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Spectroscopy of buried states in black phosphorous with surface doping

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Abstract

Electrostatic gating or alkali metal evaporation can be successfully employed to tune
the interface of layered black phosphorus (BP) from the semiconductor to a 2D
Dirac semimetal. Although Angle Resolved Photoelectron Spectroscopy (ARPES)

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3 experiments have captured the collapse of the band gap in the inversion layer, the
4 quantitative estimate of the band structure evolution has been hindered by the
5 short escape depth and matrix elements of the probed photoelectrons. Here, we
6 precisely monitor the evolution of electronic states by time-resolved ARPES at
7 photon energy of 6.3 eV. The probing depth of laser based ARPES is long enough to
8 observe the buried electronic states originating from the valence band maximum.
9 Our data show that the band gap has the maximal value of 0.32 eV in the pristine
10 sample and it shrinks down monotonically by increasing the carrier concentration
11 in the topmost layer. Most interestingly, the band velocity of valence band increases
12 by a factor two along the armchair direction, overcoming the value reported in
13 graphene on silicon carbide (SiC). This control of band structure via external gating
14 is of interest for the design of optoelectronic devices.
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25 **Keywords:** black phosphorus; time-resolved ARPES; electron doping; band gap
26 engineering; electronic structure
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30 **Introduction**

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32 Van der Waals stacked black phosphorus (BP) has attracted interest in recent years
33 because of the widely tunable band gap as function of thickness, ultrahigh carrier
34 mobility in field effect transistors (FETs), and the possible emergence of
35 topologically protected states¹⁻⁵. It has been shown by high resolution angle
36 resolved photoemission (ARPES) experiments that a large surface dipole induced
37 via alkali atoms deposition can shift the relative position of the conduction and
38 valence band above the inversion point of the electronic gap⁶⁻⁷. The crossover from
39 insulator to Dirac semimetal⁸⁻⁹ leads to a pair of Weyl points with twofold
40 degeneracy in the inversion layer. Recent reports suggest that such a transition can
41 be reversibly controlled via gating techniques¹⁰. These findings highlight the
42 potentials of BP as building block for functional devices based on exotics transport
43 channels. Nonetheless, several controversial aspects on the band structure
44 engineering^{6-7,11} via surface doping still need to be clarified.
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5 The easiest approach to observe the dispersion of electronic states in an
6 accumulation layer is based on the combination of ARPES with in-situ evaporation
7 of alkali atoms^{6-7,11-13}. In the general case, a rigid band bending occurs at the very
8 initial doping level whereas a band gap renormalization takes place upon strong
9 electron doping. Due to the formation of the accumulation layer, the wave functions
10 of conduction band and valence band spatially redistribute in the puckered layer
11 structure. This process has extreme consequences when alkali atoms are deposited
12 on the surface of black phosphorous. Despite the existing experiments, two limiting
13 issues still challenge a quantitative analysis of the band gap collapse: 1) since BP is
14 an intrinsic *p*-doped semiconductor¹⁴, conventional ARPES cannot be employed to
15 extract the band gap until the chemical potential crosses the conduction band
16 minimum. As a consequence, the doping dependent evolution of the band gap can be
17 monitored only at high carrier concentration⁶⁻⁷. 2) As shown in Fig. 1, the surface
18 dipole created by alkali metal evaporation pokes the wavefunction of the valence
19 band towards the inner layers of BP¹⁵. It is therefore questionable whether a highly
20 surface sensitive technique as ARPES can monitor the buried wavefunction of the
21 valence band. As a matter of facts, previous ARPES experiments at 20-100 eV
22 observed an anomalous band gap of ~ 0.6 eV at the initial stage of electronic doping⁶.
23 This trend is not compatible with scanning tunneling spectroscopy measurements¹⁵
24 or ab-initio calculation of the band structure¹⁶, casting doubts on the electronic
25 nature of electronic states that have been effectively probed.
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44 In the present work, we overcome the aforementioned limits by performing time-
45 resolved ARPES in pristine and *in situ* electron doped BP with probe photon energy
46 centered at 6.3 eV. Time-resolved ARPES is a powerful technique that makes use of a
47 pump-probe scheme to access the electronic states dispersion of the photoexcited
48 surface¹⁷⁻¹⁸. By these means, we transiently occupy the conduction band of BP by
49 an ultrafast pump pulse and measure the gap value with a subsequent probe pulse.
50 Furthermore, the low photon energy of the probing beam results in an electron
51 escape depth that is long enough to observe a reliable evolution of the buried
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3 valence band (see the calculated electron density in Fig. 1). Our data show that the
4 bandgap monotonically shrinks from the pristine value of 0.32 eV down to the
5 inversion point. Most interesting, the Fermi velocity of the valence band displays a
6 considerable enhancement. In the high doping regime, the holes moving along the
7 highly dispersive direction acquire a band velocity larger than the one of graphene
8 on silicon carbide (SiC). Such tunability of the electronic structure is expected also in
9 the case of gated devices.
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17 **Experimental details**

