Gate-tunable Giant Stark Effect in Few-layer Black Phosphorus

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Abstract:

Two-dimensional black phosphorus (BP) has sparked enormous research interest due to its high carrier mobility, layer-dependent direct bandgap and outstanding in-plane anisotropic properties. BP is one of the few two-dimensional materials where it is possible to tune the bandgap over a wide energy range from the visible up to the infrared. In this article, we report the observation of a giant Stark effect in electrostatically-gated few-layer BP. Using low temperature scanning tunnelling microscopy, we observed that in few-layer BP, when electrons are injected, a monotonic reduction of the bandgap occurs. The injected electrons compensate the existing defect-induced holes and achieve up to 35.5% bandgap modulation in the light-doping regime. The local density of states in few-layer BP, when probed by tunnelling spectroscopy, shows characteristic resonance features arising from layer-dependent sub-band structures due to

25 quantum confinement effects. The demonstration of an electrical gate-controlled giant Stark

26 effect in BP paves the way to designing electro-optic modulators and photodetector devices that

27 can be operated in a wide electromagnetic spectral range.

28 **Keywords:** *Black phosphorus, Giant Stark effect, bandgap, electrostatical-gating, scanning*

29 *tunnelling microscopy*

30 **TEXT**

31   The Stark effect is the shifting and splitting of atomic energy levels under the influence of

32 an externally applied electric field. In semiconductors, in the presence of an electric field, the

33 Stark effect will cause the energy levels to shift, which in turn modifies the bandgap. Hence, by

34 changing the electric field, the electro-optical response of the material can be tuned.[1,2] In

35 quantum-confined systems, the Stark effect often gives a strong optical bandgap modulation due

36 to inhibited exciton field ionization and reduced field screening as opposed to that in bulk

37 materials.[3,4] The quantum-confined Stark effect (QCSE) is the basis on which III-V

38 semiconductor-based optical modulators operate.[3] However, the relatively low energy offset

39 between the quantized transitions and the surrounding cladding (such as GaAs, with a bandgap

40 ~1.52 eV at 4K) means that even operational fields greater than only a few tens of kV cm^{-1} can

41 cause the tunnelling-out of the electrons to occur.[4] Some two dimensional (2D) materials can

42 potentially show a stronger Stark effect beyond those encountered in quantum-well structures

43 due to its weaker dielectric screening, and its strongly anisotropic properties. However, it is

44 difficult to induce a semiconductor-to-metal transition in bilayer transition metal dichalcogenides

45 (TMDs) by tuning the externally applied electric field because of the relatively large bandgap

2

46 (! 1eV) of these materials, the critical external electric field for such a transition being in the

47 range 2–3 V/nm.[5]

48 Black phosphorus (BP), a layered allotropic form of elemental phosphorus, has attracted

49 increased attention from researchers because of its layer-dependent bandgap spanning the entire

50 electromagnetic spectrum, which is unmatched by any other 2D material known to date.[6-12] BP

51 has both high mobility and a thickness-dependent direct bandgap ($\sim$2.0 eV for monolayer and

52 $\sim$0.3 eV for bulk sample owing to the strong interlayer coupling).[12-14] In view of its

53 orthorhombic crystal lattice with a puckered honeycomb structure, the conduction band

54 minimum (CBM) and the valence band maximum (VBM) of BP are mainly contributed by

55 localized P $3p_z$ orbitals (vertical to the puckered plane) rather than by $3p_x$ and $3p_y$, which means

56 that the electronic properties of BP are very sensitive to electric field applied perpendicularly.[15]

57 The Stark effect coefficient is a parameter which reflects the rate of the reduction of band gap

58 with applied field strength. The small bandgap ($\sim$0.3 eV in multilayer or bulk limit) and

59 monotonically increasing Stark effect coefficient with layer number allows the

60 semiconductor-to-metal transition of few-layer BP to be achieved at a relatively low critical field,

61 for instance, the critical field $E_c \approx 0.68$ V/nm for 10 layers.[15,16] In addition, according to

62 nonlinear Thomas-Fermi theory, in view of the moderate screening effects of BP, BP flakes

63 thinner than 10-nm will be strongly perturbed by an applied external electrical field.[17] Recently,

64 potassium dopant has been used to tune the electronic bandgap of bulk BP and the transition

65 from a moderate-gap semiconductor to a band-inverted semimetal was induced by applying an

66 ionization-induced vertical electric field.[18] It has also been demonstrated that introducing surface

67 transfer dopants such as caesium carbonate, molybdenum trioxide or depositing cross-linked

