

Supporting Information

Monolayer black phosphorus by sequential wet-chemical surface oxidation

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SI 1:

AFM video showing the complete degradation of a BP flake (see file attached).

SI 2:

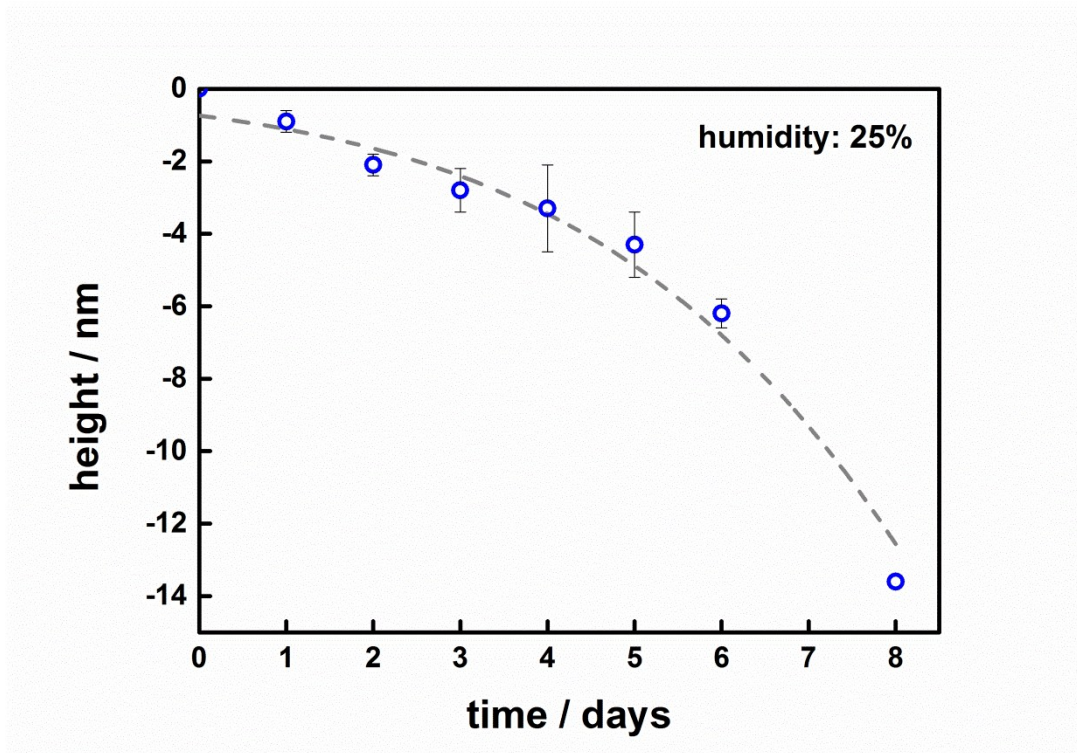


Figure SI 2:

Calibration curve showing the thickness of BP flakes versus the time when treated with DI water. It is very important to remark that the humidity highly influences these values, e.g. when reaching humidity values higher than 60 % the reduced thickness can be twice in the same amount of time for this thinning technique.

SI 3:

	R_{ms} / nm (Flake1)	R_{ms} / nm (Flake2)
pristine	1.34	1.48
1d oxidized	5.42	5.87
2d oxidized	6.10	5.37
3d oxidized	4.85	5.03
washed	1.09	1.12
PDI coated	1.07	1.04

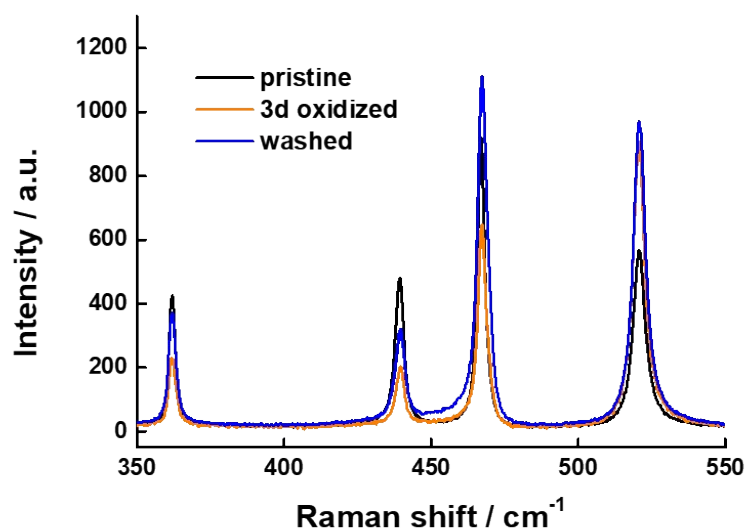


Figure SI 3:

(Top): Evolution of the surface roughness of BP flakes during oxidation, after rinsing with DI water and after the non-covalent attachment of PDI. (Bottom): Evolution of the Mean BP Raman intensities: Upon oxidation, BP Raman intensities decrease, but interestingly, when rinsed with DI water, the BP Raman intensity gets recovered which fits perfectly to the recovery of the pristine BP surface.

SI 4:

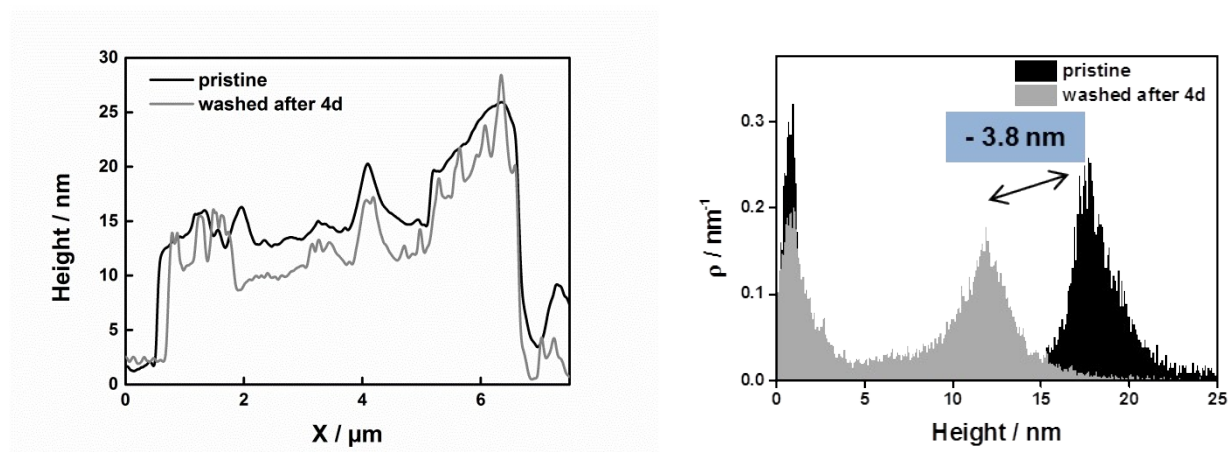
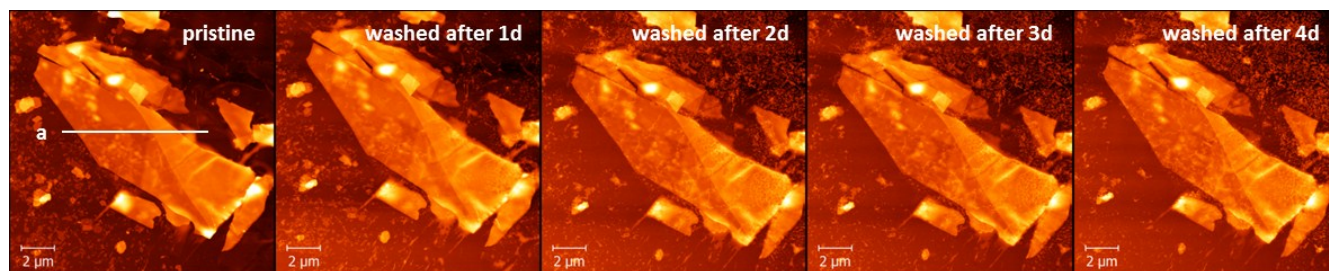


Figure SI 4:

(Top): AFM image of mechanically exfoliated FL-BP which has been washed 4 times (daily) with DI water. (Bottom): AFM height profiles along line a (left) and the related statistical AFM evaluation (right) comparing the pristine thickness to the thickness of the flake after 4 washing procedures.