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20 High-quality single crystals of BP (HQ Graphene) were cleaved and kept at the base
21 pressure of 8×10^{-11} mbar for all the duration of the experiment. The sample has
22 been mounted on a cryogenic manipulator and oriented according to low energy
23 electron diffraction patterns (LEED, see Supporting information). We deposited
24 increasing doses of Cesium (Cs) atoms by a commercial getter source. The source
25 has been carefully degassed and then approached to a distance of roughly 5 cm from
26 the sample. The evaporation of the alkali metal is obtained by a resistive heating of
27 the getter cartridge with the nominal current value. The deposition level leading to
28 the inversion point corresponds to roughly 0.3 monolayers of absorbed Cs. Each
29 step of alkali atoms deposition and Time-resolved ARPES measurement were
30 performed while constantly keeping the sample at the temperature of 125 K. No
31 sample transfer or manipulation that could destabilize temperature or base
32 pressure have been necessary between the subsequent deposition steps. All the
33 experiments have been performed on the femto-ARPES setup, using a Ti: Sapphire
34 laser system delivering 6 μ J Pulses with a 250 kHz repetition rate¹⁹. Part of the laser
35 beam (50 fs pulse, 1.57 eV) is used to pump the sample while the rest is employed to
36 generate the 6.3 eV photons as probe pulse through cascade frequency mixing in
37 BaB₂O₄ (BBO) crystals. The overall energy resolution of the experiment is $\cong 30$ meV
38 and the cross correlation between pump and probe pulses has full width at half
39 maximum (FWHM) of 150 fs. Time-resolved ARPES measurements have been
40 performed with pump fluence of 230 μ J/cm² and pump probe delay time of 1
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3 picosecond. These parameters guaranty a transient occupation of the conduction
4 band that is large enough in order to reliably extract the gap even in the pristine
5 surface¹⁷. Moreover, any photoinduced renormalization of band gap would be
6 negligible at such moderate pump fluence¹⁷.
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10 11 **Results and discussion**