68 poly(methyl methacrylate) on BP surface is capable of tuning the transport properties of BP.[19,20]

69   However, the drawbacks of chemical doping include instability in air and increased probability

70   of introducing charged scattering centres. In addition, it is difficult to achieve reversible doping

71   using chemical dopants. In contrast, electrostatic doping, which is continuously tunable,

72   non-destructive and carried out in ambient atmosphere, has been widely adopted to tune the

73   optoelectronic properties of 2D materials and their heterostructures.[21-30] It has been predicted

74   from theory that the electrical and optical properties of ultrathin BP can be effectively tuned by

75   electrostatic doping.[15,16,31,32] However, difficulties in the preparation of 2D BP device and its

76   high reactivity when exposed to air have so far limited systematic experimental

77   investigations.[28-30,33-36]

78   Here, we report a LT-STM study on a few-layer BP device to demonstrate a giant Stark

79   effect in few-layer BP flakes induced by electrostatic gating. We find that the application of an

80   external perpendicular electric field across few-layer BP flakes leads to a monotonic narrowing

81   of the bandgap with increasing field intensity. We achieve a notable bandgap reduction of

82    $\sim$35.5% (from 310 ± 20 meV to 200 ± 20 meV) by applying a vertical field of 0.1 V/nm. It

83   is expected therefore, that few-layer BP can be transformed from moderate-gap semiconductor to

84   a band-inverted semimetal under a more intense electric field. Furthermore, we observe

85   resonance features in the dI/dV spectra, which originate from the thickness-dependent sub-band

86   structures in few-layer BP. The gate tunable Stark effect of BP implies that it can be used as an

87   electro-optical modulator operating in the far and mid-infrared regions.

88   To probe the effect of the applied electric field on the electronic properties of BP, we

89   prepared a field effect transistor (FET) device consisting of a few-layer-layer BP flake stacked

90   on a SiO_2 substrate with a doped Si back gate as shown in **Figure 1**a (see methods in SI for more

91   details). Using the well-established dry transfer technique, a few-layer BP flake was placed on

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92   the surface of a pre-patterned gold electrode deposited on a SiO_2/Si substrate.[37] The gold

93   electrode served as the electrical contact required for STM measurements (Figure 1b). The

94   crystallinity of the BP flake was characterized using Raman spectroscopy. Figure 1c shows the

95   Raman spectrum with the three intrinsic peaks at $\approx$ 362.9, 438.7, and 467.4 cm^{-1}, which are

96   attributed to the A_g^1, B_{2g} and A_g^2 phonon modes respectively, in few-layer BP resulting from its

97   orthorhombic crystal structure (shown in the upper panel of Figure 1b).[7,11,38] To minimize

98   surface degradation, BP devices were immediately loaded into the LT-STM chamber after device

99   fabrication. The thickness of BP flakes probed in our STM study was determined to be

100 equivalent to 11 layers using atomic force microscopy (AFM) (see supporting Figure S1).

101 **Figure 2**a shows a typical STM topographic image of a thin BP flake for a scan area of 50

102 nm $\times$ 50 nm. It is seen that arrays of one-dimensional (1D) zigzag atomic rows corresponding

103 to the upper rows of atoms in the puckered BP layer are clearly resolved, similar to the atomic

104 STM images of *in-situ* cleaved bulk BP sample in previous reports.[39,40] Our high resolution STM

105 images reveal that an intact BP lattice is present in a majority of the flat surface regions. The

106 defect-related feature showing a bright topographic contrast in STM imaging (Figure 2a), is

107 presumably due to buried impurities or atomic substituents in the BP host lattice. These defects

108 may contribute to hole doping in pristine BP crystals; this aspect is described in a later section.

109 According to the atomic structural model of BP (Figure 2b), each P atom is covalently

110 bonded to three nearest neighbour atoms through $3p$ orbitals to form a puckered structure

111 consisting of an upper row of P atoms (red and white balls) and a lower row of P atoms (violet

112 balls).The wave function of the lower P atoms is expected to decay exponentially in the vertical

113 direction and thus only the P atoms located on the top are clearly resolved in the STM

114 topographic image as shown in the close up image (Figure 2c). The lattice constants measured

5

115 along two directions (armchair "xx" and zigzag "xy" shown in Figure 2b, top view) are

116 determined to be 4.46 $\pm$ 0.13 Å and 3.32 $\pm$ 0.05 Å, respectively, which are in good agreement