SI 5:

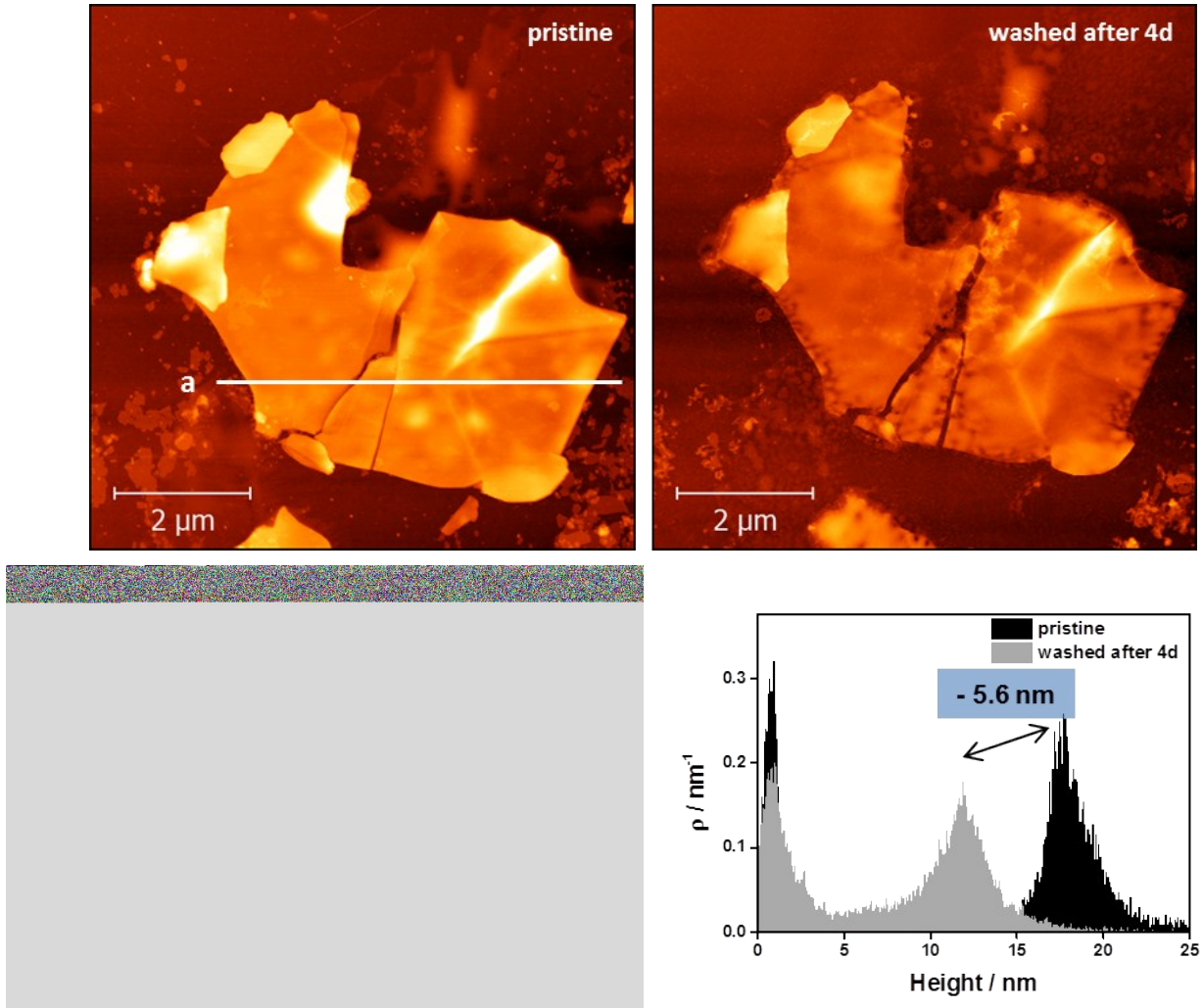


Figure SI 5:

(Top): AFM image of mechanically exfoliated FL-BP which has been washed after 4 days with DI water. (Bottom): AFM height profiles along line a (left) and the related statistical AFM evaluation (right) comparing the pristine thickness to the thickness of the flake washed after 4 days. Comparing to the flake shown in figure SI 6 it is worth to remark that washing the BP flake every day results in a slower degradation than washing only one time in the same amount of time.

SI 6:

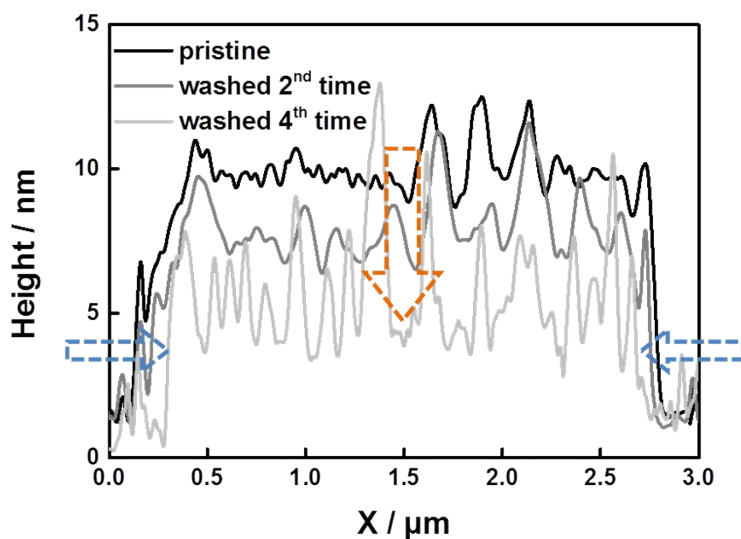
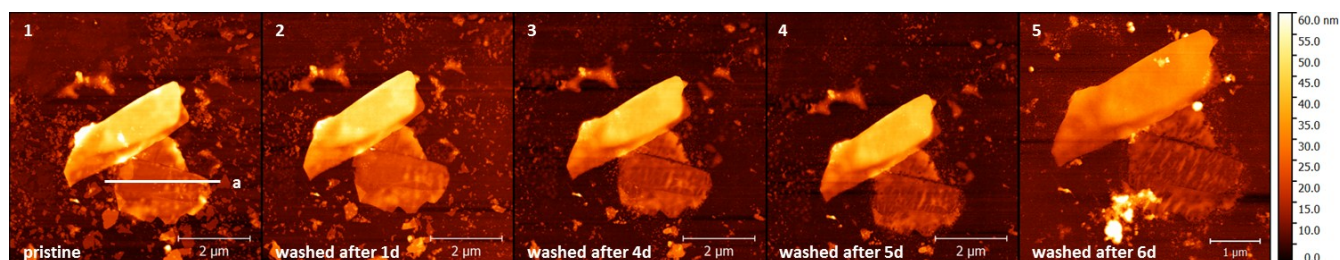


Figure SI 6: (Top): Sequence of AFM images depicting a mechanically exfoliated BP flake which has been washed several times with DI water in order to produce SL-BP. (Bottom): Corresponding AFM height profiles along line a. Interestingly, not only a decrease in the thickness of the flake can be observed, but also a reduce in the lateral dimensions of the flake. This confirms on the one hand that the degradation of black phosphorous follows the layer by layer thinning effect described by Castellanos^[1] but on the other hand oxidation of the edges also plays a role.

SI 7:

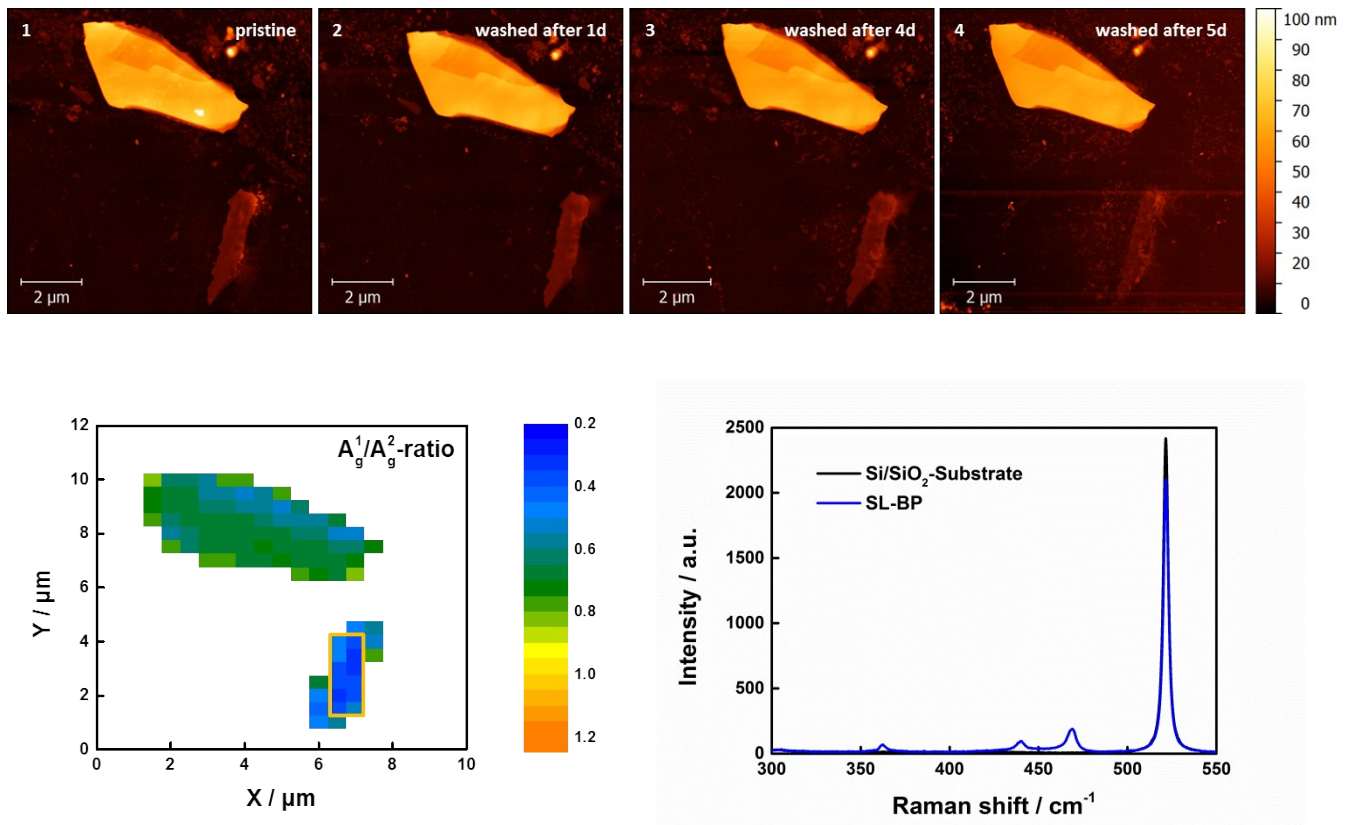


Figure SI 7:

(Top): Sequence of AFM images depicting mechanically exfoliated BP flakes which have been washed several times with DI water in order to produce SL-BP. (Bottom-Left): Raman mapping of the A_g^1/A_g^2 -ratio of the BP flakes which has been conducted after the last washing step. (Bottom-Right): Mean Raman spectrum (orange area) of the thin BP flake in comparison to the Si/SiO₂ substrate. The high remaining silicon intensity (>82%) indicates that the flake consist only of one BP layer.

SI 8:

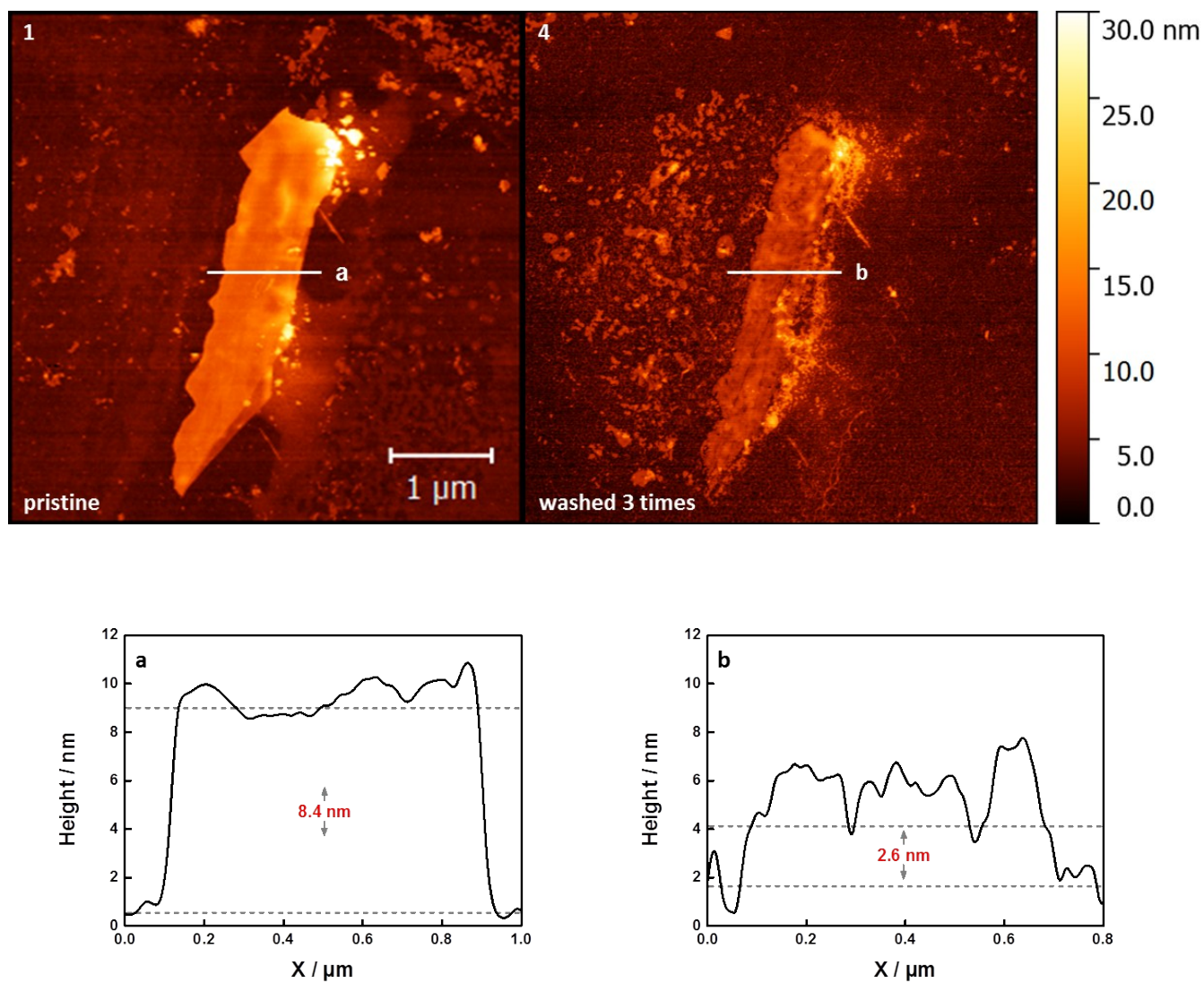


Figure SI 8:

(Top): Zoom-in of the AFM images shown in figure SI 3. Comparison of the pristine BP flake and the same flake after it has been dip-casted 3 times in DI-water to reduce the thickness down to SL-BP. (Bottom): Corresponding AFM height profiles taken along line a and b.

SI 9:

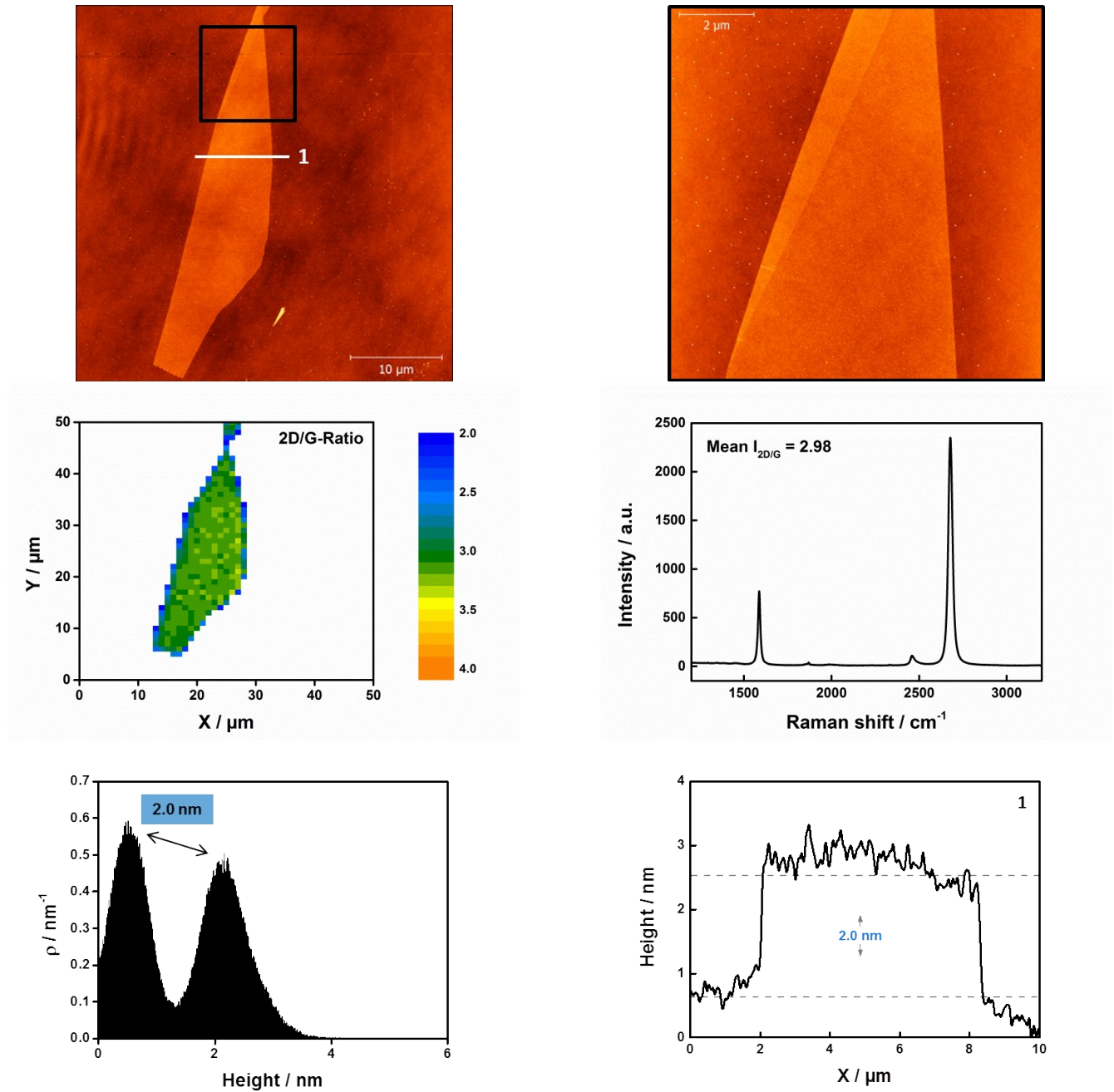
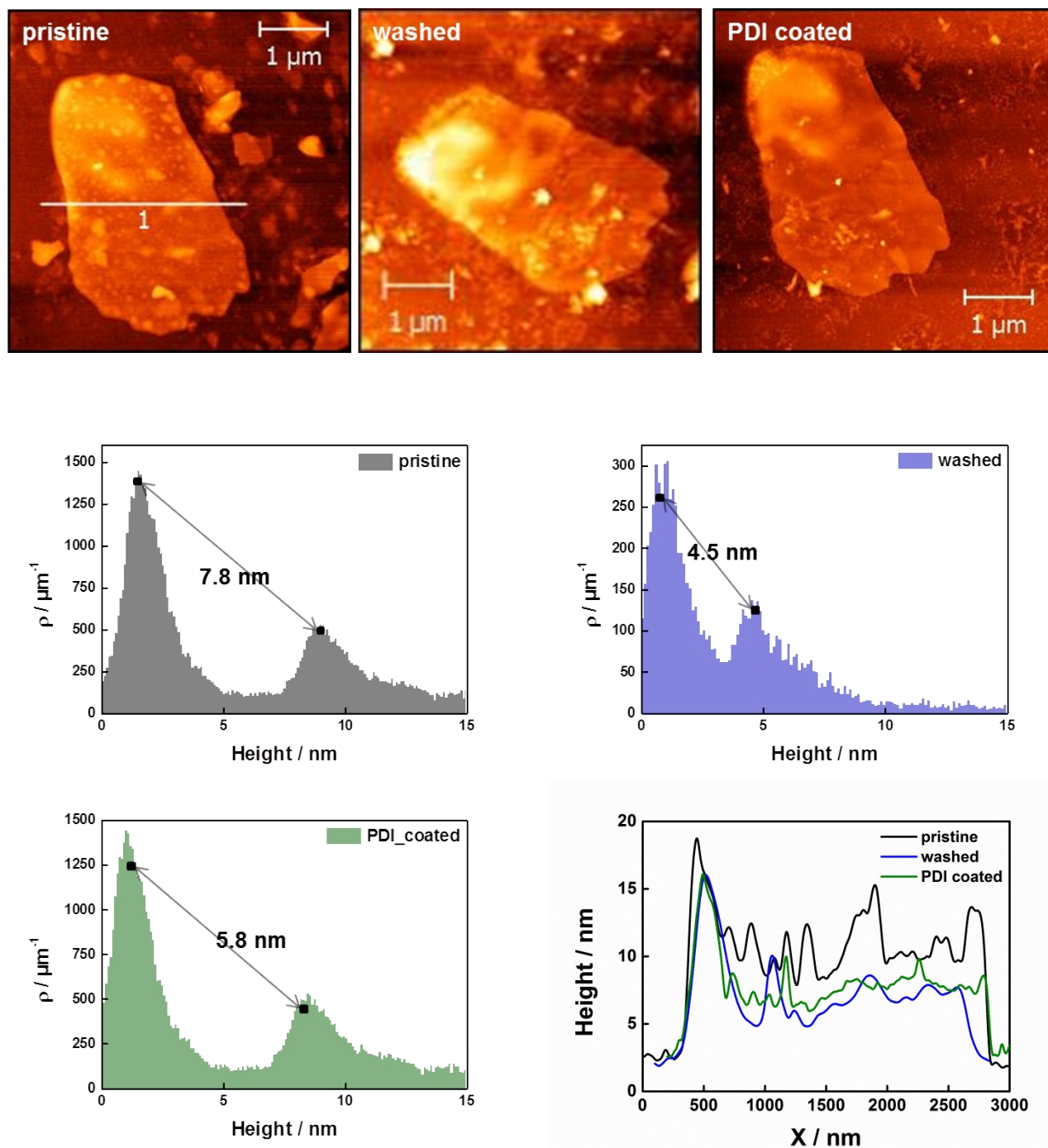


Figure SI 9:

(Top): AFM image of a mechanically exfoliated SL-graphene flake (left) and a zoom-in highlighting that a small part of the flake is folded. (Middle): Corresponding Raman mapping of the SL-graphene showing the 2D/G-ratio (left) and the related Mean Raman spectra (right) with a mean $I_{2D/G}$ -ratio of 2.98 confirming that SL-graphene is present. (Bottom): Statistical AFM evaluation (left) visualizing the thickness of the SL-graphene flake and the corresponding AFM height profile along line 1.

SI 10:

**Figure SI 10:**

(Top): AFM image of mechanically exfoliated FL-BP which has been washed with DI water and afterwards coated with PDI by dip-casting the wafer in a 10^{-5} M PDI solution. The non-covalently attached PDI temporarily prevents oxidation of the BP. (Middle & Bottom): Statistical AFM evaluation showing in a first step the reduced thickness of the BP flake when washed with DI water and in the second step an increased thickness because of the PDI layer on top of the BP flake. Corresponding AFM height profiles along line 1 confirm this trend.

SI 11:

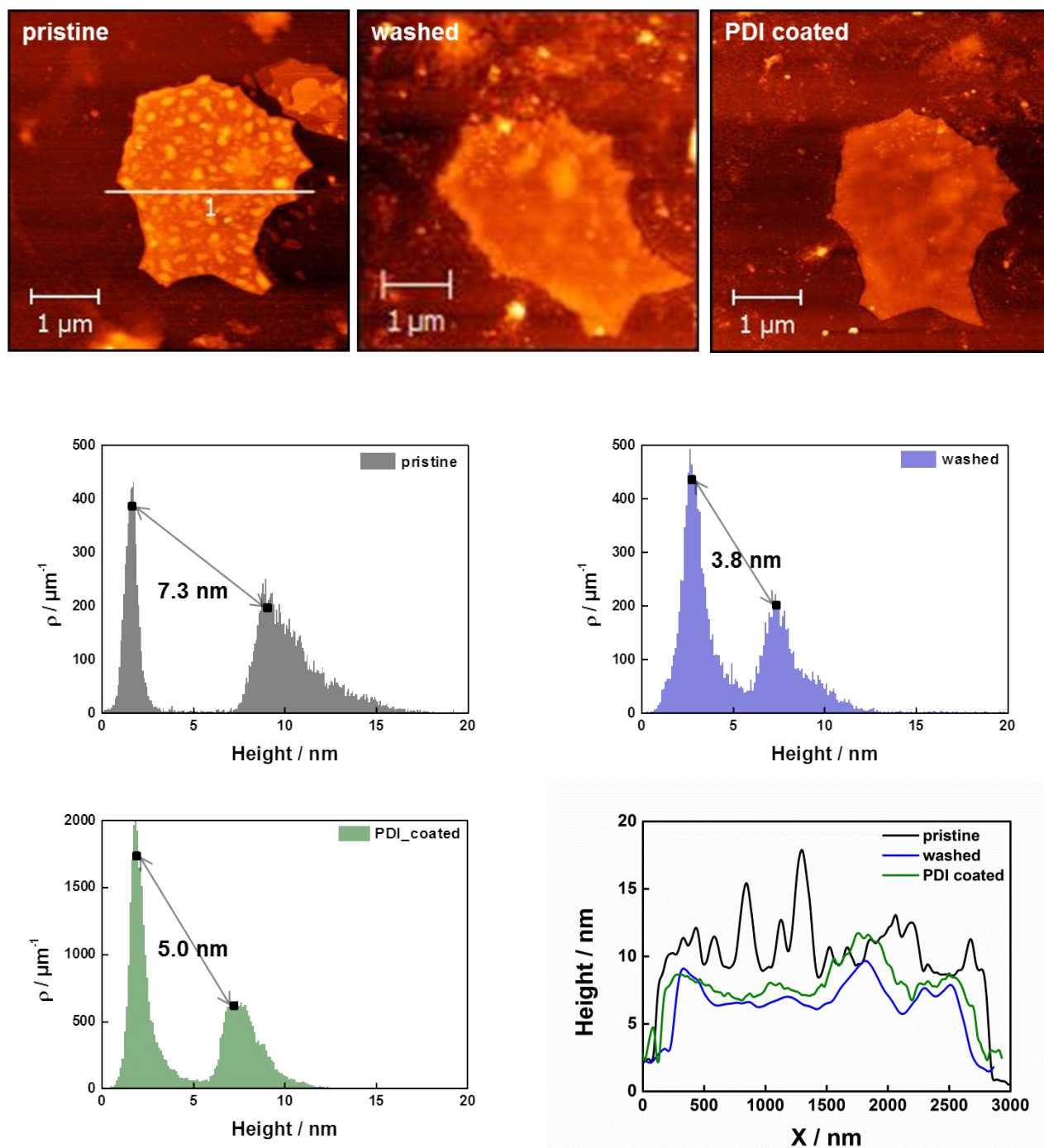


Figure SI 11:

(Top): AFM image of mechanically exfoliated FL-BP which has been washed with DI water and afterwards coated with PDI by dip-casting the wafer in a 10^{-5} M PDI solution. The non-covalently attached PDI temporarily prevents oxidation of the BP. (Middle & Bottom): Statistical AFM evaluation showing in a first step the reduced thickness of the BP flake when washed with DI water and in the second step an increased thickness because of the PDI layer on top of the BP flake. Corresponding AFM height profiles along line 1 confirm this trend.

SI 12:

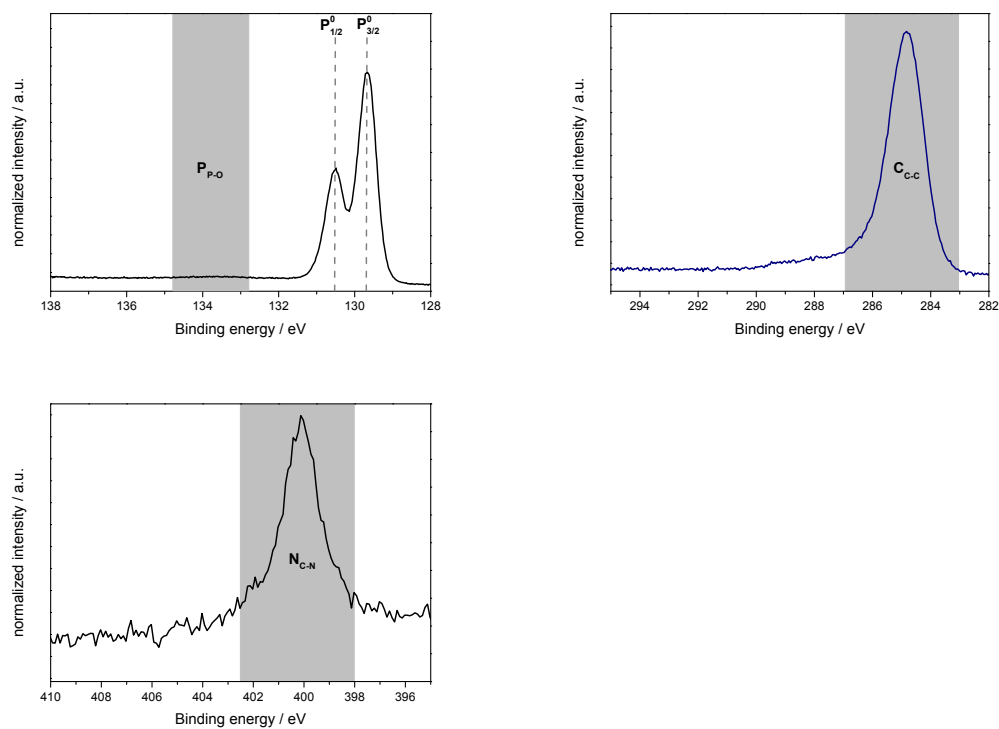


Figure SI 12A XPS BP-PDI hybrid showing the regions of P, without any oxidation, and the regions of C and N indicating that the perylene is interacting with BP.

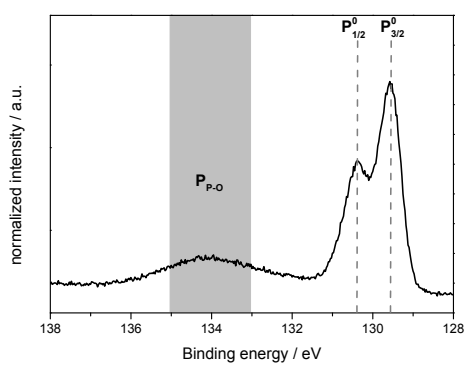


Figure SI 12B XPS of pristine BP showing the regions of P, with the typical oxidation P-O bonds.

SI 13:

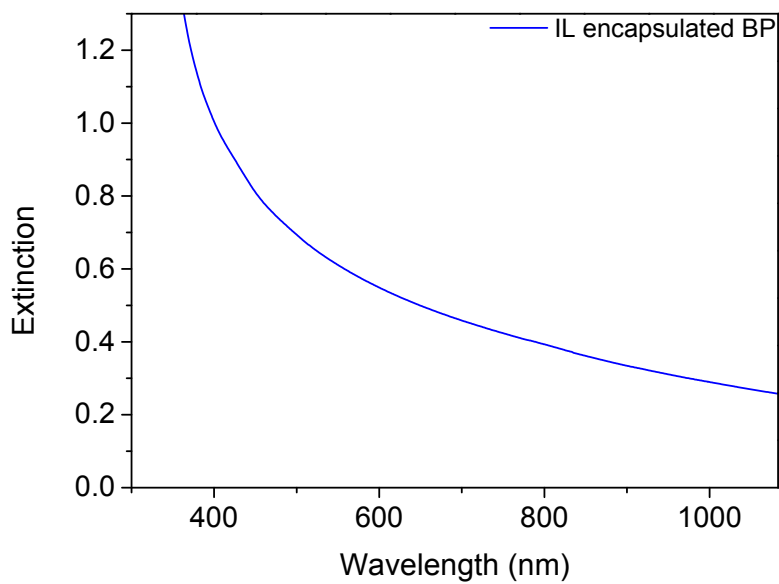
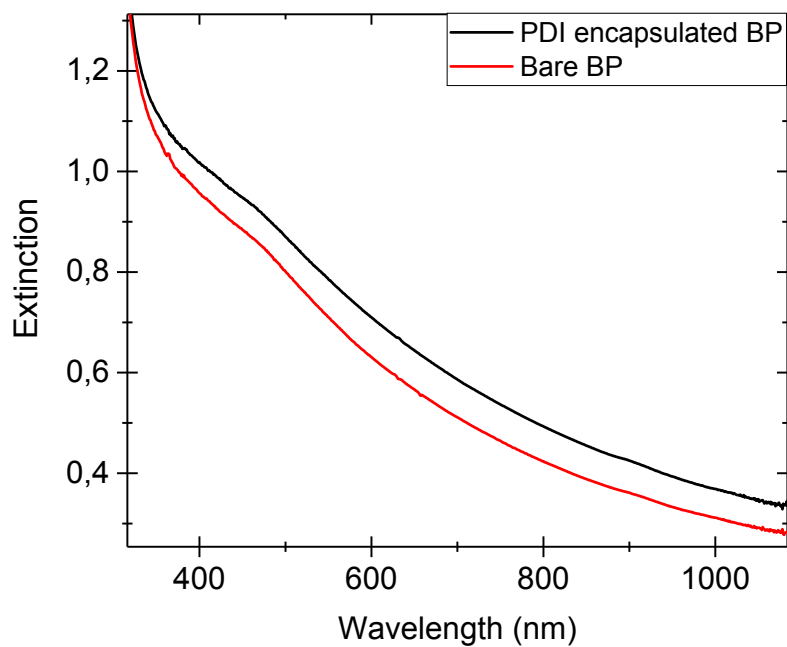


Figure SI 13 Extinction spectra of bare BP and BP encapsulated with perylene.

SI 14:

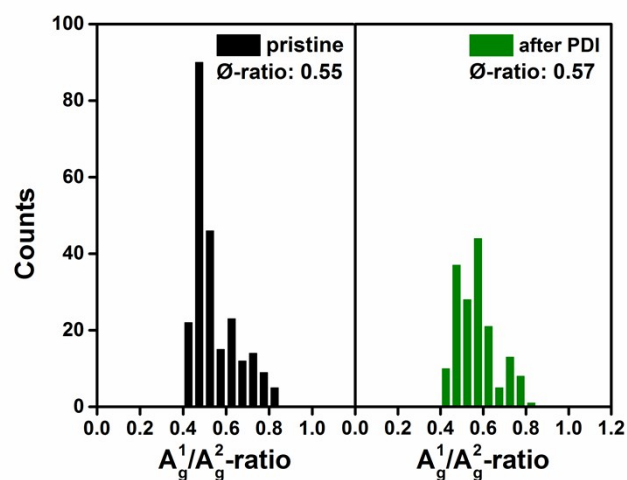


Figure SI 14 Comparison of the A_g^1/A_g^2 -ratio of the BP flakes before and after treatment with BP showing nearly no difference.