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14 The evaporation of alkali metals is a common approach to generate accumulation
15 layers at the surface of semiconductors. Generally, the carrier concentration in the
16 topmost layer is linearly dependent on the surface density of alkali atoms. Fig. 2
17 shows a series of photoelectron intensity maps of the photoexcited state as function
18 of surface doping along the armchair and zigzag direction. We choose *p*-polarized
19 photons for photoelectron intensity map along the armchair direction (panels a-h in
20 Fig. 2). However, in the zigzag direction, the *p*-polarized probe couples strongly to
21 the conduction band. As a consequence, we choose *p*-polarized photons when the
22 occupation of the conduction band is weak (panels i-m in Fig. 2) while we polarize at
23 30° with respect to *p* orientation at higher filling level (panels n-p in Fig. 2). The
24 wave vector asymmetry and drop of signal at the conduction band minimum are due
25 to matrix elements of the photoemission process. The chemical potential μ_e of BP in
26 equilibrium conditions (pump off) is obtained by the reference spectrum of a
27 metallic compound. Upon photoexcitation a steady state Surface PhotoVoltage (SPV)
28 shifts the photoelectron intensity map with respect to the equilibrium case (see also
29 the Supporting information). The internal reference μ (see white dashed line in the
30 plots of Fig. 2) is given by μ_e plus the SPV shift.
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46 In agreement with previous finding, the alkali metal evaporation induces a surface
47 dipole that dramatically restructures the electronic states in the accumulation layer.
48 In Fig. 3, we plot the gap value Δ (energy of the conduction band minimum E_{CB}
49 minus energy valence band maximum E_{VB} , and also see the Supporting information
50 for the positions of E_{CB} and E_{VB}) as a function of the energy distance $\mu - E_{CB}$. Note that
51 the band gap of BP keeps constant at ~ 0.32 eV as long as the chemical potential lies
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3 within the gap ($\mu - E_{CB} < 0$). In this regime the surface doping mainly compensates
4 the acceptor states due to intrinsic vacancies. The electrons are transferred in the
5 topmost layer of black phosphorus when $\mu - E_{CB} > 0$ and the associated surface
6 dipole induces a measureable shrinking of the bandgap for $\mu - E_{CB} > 0.07$ eV. Note
7 that the initial $\Delta = 0.32$ eV is in good agreement with scanning tunneling
8 spectroscopy data acquired on a pristine surface¹⁵ and with infrared measurements
9 of a bulk sample¹⁴. The band gap decreases linearly with $\mu - E_{CB}$ when the charge
10 transfer keeps on filling the conduction band of the topmost layers. The inversion
11 point $E_{CB} = E_{VB}$ takes place when $\mu - E_{CB} = 0.3$ eV, while Δ reaches the negative value
12 of -0.2 eV at the largest doping level. We can estimate the electronic density in the
13 accumulation layer from the area of the electronic pocket at a given filling of the
14 conduction band (Luttinger theorem). The area of the ellipse $\pi k_x^F k_y^F$ results in an
15 electronic density of 4.5×10^{13} 1/cm² at the inversion point. This value is roughly a
16 50% lower than the critical surface density reported by ARPES experiments at
17 higher photon energy⁷. In our opinion, the ARPES signal of Ref. 6,7 does not peak at
18 the valence band maximum but is dominated by electronic states at higher binding
19 energy. A manifold of such states exists because of the sizable dispersion of the
20 valence band along the interlayer direction. These states would cross the
21 conduction band at an electronic density higher than the real inversion point and
22 may largely dominate the photoelectron intensity at 100 eV if their electronic
23 density extends nearer to the surface plane.
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42 As shown by Fig. 3(a) the evaporation of potassium (K) instead of Cs atoms generate
43 very similar results. It is interesting to compare in Fig. 3 the band gap evolution of
44 our experiment with Scanning Tunneling Microscopy (STM) of a gated BP flake¹⁵.
45 The agreement between the two different measurements is excellent if we assume
46 that a stark field of 0.1 V/nm displaces the chemical potential by 0.2 eV.
47 Furthermore, our data are consistent with the monotonic decrease of gap value that
48 has been reported by density-functional theory (DFT) calculations¹⁶.