117 with previously reported values for bulk BP.[12,13,39,40] Figure 2d shows a wide energy range dI/dV

118 spectrum (which reflects the local density of states, LDOS) collected from areas on the BP

119 surface far away from defective regions. The intrinsic spectrum is highly asymmetric and shows

120 a wide "gap-like" signature surrounded by a series of well-defined resonant peaks labelled as V_n

121 in the valence band and C_m in the conduction band. The origin of these prominent resonance

122 features will be discussed later in the article. Due to the relatively large tip-sample separation,

123 the dI/dV signal in the vicinity of the Fermi energy (E_F, V_S= 0 V) is low and thus the prominent

124 features in the spectrum occurs at high energy away from E_F.[21,39-41] To better resolve the

125 electronic states close to E_F, a lower set point (V_S= -1.0V, I= 1.0 nA) has been used to collect

126 the dI/dV spectrum from the same surface region as shown in Figure 2f. The bandgap of the

127 as-prepared BP (E_g= E_{CBM} $-E_{VBM}$, see supporting Figure S2 for details of the calculation) is

128 determined to be 310 $\pm$ 20 meV, consistent with previously reported behaviour and values for

129 bulk BP.[12,40] The slight fluctuation of E_g may be attributed to a tip-induced band bending effect,

130 which has been carefully investigated in this work (see supporting information for details). Our

131 STS data also reveal that the as-prepared BP flakes are heavily p-doped, which is confirmed

132 from the closeness of the VBM energy and E_F (Figure 2f).

133 Next, we probe the evolution of the local electronic properties of BP as a function of the

134 applied back gate voltage (V_g). In contrast to n-doping using K atoms, electrostatic gating

135 enables us to tune the doping levels in thin BP flakes to obtain p-type or n-type behavior.[18]

136 **Figure 3**a shows the gate-voltage-dependent STS spectra acquired in the defect-free region of

137 the 11-layer BP flake. At positive gate voltages (V_g > 0 V), negative charge carriers are injected

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138   into the BP flake leading to n-type doping of BP. Hence, the band structure shifts towards the

139   negative sample bias region [from the green line (0 V) up to the red line (+60 V)]. To our

140   surprise, the shift of the band structure towards higher potential energy [(from the green line (0 V)

141   down to the blue line (−60 V)] is negligible. This observation is tentatively attributed to the

142   heavily p-doped nature of the thin BP flakes (E_F is located at the edge of the VB and the presence

143   of shallow acceptor states), which leads to Fermi level pinning. In order to determine the values

144   of the VBM, CBM and bandgap more accurately, the logarithm of the dI/dV spectra collected at

145   different gate voltages on thin BP flakes were plotted (shown in Figure 3b and 3c) (refer to

146   supporting Figure S2 for more details). Using this method, we extracted the gate-dependent

147   energies corresponding to CBMs, VBMs and the resonance peaks as shown in Figure 3d. It can

148   be clearly observed that the CBMs and VBMs (pinned at the E_F) barely shift at $V_g \leq 0$ V, and

149   consequently, the overall shift in the band structure of BP is negligible. In contrast, at $V_g \geq 0$ V,

150   a pronounced downward shift of the entire band structure is observed. Interestingly, we also

151   observed that the bandgap reduces significantly with increase in applied gate voltages at $V_g \geq 0$

152   V. In addition, the observed resonance peaks at different gate voltages move with the band edges

153   depending on whether they are in the conduction band or the valence band region.

154   Here we employ Scanning Tunnelling Spectroscopy (STS) to measure field-dependent

155   single-particle electronic bandgap of few-layer BP as opposed to two-particle optical bandgap

156   *via* optical adsorption.[41] Hence, the reduction in the bandgap of 11-layer BP flakes as a function

157   of gate voltages can be explained on the basis of a giant Stark effect rather than Franz-Keldysh

158   effect reported in the recent work on optoelectronic modulation of BP.[28,29,42] In the absence of a

159   giant Stark effect, a rigid band shift typically occurs with gate voltage and E_g remains unchanged

160   even when electric field is applied (**Figure 4**a, left. $E_g = E'_g =$ constant).[24,43] In the presence of

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161   the Stark effect, the band edges of VB and CB gradually move towards each other with

162   increasing gate voltage due to the spatial redistribution of their wave functions in the puckered

163   layer structure, as shown in Figure 4a (right). To understand the asymmetry in gap reduction

164   observed in Figure 3a and 3d, we provide a schematic to explain the experimental results at

165   different gate bias. Initially (V_g= 0 V, left panel of Figure 3e), the few-layer BP sample is