SI 15:

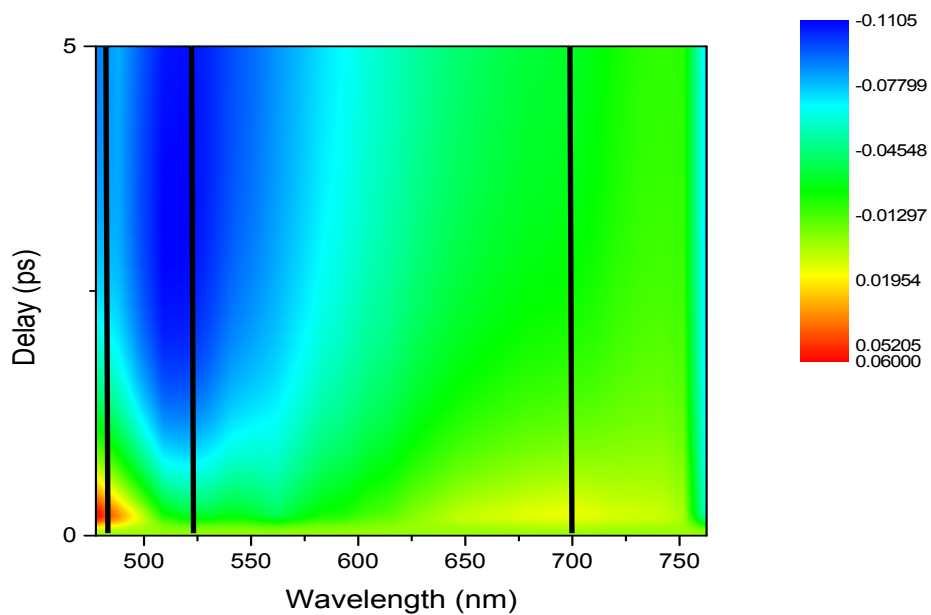


Figure SI 15 Contour plot of $\Delta T/T$ for a pristine exfoliated BP sample encapsulated in PMMA as an optically inert transparent matrix.

SI 16:

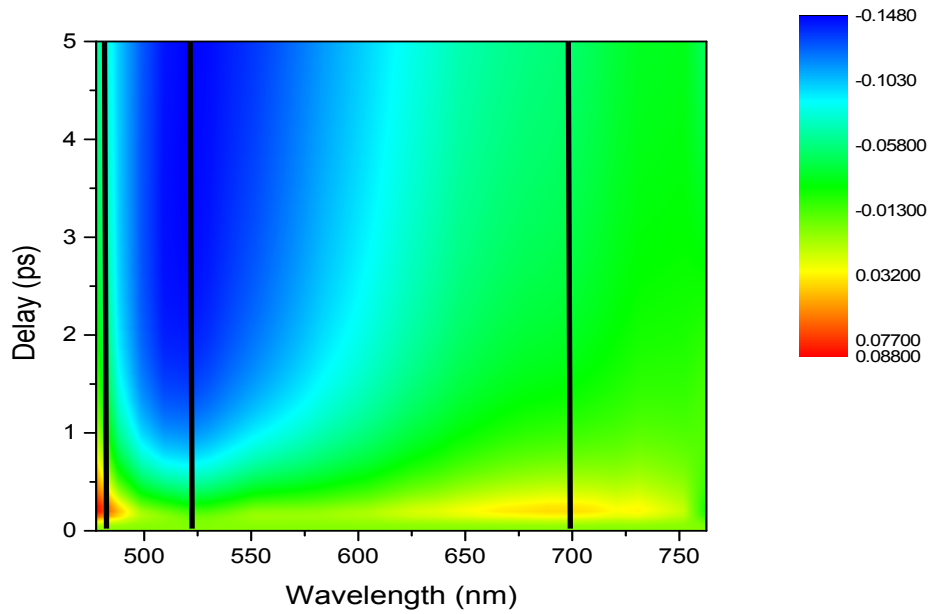


Figure SI 16 Contour plot of $\Delta T/T$ for a PDI functionalized BP sample encapsulated in PMMA as an optically inert transparent matrix.

SI 17:

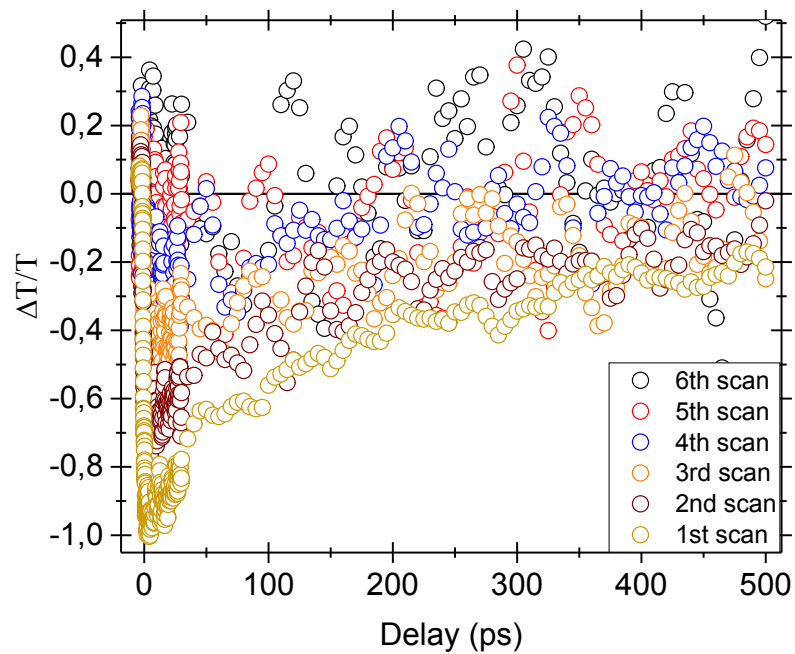


Figure SI 17 Degradation of blank black phosphorous embedded in PMMA (dry sample) ($\lambda_{\text{probe}}=562$ nm)

SI 18:

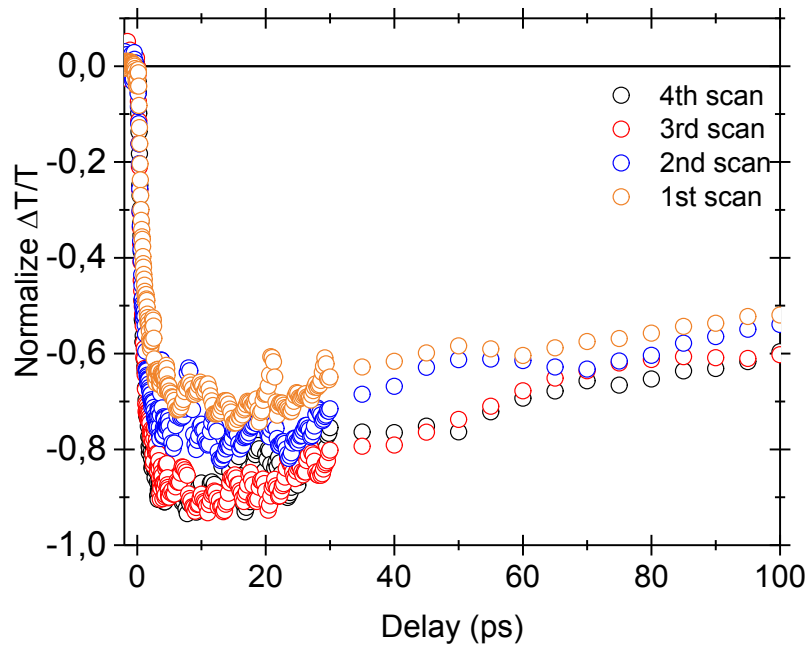


Figure SI 18 Degradation of pdi black phosphorous embedded in PMMA (dry sample) ($\lambda_{\text{probe}}=562$ nm)

SI 19:

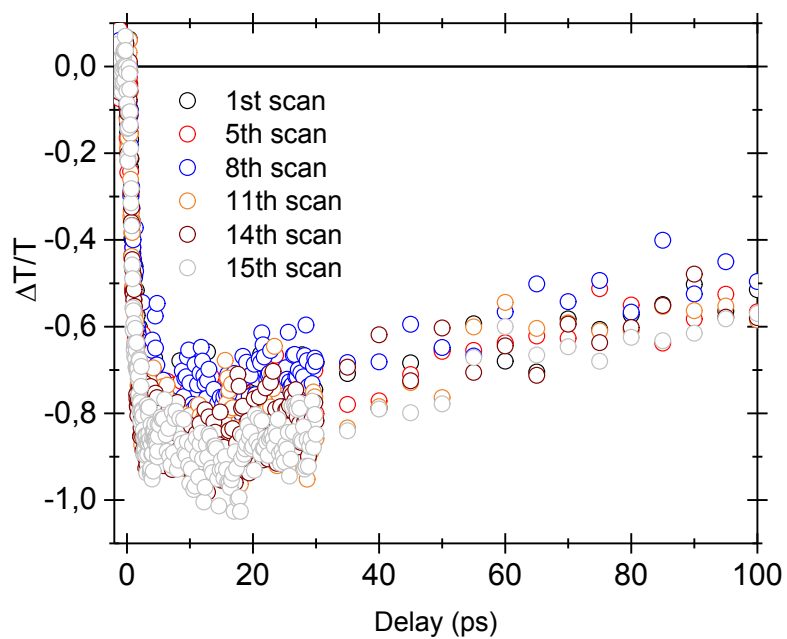


Figure SI 19 Degradation of pdi black phosphorous embedded in PMMA (liquid sample) ($\lambda_{\text{probe}}=562$ nm)

SI 20:

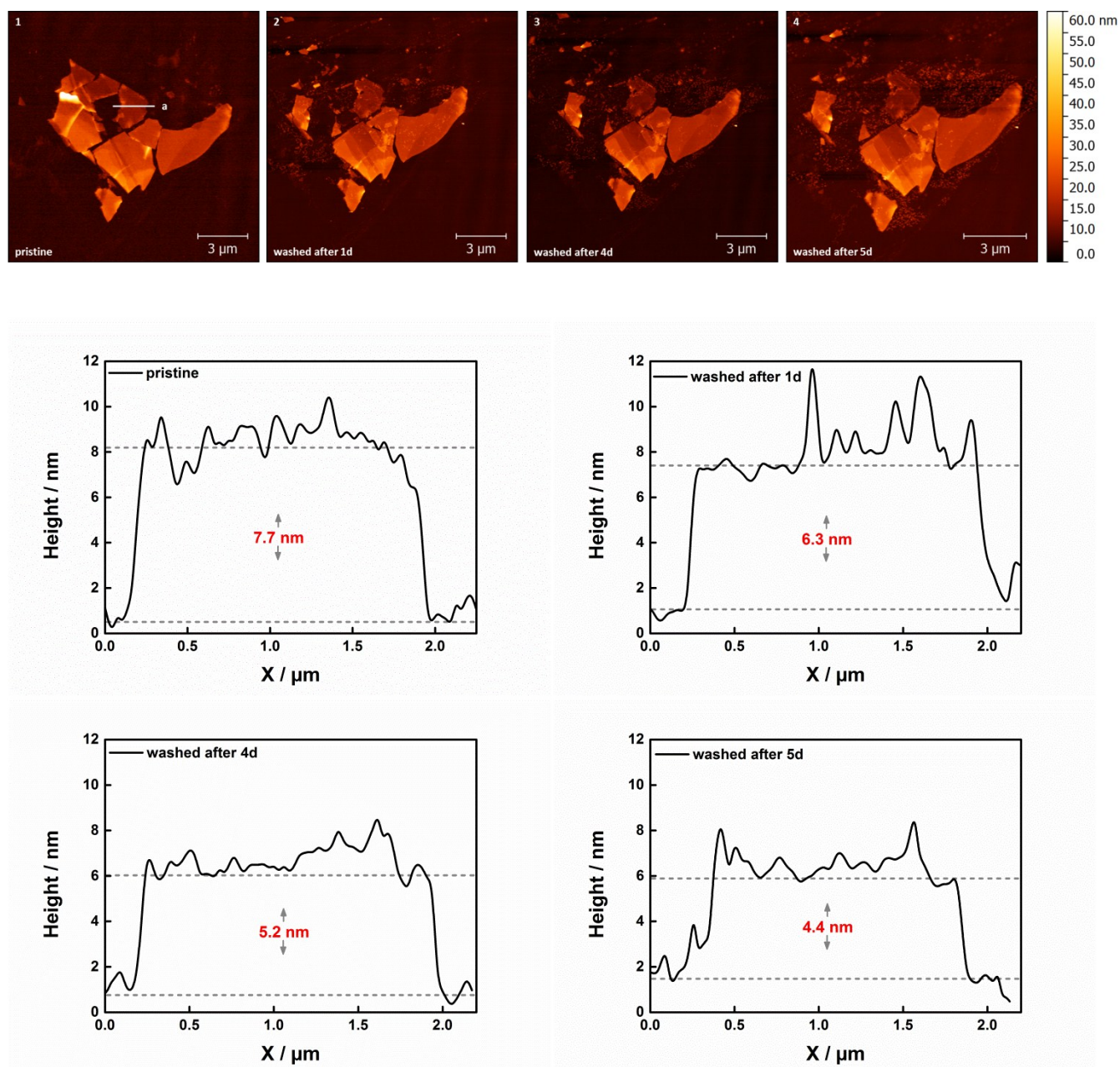


Figure SI 20:

(Top): AFM image of mechanically exfoliated FL-BP which has been washed 4 times with DI water to reduce the thickness. (Middle & Bottom): Corresponding AFM height profiles along line a illustrating the stepwise reduction of the thickness.

SI 21:

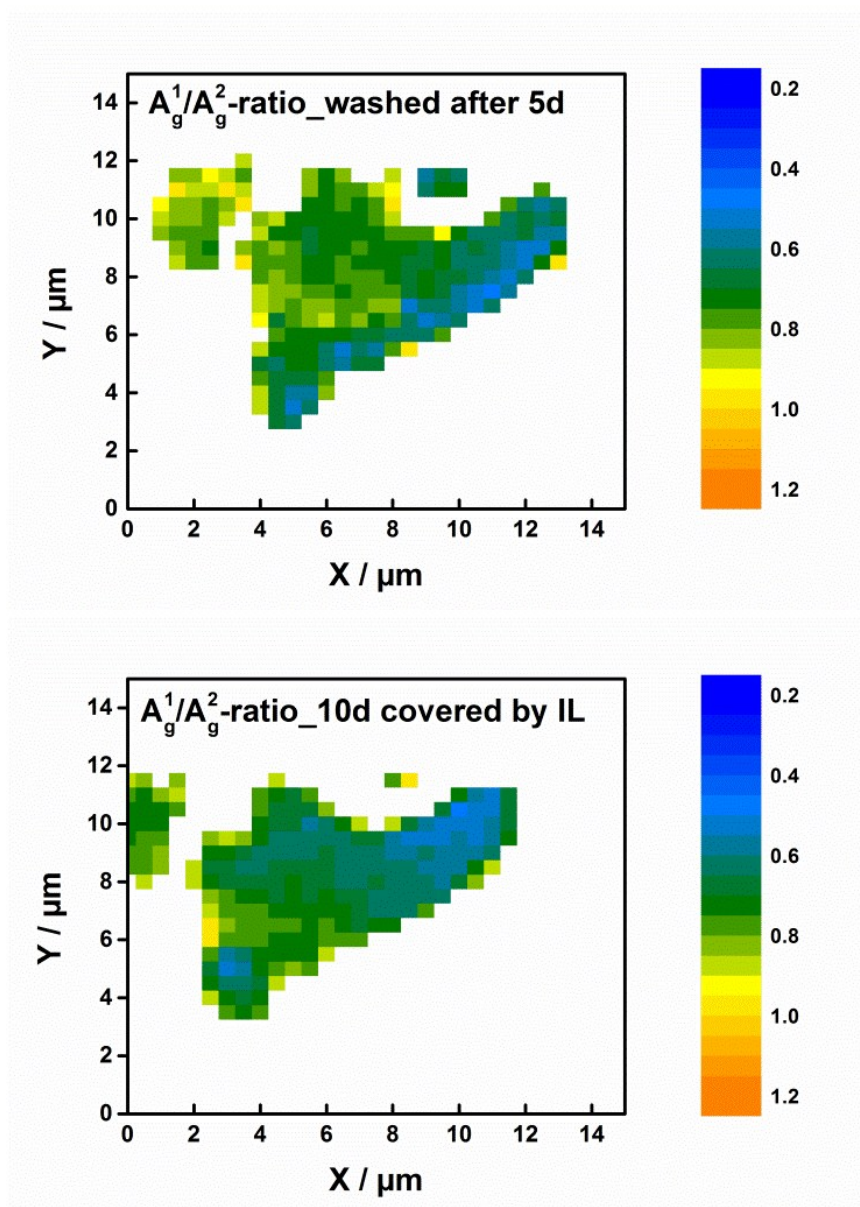


Figure SI 21:

A_g^1/A_g^2 -ratio Raman mappings of the BP flakes shown in figure SI 8 after the last washing procedure with DI water (left) and after the removal of IL which covered the flakes for 10 days (right) in order to successfully prevent any degradation of the flakes.

