Supplementary Information

Supplementary Figure 1 | Formation of transfer bubbles at the graphene/bP interface. (a) AFM image of graphene on few-layer bP ample as transferred. (b) The same sample after 4 hour of Ar+H₂ (9:1) gas annealing at 300 C.

Supplementary Figure 2 | Raman spectra of the passivating crystals. (a) Raman spectrum of monolayer graphene on top of black phosphorus (red curve) and SiO₂ (blue curve) for the sample from Fig.1 and Fig.2 of the main text after approximately 48 hours in ambient air. (b) Raman spectrum of few-layer hexagonal BN on top of black phosphorus (red curve) and SiO₂ (blue curve) for the sample from Fig.1 of the main after approximately 48 hours in ambient air.
Supplementary Figure 3 | Estimation of the field effect mobility. (a-b)
Conductance and field effect mobility versus gate, $V_g$, voltage for the passivated (blue curve) and exposed (red curve) channels of sample #1 from Fig.3 in the main text. (c-d) Conductance and field effect mobility versus gate voltage for the passivated (blue curve) and exposed (red curve) channels of sample #2 from Fig.3 in the main text.

Supplementary Figure 4 | Two-point electrical characterization of more passivated samples. Two-probe conductance versus gate voltage for the passivated (blue curves) and exposed (red curves) channels of three transport samples different from those presented in the main text. The temperature ($T$) and sample thickness ($t$) are indicated inside the plots.
Supplementary Figure 5 | Hysteresis in the back gate sweep direction. Source-drain current ($I_{sd}$) versus gate voltage ($V_{g}$) for the device discussed in Fig. 4 of the main text at $T=280$ K (green curves) and $T=200$ K (blue curves) for both sweep directions of the back gate voltage: from positive to negative gate voltage (solid curves) and from negative to positive (dashed curves).
**Supplementary Figure 6 | Electronic band structure few-layer black phosphorus with an oxygen point defect.** Band structure of ultrathin bP with a chemisorbed diagonal oxygen bridge defect (O_{b-d}) from monolayer (1L) up to three layers (3L). Occupied bands are represented by solid black lines and unoccupied by solid red lines. The bands of the pristine black phosphorus are overlaid as shade, and the labels indicate the p-orbital character of the oxygen related bands at the G point.
Supplementary Figure 7 | Absence of degradation in Ar gas atmosphere. (a) Optical image of an ultrathin bP crystal taken in an Ar glovebox with O$_2$ and H$_2$O concentration of less than 2 ppm ~30 min after exfoliation. (b) Optical image of the same ultrathin crystal after ~18 days in Ar atmosphere without any exposure to ambient air and. The scale bar is 10 µm.
**Supplementary Note 1 | Formation of transfer bubbles at the graphene/bP interface.**

The transfer of graphene and hexagonal BN (hBN) onto black phosphorus (bP) leads to the formation of transfer bubbles which indicate a self-cleaning effect\(^1\). Upon heat annealing the small transfer bubbles congregate into larger ones as has been reported for transfer of graphene onto other two dimensional crystals\(^2,1\). In Supplementary Fig. 1 we show atomic force microscopy (AFM) scans of graphene on bP before and after heat annealing, demonstrating the formation of the transfer bubbles.

**Supplementary Note 2 | Raman spectra of the passivating crystals.**

In order to exclude the presence of chemical or electronic interactions between the few-layer bP crystal and the top passivating layer we have analyzed the Raman spectra of the passivating graphene and hexagonal BN (hBN) layers on top of bP 48 hours after transfer. In particular, the Raman spectrum of graphene is known to be very sensitive to perturbations such as doping, strain, disorder, and adsorbed functional groups\(^3\). As shown in Supplementary Fig. 2 we do not observe any shift or broadening of the G or 2D peaks for graphene on bP. There are also no D or D’ peaks to indicate increased disorder of the graphene on bP. In fact, the observed ratio of the 2D to G peak on bP is even higher than on SiO\(_2\). The Raman spectrum of few-layer hBN on top of bP also does not show any changes when compared to the one on SiO\(_2\).

**Supplementary Note 3 | Electric field effect mobility estimation.**

Transport measurements of exfoliated bP using a SiO\(_2\) back gate show significant hysteresis which depends on the back gate sweep rate, the sweep direction, and the starting or extreme point of the sweep. Hysteresis is significantly suppressed by
measuring at lower temperature. Supplementary Fig.3 shows the effect of hysteresis on the drain current modulation at $T = 280$ K and $T = 200$ K.