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3 These favorable comparisons indicate that our experiment is indeed detecting the
4 conduction band minimum and valence band maximum of the accumulation layer.
5 The calculated local density of electronic states supports our claim. As shown in Fig.
6 1, the square wavefunction of electronic states at the top of the E_{VB} shifts by roughly
7 5 nm away from the surface upon the application of an external electric field of 0.1
8 V/nm¹⁵. This distance is comparable to the escape depth of photoelectrons
9 generated by 6.3 eV photons whereas is 5 times longer than the photoelectron
10 escape depth of a ~ 100 eV probing source. We have recently shown that topological
11 states buried by absorbed molecules can be visible by laser based ARPES while they
12 go undetected at higher photon energy²⁰. By the same token, we think that the
13 synchrotron based experiments^{6,7} could fail to observe the top of valence band of
14 the accumulation layer.
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26 In order to gain quantitative insights on the evolution of electronic states, we fit the
27 dispersions along the armchair direction by the pseudorelativistic expression
28 $E = E_0 \pm (\delta + \sqrt{m_x^2 v_x^4 + v_x^2 p^2})$, where $m_x = m_x^c$ ($m_x = m_x^v$) is the effective mass
29 for conduction band (valence band), $v_x = v_x^c$ ($v_x = v_x^v$) is the band velocity in the linear
30 section of conduction band (valence band). E_0 and δ are constants. Along the zigzag
31 direction, the dispersion follows the parabolic form $E = E_0 \pm (\Delta/2 + p^2/2m_y)$,
32 where Δ is the electronic gap, and $m_y = m_y^c$ ($m_y = m_y^v$) is the effective mass of the
33 conduction band (valence band). As shown by the dotted lines in Fig. 2, the fitting
34 curves reproduce with high accuracy the band dispersion along both
35 crystallographic axes. The band gap turns out to be $2(\delta + m_x v_x^2)$ in the armchair
36 direction and $\Delta = 2(\delta + m_x v_x^2)$ is satisfied for each of the doping levels (with error
37 bars of ± 0.03 eV). The deformation of band dispersion upon electron doping is
38 quantified by extracting fitting parameters for each band and high symmetry
39 direction. Along zigzag direction, the fitting parameters m_y does not depend on Cs
40 deposition, neither for the conduction band ($m_y^c = 0.9 \pm 0.2m_e$) nor for valence
41 band ($m_y^v = 0.4 \pm 0.1m_e$). Along armchair direction, the Cs evaporation does not
42 modify the fitting in the conduction band parameter $m_x^c = 0.055 \pm 0.01m_e$ and
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3 $v_x^c = 0.7 \pm 0.1 \times 10^6$ m/s. Nonetheless, Fig 2(a-h) show a very interesting evolution
4 of the valence band along the armchair direction. Figure 3(b-c) shows the values of
5 v_x^v and m_x^v as a function of $\mu - E_{CB}$. Upon increasing doping level, the effective mass
6 m_x^v shrinks below the detection limit while v_x^v increases by nearly two times (from
7 $v_x^v = 0.7 \pm 0.1 \times 10^6$ m/s to $v_x^v = 1.25 \pm 0.1 \times 10^6$ m/s). A similar tuning of Fermi
8 velocity has been previously achieved in graphene by employing substrates of
9 different dielectric constant²¹. The maximal $v_x^v = 1.25 \times 10^6$ m/s value of this work is
10 already higher than the Fermi velocity reported for graphene on SiC substrate and it
11 is only a factor of two lower than the value reported in suspended graphene sheets²².
12 The electron-electron interaction and the substrate polarizability explain the
13 modified dispersion observed in graphene. Here instead, the formation of an
14 accumulation layer shapes Fermi velocity and effective mass. Eventually, the
15 anisotropic screening due to the self-organization of alkali metals should also be
16 considered²³. The STM imaging of ref. 23 reveals that anisotropic charge screening
17 from the surface layers induce the development of 1D potassium structures.
18 Potassium atoms reorganize in short chains oriented along the armchair direction.
19 Possibly, the potassium chains modify the electronic band dispersion in the
20 accumulation layer, leading a larger Fermi velocity along the armchair direction.
21 This hypothesis should be tested by ab-initio calculations of the electronic states in
22 such specific configuration. Further theoretical and experimental investigations will
23 be necessary in order to clarify this issue.
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42 **Conclusions**