SI 22:

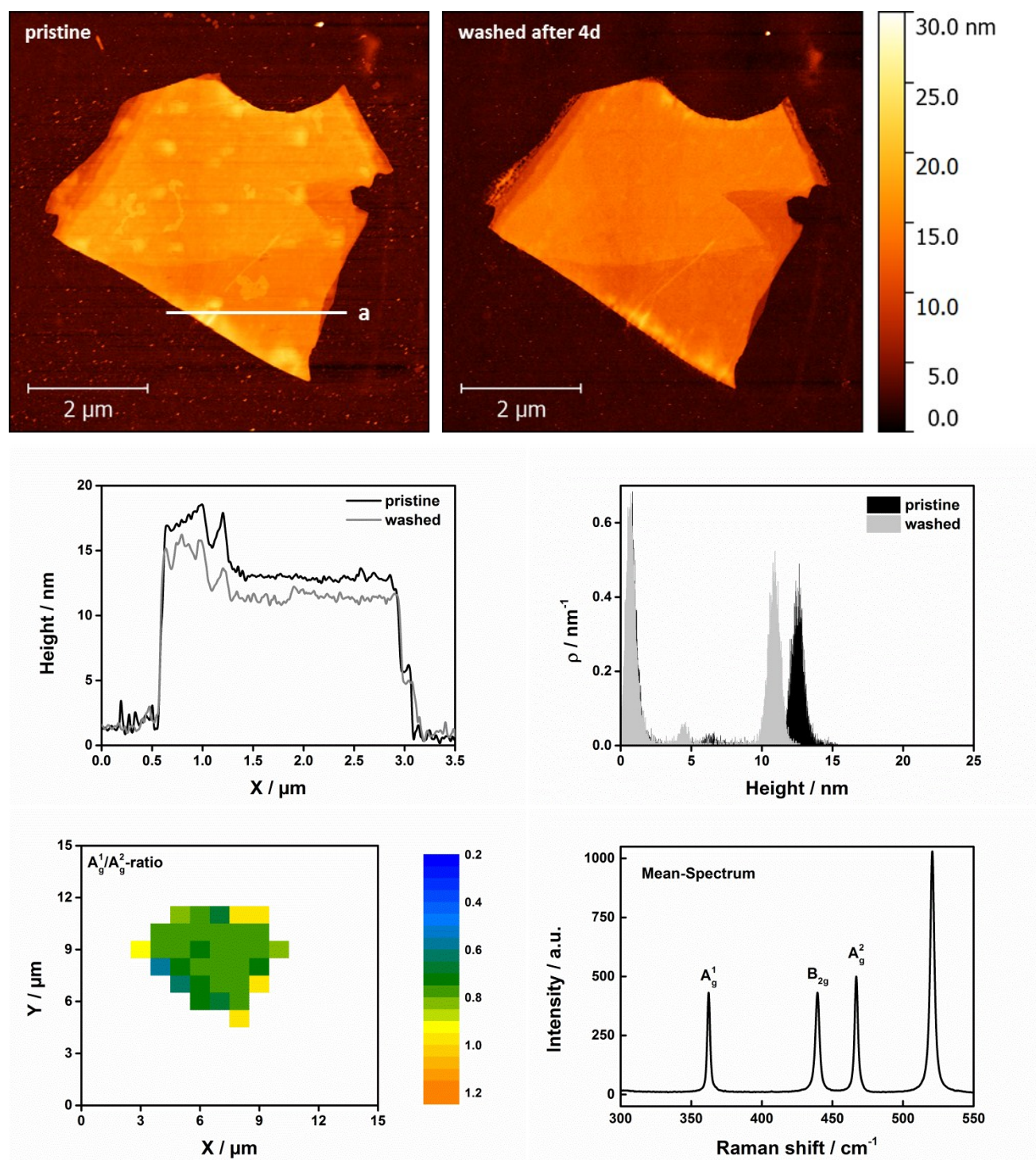


Figure SI 22:

(Top): AFM image of a mechanically exfoliated BP flake which has been washed with DI-water before it was electrically contacted to perform transport measurements. (Middle): Corresponding AFM height profiles along line a (left) and the statistical AFM evaluation (right) visualizing the reduced thickness of the flake. (Bottom): A_g¹/A_g²-ratio Raman mapping of the BP flake after it was treated with DI-water and the related mean Raman spectrum showing the three characteristic vibrational modes of BP.

SI 23:

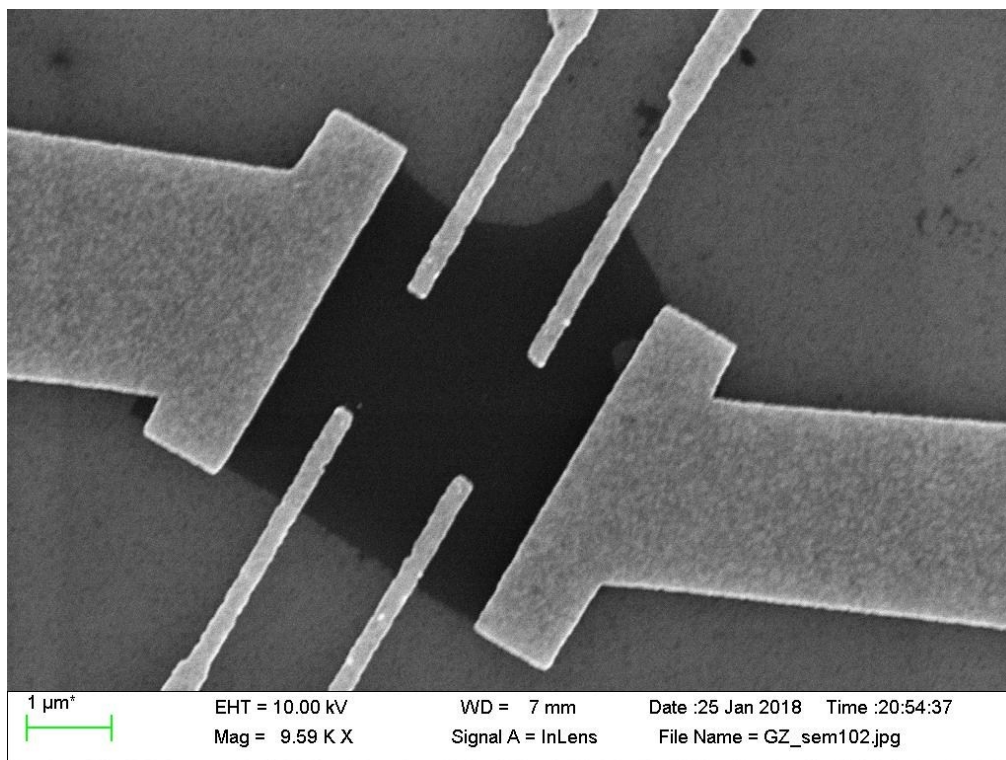
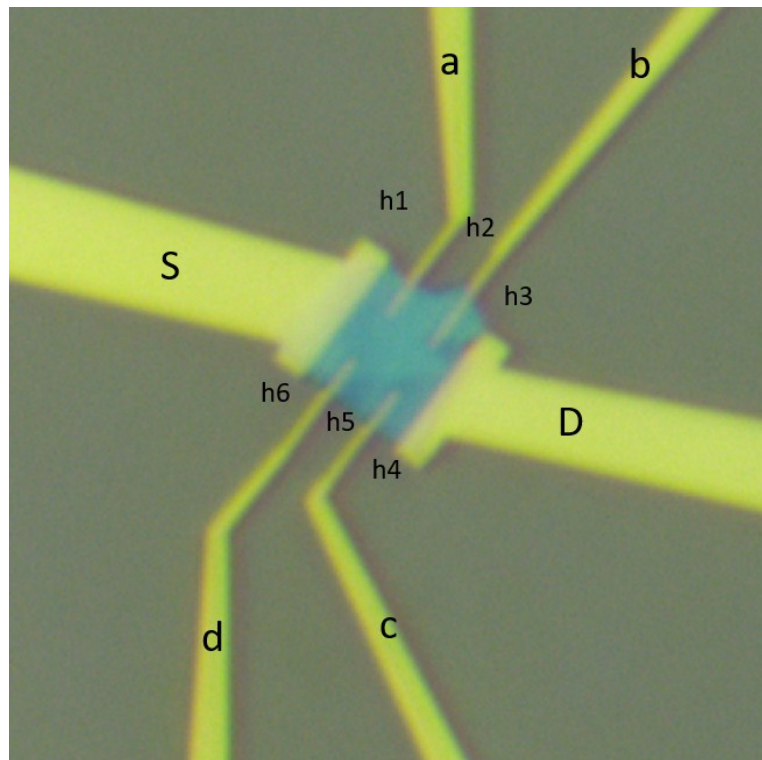


Figure SI 23:

(Top): Optical image of the rinsed BP flake which was contacted afterwards in a FET device. The mobility and carrier density were determined for the different heights of the flake. (Bottom): SEM-image of the rinsed BP flake.



References:

- [1] O. I. Joshua, A. S. Gary, S. J. v. d. Z. Herre, C.-G. Andres, *2D Mater.* **2015**, 2, 011002.