166   p-doped (VBM of BP flake nearly touches the Fermi energy, Figure 2f and green line in Figure

167   3b) and therefore, free positive charge carriers distribute uniformly in the real space of few-layer

168   BP. When a negative gate voltage is applied (V_g < 0V, electrons accumulate in the p++ silicon

169   layer and thus holes will be induced in the BP layers), additional holes fill the valence states. As

170   a result of the accumulation of holes, screening of the gate electric field occurs (right panel in

171   Figure 3e) and the measured bandgap of BP remains approximately constant (Figure 3b). On the

172   other hand, a positive gate voltage injects electrons into the BP flake. A depletion layer is formed

173   with different heights depending on the field strength (left panel, Figure 3f), which facilitates the

174   penetration of the electric field into the whole BP flake (right panel, Figure 3e). During this

175   process, two effects can occur: i) a potential drop that shifts the CB and the VB towards lower

176   energy and ii) a gap reduction due to the Stark effect as shown in Figure 3c (V_g= 0V, 20V and

177   30V). With increasing voltage (E_F locates right in the middle of bandgap, here, $V = 29 \pm 1V$),

178   the holes become completely depleted by back-gating. At even higher positive gate voltages, the

179   BP flake becomes electron doped, (as shown in Figure 3f, right panel) and both the VB and the

180   CB move towards the negative sample bias region with the latter approaching the Fermi level.

181   Once the CB touches the Fermi level, the "pinning" effect dominates and the gap reduction is

182   arrested. For the latter two cases shown in Figure 3f (Vg > 0 V), the bandgap of few-layer BP is

183   reduced to 200 $\pm$ 20 meV even at a moderate gate voltage (V_g = 60 V), due to the giant Stark

184 effect.[1,2,16] The magnitude of bandgap modulation achievable by the Stark effect is predicted to

185 be larger in thinner BP flakes due to its larger bandgap as compared to thicker BP, where

186 electro-optical modulation from the visible to far infrared regime can be achieved in monolayer

187 and bilayer BP.[7,15,16] Our theoretical calculations reveal that the Stark coefficient defined as $S_{nL} =$

188 $-(dE_g/dE_{ext})/e$ increases monotonically as a function of layer thickness (see supporting Figure

189 S3), suggesting that a large critical field strength is required to induce the

190 semiconductor-to-semimetal phase transition for thinner samples.

191 In order to estimate the magnitude of reduction of E_g by Stark effect and to identify the

192 origin of the resonance peaks in the dI/dV spectra, we calculate the electronic structure of

193 few-layer BP under different external electrical fields, using density functional theory (DFT)

194 calculations within the Perdew-Burke-Ernzerhof parametrisation (PBE).[12,16] Figure 4b shows the

195 highest occupied states at the Γ point for a 11-layer BP sample without (top) and with (bottom)

196 0.1 V/nm electrical field, where a strong redistribution of the VBM states along the z direction is

197 observed in the latter. Even though the value of the estimated bandgap is slightly underestimated

198 using the PBE approximation, modifications of the band structure due to small perturbations can

199 be correctly predicted. For low fields, it is found that the bandgap varies quadratically with the

200 electric field as expected from the system symmetry. Since phosphorene is centrosymmetric and

201 has no dipole in the direction of the field, the first order term in the expression for the energy

202 levels ε_i in E vanishes, and the leading terms are (as found by perturbation theory) given by :

203 $$\varepsilon_i = \varepsilon_i^0 + \sum_{k \neq i} \frac{M_{ik}^{zz}}{\varepsilon_i - \varepsilon_k} E^2 \qquad (1)$$

204 where M_{ik}^{zz} is the dipole matrix element between states i and k.

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205   This is qualitatively similar to the experimentally observed behaviour (Figure 4c). If the intensity

206   of the electric field is calculated from the experimental values for V_g assuming that the system

207   can be approximated by two planar capacitors in series (see supporting Figure S4 for more

208   details), the experimentally obtained rate dE_g/dE is of the same order of magnitude as

209   expected from the theoretical prediction (inset in Figure 4c), despite despite the bandgap

210   underestimation, the uncertainty in the estimation of the capacitance, and tip-induced band

211   bending effects which may contribute to decrease the measured dE_g/dE.[24,44,45] In fact, a large

212   magnitude of bandgap reduction should be achievable by applying a high electric field. By

213   performing transport studies on a dual-gated BP transistor, Deng *et al.* reported that the band gap