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45 In conclusion, we performed Time resolved photoelectron spectroscopy of BP with
46 surface doping. Aiming for the larger escape depth of electrons emitted by a probe
47 photon energy of 6.3 eV, we could observe the evolution of the buried valence band
48 as a function of alkali metal deposition. Our data show that the band gap decreases
49 monotonically from the bulk value of 0.32 eV down to the inversion point. This
50 finding is in excellent agreement with scanning tunneling spectroscopy
51 measurements of gated BP and first principle calculations. A closer inspection
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reveals that the Fermi velocity of the electrons in the valence band increases by a factor of two upon doping the BP surface by Cs atoms. At the highest carrier concentration Fermi velocity of doped BP exceeds the value of the Dirac fermions in graphene on SiC. This observation suggests that mobility of excited electrons in the accumulation layer of black phosphorous may considerably increase at large carrier density.

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Supporting Information

Low energy electron diffraction (LEED) on black phosphorus; The shift of conduction band and valence band as function of electron doping; Surface PhotoVoltage (SPV) and band bending as function of electron doping.

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Figure 1

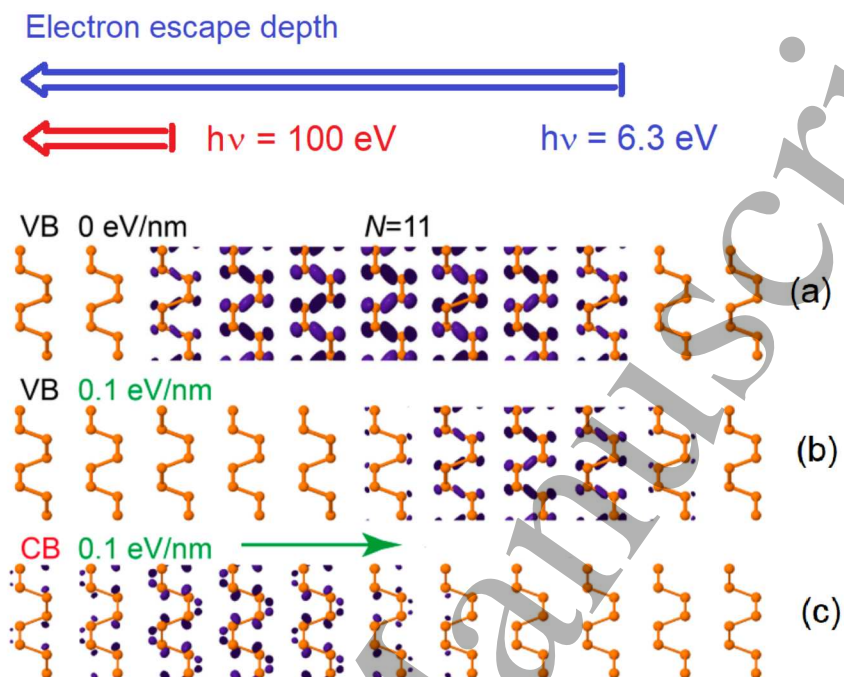


Figure 1. (a) Calculated spatial distribution of electronic density obtained by projecting the states at the top of the valence band on the atoms of a slab. (b) Puckering of valence band states after the application of 0.1 eV/nm field directed towards the right side of the slab. (c) Projected states of the conduction band minimum in the presence of the polarizing electric field. The blue and red arrows indicate the escape depth of photoelectrons probed by 6.3 eV and 100 eV , respectively. This image has been readapted from the calculations and pictures of reference [15]. Copyright (2017) American Chemical Society.