**Supplementary Note 4 | Robustness of the improved electron transport.**

The improved electron transport for channels passivated in Ar gas atmosphere has been reproduced in all 5 out of 5 fabricated transport samples. Two of the transport samples allowed four-probe characterization and were therefore chosen for the discussion in the main text. In Supplementary Fig.4 we show two-probe transfer curves for three additional devices of different thickness showing similar qualitative behavior of improved electron transport and reduced p-doping in the passivated channels, as discussed in the main text. The thickness of the two thinnest devices was estimated by the optical contrast on top of SiO$_2$.

**Supplementary Note 5 | Hysteresis in the charge transport measurements.**

The 300 nm SiO$_2$ gate does not allow us to fully reach the conduction or valance band and the linear conduction regime. In Supplementary Fig.5 we plot the electric field effect mobility versus gate voltage for the transport samples from Fig.3 of the main text. From Fig.S5 can be seen that even at the highest gate voltage the mobility does not saturate and is still increasing. Combined with the fact that the non-passivated channels are p-doped due to oxidation, this leads to slightly higher hole mobility in the exposed channels of our devices.

**Supplementary Note 6 | DFT bandstructure of oxidized black phosphorus.**

Electron trap states in bP were shown to be induced by oxygen point defects in a recent theoretical study of monolayer phosphorene$^5$; it was found that two configurations of chemisorbed oxygen, the diagonal oxygen bridge (O$_{b-d}$) and the
horizontal oxygen bridge (O_{b-h}) lead to the formation of electron traps. As atmospheric oxygen molecules adsorb onto the surface of few-layer bP, the formation of electrically active oxygen bridge defects could be competing with the formation of other defects, like the dangling oxygen configuration, which are energetically more stable but are neutral and undetectable by electrical measurements.\textsuperscript{5} Since electronic relaxation processes are typically orders of magnitude faster than atomic relaxation processes, meta-stable electrically active bridge defects in air-exposed bP could be significantly altering the electronic behavior, similarly to the meta-stable epoxide defect in graphene.\textsuperscript{6,7}

Here we consider how the exposure to ambient atmosphere could produce electron traps by first principles density functional theory (DFT) calculations. In Supplementary Figure 6 we show electronic band structure of mono and few-layer bP with a chemisorbed oxygen diagonal bridge O_{b-d} defect. In monolayer the oxygen atom introduces two states within the bandgap which have O-p_x and O-p_z orbital character. With increasing number of layers, as the gap decreases, both the p_x and p_z states plunge and hybridize with the bP valence band. Since the p_z state is filled it does not affect the conduction of electrons, whereas the p_x state is an electron trap, consistent with experimental observation. We note that semilocal DFT calculations are known to underestimate the bandgap and the calculated electron trap state is highly dispersive which may be an artifact of the finite size of the calculation supercell. Nevertheless, despite these shortcomings the calculation qualitatively reproduces the inclusion of oxygen defects to pristine multilayer bP and suggests that the experimental observations could be due to formation of the oxygen bridge defects on the exposed channel, which are absent in the passivated channel.
**Supplementary Note 7 | Absence of bP degradation in Ar atmosphere.**

We do not observe any degradation when exfoliated black phosphorus (bP) crystals are kept in an Ar-filled glovebox with H₂O and O₂ concentration of less than 2 ppm. This is consistent with studies showing the importance of both H₂O and O₂ in the degradation process. In Supplementary Fig. 6 we show optical images of a thin crystal taken 18 days after exfoliation which do not show any noticeable change in the surface integrity.

**Supplementary Methods**

**Density-functional theory calculations**

Black phosphorus multi-layers were modeled within the framework of density-functional theory, as implemented in the siesta package. The generalized gradient approximation of Perdew, Burke and Ernzerhof is used for the exchange-correlation functional. The electronic core is accounted for by using ab-initio norm-conserving pseudopotentials with the Troullier-Martins parameterization in the Kleinman-Bylander form. The charge density was assumed to be independent on spin. The basis sets for the Kohn-Sham states are linear combinations of numerical atomic orbitals (double zeta polarised basis). The charge density is projected on a real-space grid with an equivalent cutoff energy of 250 Ry to calculate the exchange-correlation and Hartree potentials. A Monkhorst-Pack scheme with 4x4x1 points is used to sample the Brillouin Zone.
Supplementary References