214   can be narrowed to ~50 meV under a high electric field strength of 1.1 V/nm by measuring the

215   minimum transport conductivity and carrier density at different temperatures.[30]

216   In the STS spectra (Figure 2d and 2f) of the 11-layer BP flake, in addition to the gap feature,

217   resonance peaks are observed. The tendency of these peaks to move in the same direction as the

218   band edges as a function of the gate voltage indicates that they originate from electronic states

219   and are not due to tip-induced charging effects (see supporting Figure S5).[22,41] The energy

220   separation between the adjacent resonances observed here is larger than 150 meV, which is much

221   higher than the energy of the most energetic phonon mode of BP (~66.1 meV).[38] The

222   nearly-rigid shifting of the resonance peaks together with the band edges also rules out possible

223   contribution from electron-plasmon coupling (see supporting information for more details on

224   other possible origins of these peaks).[46-48] Instead, a sub-band model due to the quantisation of

225   BP layers with finite thickness can be used to explain the thickness-dependent resonance features

226   in the STS spectra, which is verified both by our DFT calculations with PBE and through a

227   phenomenological tight-binding model.[14,49] LDOS obtained from DFT calculations are in good

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228   agreement with the STS spectra recorded on BP with different layer numbers (see supporting

229   Figure S6). Due to the strong interlayer interaction, both the CBs and VBs of N-layer

230   phosphorene are quantized and split into N 2D sub-bands. This quantum-well like structure

231   creates the characteristic sub-band structures of few-layer BP, which in turn modifies its density

232   of states. In the absence of other interactions and thermal effects, this DOS modulation may

233   manifest as singularities in a system with a parabolic band dispersion. The spacing between the

234   peaks can be approximated by a simple one dimensional tight-binding band model

235    $E_{N,n} = E_{N,n}^{0} + 2\gamma \cos(\frac{n\pi}{N+n})$ (2)

236   where $n =$1, 2..., N, is the subband index, $E_{N,n}^{0}$ is the average band energy, and $\gamma =$0.55

237   (HSE), 0.49 (PBE). Based on this simplified tight-binding model, an integrated evolution of the

238   sub-band structures of few-layer BP is empirically described (Figure 4d). This model describes

239   the band energy at the Γ point of the 2D Brillouin zone considering only the nearest-neighbour

240   layer-layer interaction while neglecting electron-electron and electron-hole (exciton effect)

241   interactions, in accordance with our experimental conditions.

242   To further elucidate the nature of the resonance peaks in STS, we compare the experimental

243   dI/dV spectra with the DOS obtained from DFT calculations for few-layer BP ranging from 1–12

244   layers (Figure 4e, see supporting Figure S7 for a full version). The large hole effective mass

245   along the $\Gamma - Y$ direction leads to additional contributions in DOS, which gives rise to the

246   observed peaks in STS (shown in Figure 2f). Moreover, the sharp peaks which are seen

247   appearing in the -1.5 to -2 eV energy range (V'_{n}, Figure 2d) originate from deep-lying flat

248   sub-bands. Our calculations confirm the presence of sub-bands with energy spacing similar to the

249   experimentally observed resonance peaks. One remarkable feature is the possibility for optical

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250 transitions between quantized sub-bands in the same band, leading to multiphoton absorptions.

251 The unique sub-band structure also suggests that BP may qualify as an emerging candidate

252 material for quantum cascade lasers.[50]

253 The giant Stark effect in few-layer BP device allows the bandgap of BP to be electrically

254 tuned. For 11-layer-thick BP, the bandgap can be reduced from 310 ± 20 meV to 200 ± 20

255 meV. Interestingly, layer-dependent sub-band structures (especially the sub-bands at Γ point)

256 have been experimentally observed in our STS measurements, where we found that the number

257 of sub-bands is directly correlated to the number of layers in BP. This suggests that STS can be

258 used as a tool to accurately determine the layer number in few-layer BP. The reduced bandgap of

259 few-player BP due to the giant Stark effect shifts its working spectral range to far-IR while the

260 sub-band transition induces multiphoton absorptions.[50-52] Moreover, the giant Stark effect breaks

261 the symmetric BP quantum well-like electronic structure, leading to the relaxation of selection

262 rules and consequently activates "forbidden" optical transitions from the valence sub-band to the

263 conduction sub-band with different quantum numbers.[52] Our work suggests that the inter-band

264 and inter sub-band transitions in BP can be continuously varied over a wide electromagnetic

265 spectral range from visible to far IR by varying the electric field, making BP a versatile material

266 platform for applications in IR optical modulators and quantum cascade lasers.