Figure 2

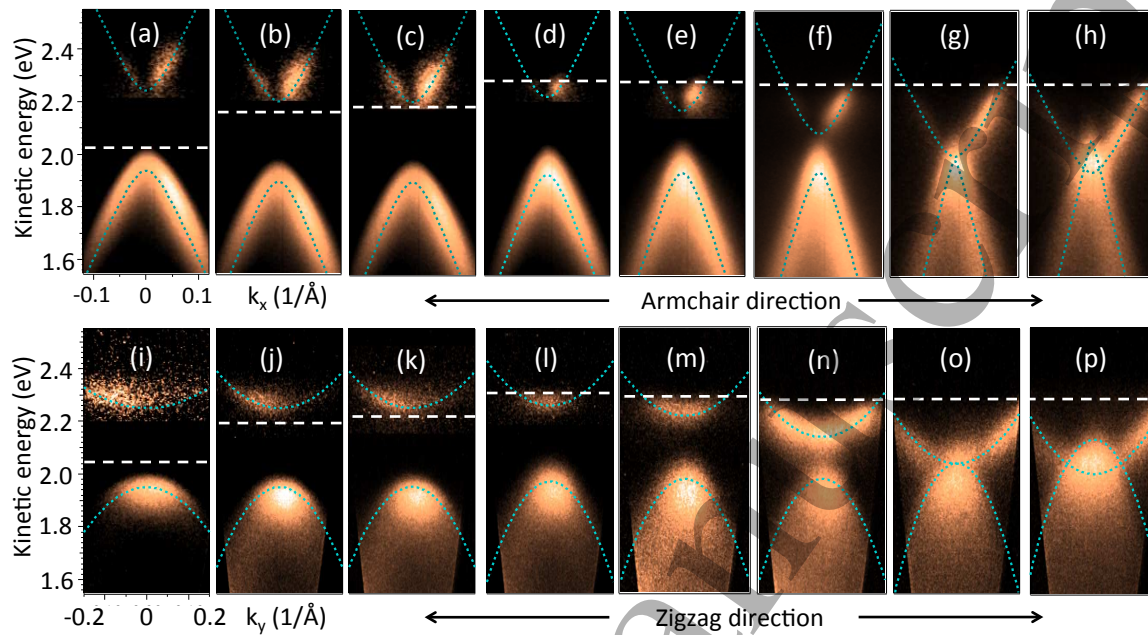


Figure 2: (a-h) Time-resolved ARPES data of BP along the armchair direction, as function of surface doping. (i-p) Time-resolved ARPES data of BP along the zigzag direction, as function of surface doping. The dashed lines indicate the position of chemical potential μ . At low doping levels in (a-c) and (i-k), the gap has been visualized by measuring the photoelectron intensity maps at delay time of 1 ps after photoexcitation. At high doping levels in (d-h) and (l-p), the gap has been visualized by measuring the photoelectron intensity maps at negative delay. The conduction band signal of (a-e) and (i-l) has been multiplied by factors between 5 to 200, in order to equalize the intensity of the color scale.

Figure 3

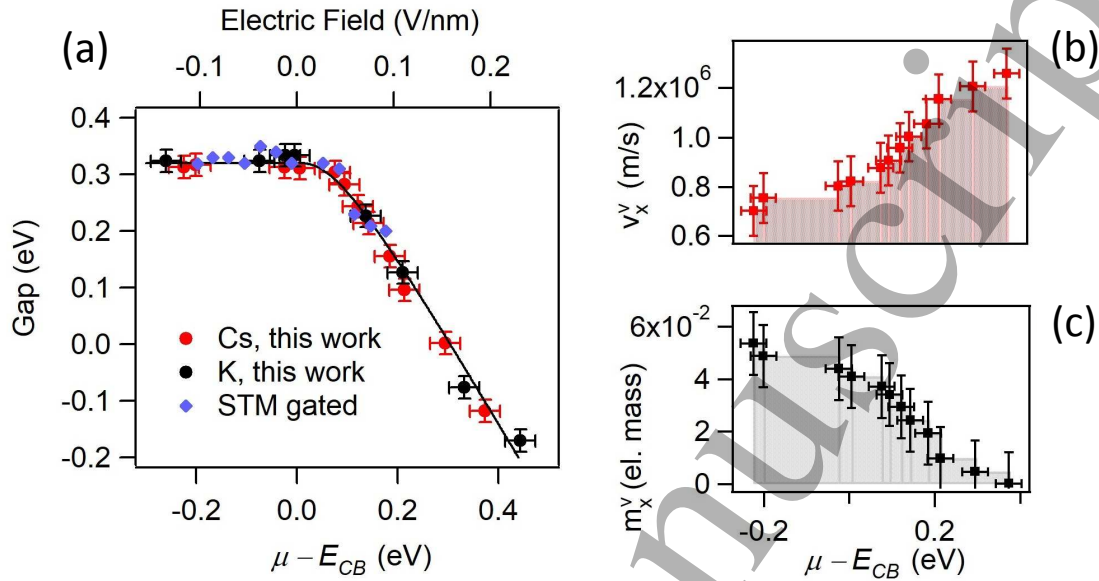


Figure 3: (a) Band gap at the surface of BP as function of surface doping by deposition of Cs atoms (red filled circles) and K atoms (black filled circles), respectively. The surface doping (bottom axis) is quantified by the difference between chemical potential μ and the minimum of the conduction band energy E_{CB} . The solid line is a guide to the eye. As a term of comparison, the gap value (blue diamond) as function of polarizing field (top axis) is extracted from Ref. [15]. (b) The fermi velocity of the valence band along armchair direction and as function of doping level. (c) The effective mass of the valence band along armchair direction and as function of doping level.