratio. Here 0° corresponds to the configuration with the incident laser polarization along the zigzag direction. Excitation wavelength = 532 nm.
SI 5: Wavelength dependent Raman spectra of BP:

**Figure SI 3:** Top: Raman spectra measured at different excitation wavelengths for the monolayer. Bottom: exact intensity values for the $A_{1g}$, $B_{2g}$ and $A_{2g}$ Raman modes measured at different excitation wavelengths.

**Figure SI 4:** Top: Raman spectra measured at different excitation wavelengths for the few-layer flakes under the LRR (left) and HRR (right). Bottom: exact intensity values for the $A_{1g}$, $B_{2g}$ and $A_{2g}$ Raman modes measured at different excitation wavelengths.
Figure SI 5: Top: Raman spectra measured at different excitation wavelengths for bulk BP under the LRR (left) and HRR (right). Bottom: exact intensity values for the $A_{1g}$, $B_{2g}$ and $A_{2g}$ Raman modes measured at different excitation wavelengths.

Figure SI 6: $A_{1g}$ Raman intensity plot for all the samples measured at different excitation wavelengths (LRR).
Figure SI 7: Raman spectra of a BP monolayer at different excitation wavelength.

Figure SI 8: Comparison of BP bulk and single layered BP Raman spectra.
Figure SI 9: $A^1_g/A^2_g$ ratio Raman mappings of a flake, which has been characterized also by AFM (shown on the left) at different orientations separated by 60°. One can nicely distinguish between the “High-Ratio-region” (HRR) and “Low Ratio-region” (LRR) because of the different color coding. Corresponding mean Raman spectra confirm the angular dependency of each individual Raman mode. Generally, rotation of the sample drastically influences total intensities of each individual Raman mode as well as the $A^1_g/A^2_g$ ratio. Due to the two-fold symmetry of BP, spectra separated by an angle of 180° are very similar.
SI 7: Oxidation of pristine BP followed by SRM:

For the oxidation study of pristine FL-BP Raman mappings were conducted every 24 h. The first measurement in this series was performed under inert conditions. BP flakes were exfoliated inside the Argon filled glove box, transferred onto a Si/SiO$_2$ wafer and afterwards put in a small inert chamber with a small window on top. Due to diffraction of the laser when penetrating the window of the inert chamber, the spatial resolution in the mapping on the left is lower.

![Graph showing Raman mappings under inert and oxidized conditions]

**Figure SI 10:** $A^{1g}/A^{2g}$ ratio Raman mappings under inert conditions (left) and after 72 hours of oxidation time (right). Comparison of the color coding indicates a change in the $A^{1g}/A^{2g}$ ratio tending towards lower values. With the intent to exactly monitor the development of the characteristic $A^{1g}/A^{2g}$ ratio, all Raman mappings were evaluated using LabSpec5 under exact same conditions. The borders around the $A^{1g}$ peak were set at 355-370 cm$^{-1}$ and for the $A^{2g}$ peak at 455-470 cm$^{-1}$, respectively. It is essential to keep these conditions constant because changing the borders will result in a slight change of the $A^{1g}/A^{2g}$ ratio.
SI 8: Oxidation of pristine BP monitored by AFM:

Figure SI 11: AFM images of FL-BP recorded over time demonstrating their environmental instability. According height profiles across lines A and B demonstrate the typical oxidation behavior of pristine BP.
The sequence of AFM images above displays the oxidation of pristine FL-BP (ca. 7nm) in a rhythm of 24 hours. The first AFM scan represents the flakes directly after removing the sample from inert conditions. Here, it is already possible to observe some droplets, which exhibits diameters of around 150 nm and are about 5 nm high, on top of the exfoliated BP sheets. After 24 hours all flakes within the scanned area exhibit substantial signs of the ongoing oxidation. Formed droplets now have about twice the height than one day earlier and reach lateral dimensions up to μm size. Another two days of oxidation time leads to a further growth of droplets until their coalescence leads to the constitution of a huge bubble, which covers the whole flake. Typically, this fully oxidized state of the flake is accompanied by a drastic increase of the volume with the height of the flakes being around three to four times the original value as both exemplary height profiles underline.
SI 9: Development of $A_1^g/A_2^g$ histograms for flakes thicker than 10 nm:

SI 10: Development of $A_2^g$ and $B_{2g}$ mode of pristine BP versus time:
SI 11: AFM image of flakes with comparable thickness for lateral dimension study:

SI 12: Lateral dimension plot – time versus $A^1_g$ mode intensity:
SI 13: Remaining Si intensity upon oxidation:
SI 14: AFM sequence of NMP protected BP flakes: Comparison of illuminated (top) and dark (bottom) samples
References

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