267

268 **ASSOCIATED CONTENT**

269 The Supporting Information is available free of charge on the ACS Publications website.

270 Details of the experiment method, thickness determination, bandgap calculation method,

271 layer-dependent properties of BP, exclusion of possible origin of resonance peaks, calculated

272 band structure of 1-12 layer BP.

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284   **Notes**

285   The authors declare no competing financial interests.

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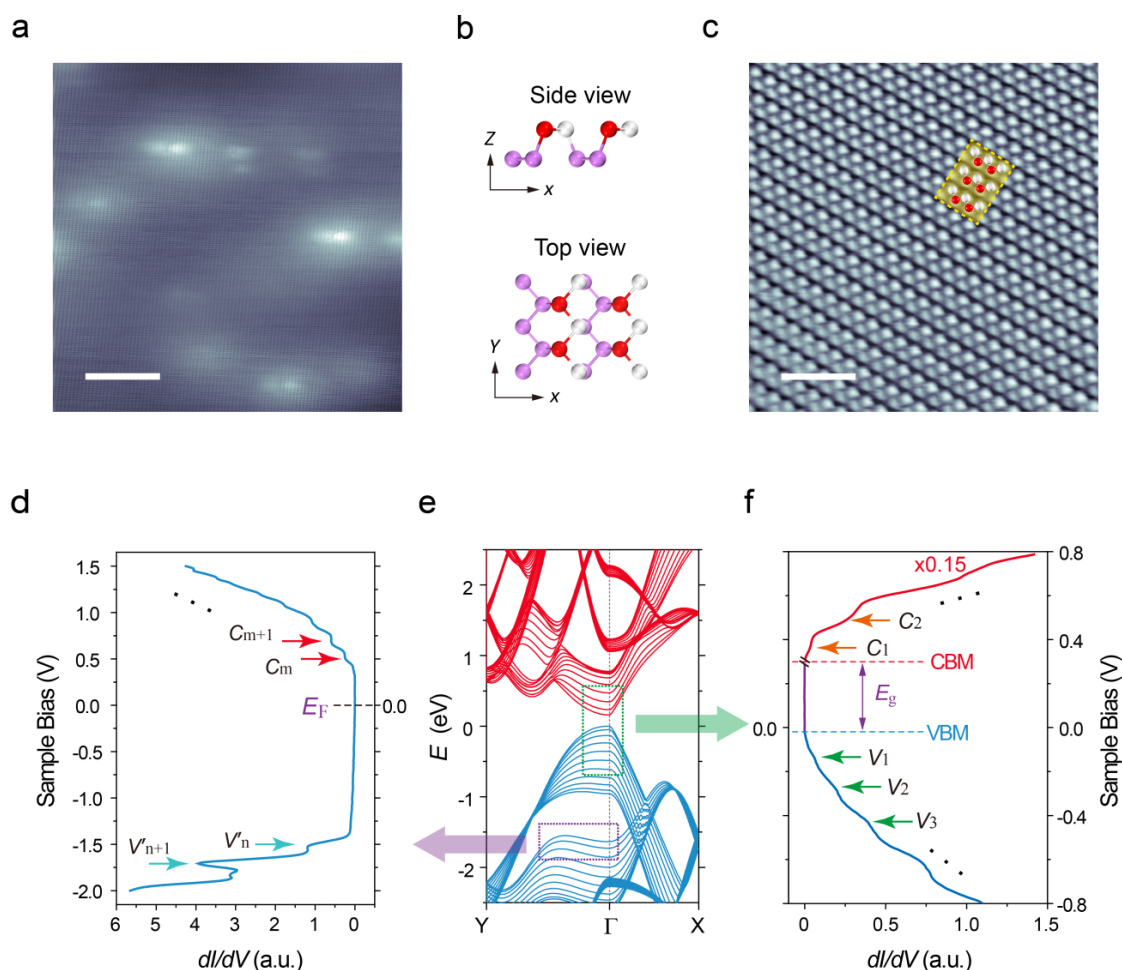16

379   **Figures and Legends**

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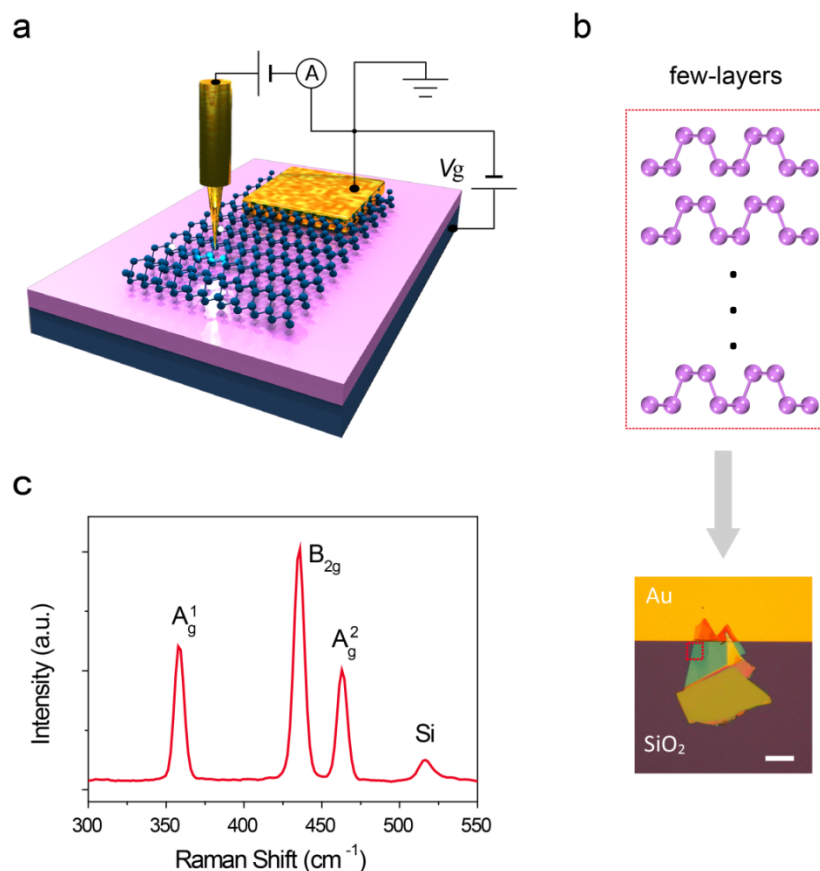
382   **Figure 1.** Schematic drawing and structural characterisation of a few-layer BP device. (a) Schematic
383   illustration of a gated BP device during STM analysis. The sample bias V_S is applied between the STM tip
384   and the thin BP sample contacted by a gold electrode. The electrostatic gate voltage is applied to the BP
385   flake through a p-doped silicon wafer. (b) Optical image of few-layer BP flakes on silicon substrate
386   partially in contact with a gold electrode. Scale bar is 20 μm. (c) Raman spectrum of the as-prepared BP
387   flake; the peak at ~520 cm^{-1} originates from the underlying silicon substrate.

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Figure 3. Gate-controlled Stark effect in an 11-layer BP flake device. (a) Gate-dependent dI/dV spectra obtained on a defect free region in an 11-layer BP flake. (Set point: $V_S=$ -1.0 V, $I=$ 1.0 nA). The curves are vertically offset and the gate voltage step is 10 V. (b) and (c) Logarithmic dI/dV spectra under negative and positive gate voltages, respectively. (d) VBM (red balls), CBM (black balls), resonance peaks (solid symbols) and bandgap (E_g) of 11-layer BP at different gate voltages. (e) and (f) Schematic models (note: thickness and charge carrier density not to scale) to illustrate the charge carrier distribution and gate-dependent behaviour of 11-layer BP shown in Figure 3b and 3c, respectively.
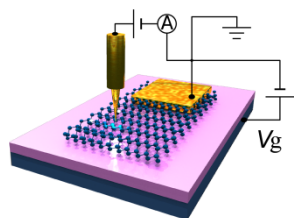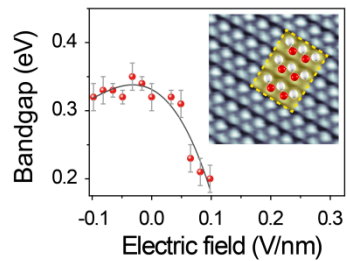
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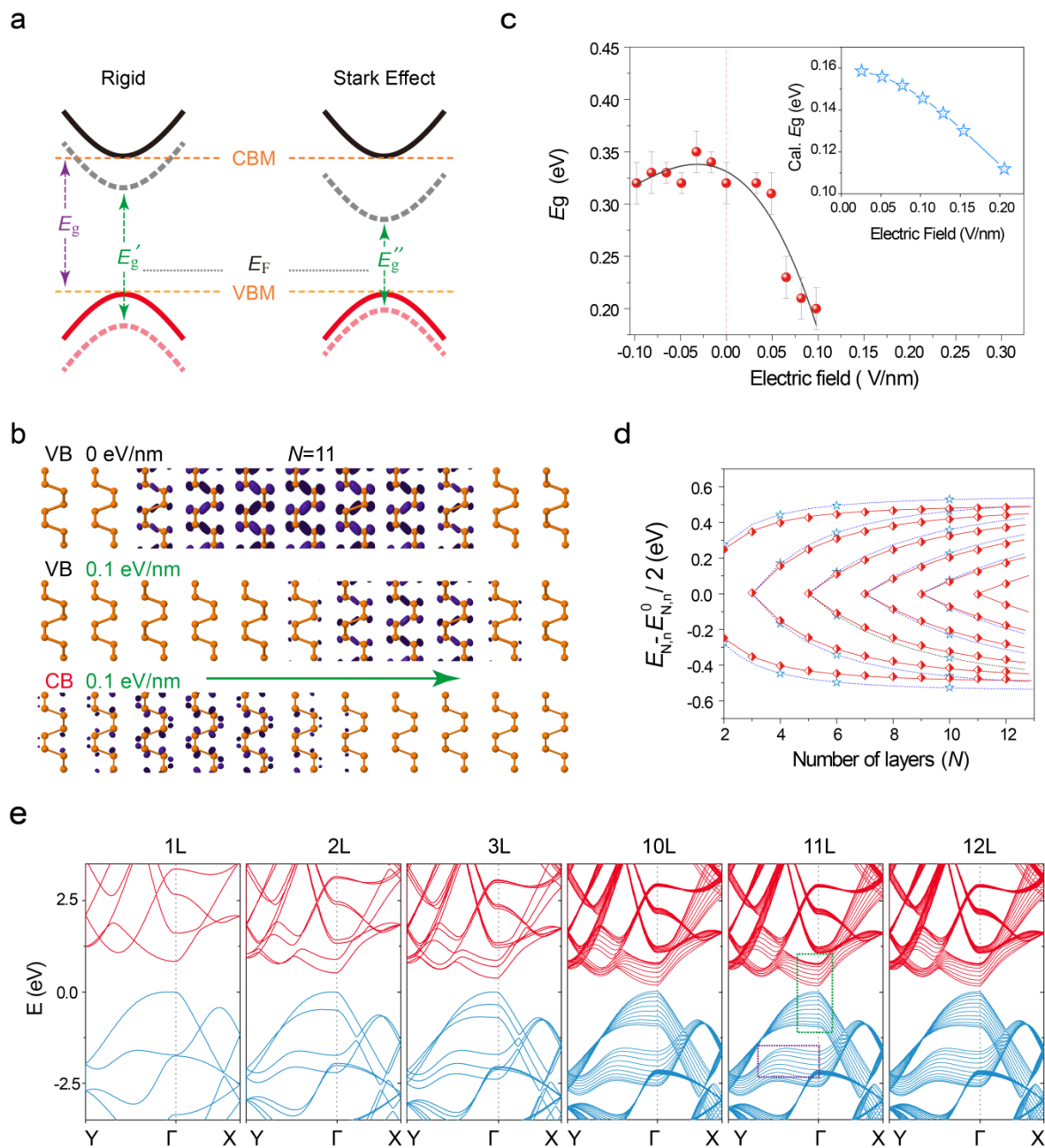
Figure 4. Calculated electronic structures of few-layer BP with and without field modulation. (a) Schematic illustration of the field modulation of electronic structures of few-layer BP with and without a giant Stark effect. The solid red and black lines indicate the initial positions of VBM and CBM (E= 0 V) while the dashed red and black lines represent the VBM and CBM under an electric field (E≠ 0 V), respectively. (b) The wave function modulus square of the highest occupied state at Γ point for 11-layer BP sample at 0 V/nm (top) and 0.1 V/nm (middle) electrical fields. The wave function modulus square of the lowest unoccupied state at Γ point for the 11-layer BP sample at 0.1 V/nm electrical field (bottom). (c)

419   Measured bandgap of 11-layer BP as a function of applied electrical field. Inset shows the calculated

420   bandgap of a BP sample of the same thickness in the presence of electrical fields of different strength. (d)

421   Level spacing in few-layer BP (layer number N= 2–12) obtained from PBE (red) and HSE (blue)

422   calculation methods. (e) Representative layer-dependent PBE band structures of BP; please refer to the

423   supporting information Figure S7 for a more detailed version of the calculation.

424

425   **Table of Contents Graphic**

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