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## PAPER

## Excitonic effect in black phosphorus oxides

Longxing Chi<sup>1,2</sup> , Ming-Hsien Lee<sup>3</sup> , Ta-Ya Chu<sup>1,\*</sup> and Ye Tao<sup>1</sup> <sup>1</sup> Advanced Electronics and Photonics Research Centre, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada<sup>2</sup> Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario M5S 3E4, Canada<sup>3</sup> Department of Physics, Tamkang University, Tamsui, New Taipei City 25137, Taiwan (ROC)

\* Author to whom any correspondence should be addressed.

E-mail: [ta-ya.chu@nrc-cnrc.gc.ca](mailto:ta-ya.chu@nrc-cnrc.gc.ca)**Keywords:** excitonic effect, exciton binding energy, black phosphorus oxidesSupplementary material for this article is available [online](#)

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## Abstract

Two-dimensional (2D) few-layer black phosphorus (BP) with extraordinary electronic and optical properties is an excellent candidate for optoelectronic applications. However, rapid surface oxidation under ambient environment significantly restricts its practicability. Here, we investigate excitonic effect in few-layer BP oxides via first-principle calculation and effective mass approximation. Influence of layer numbers and degree of oxidation on exciton binding energy (EBE) is discussed in detail for the first time. It is found that EBE in BP oxides decreases exponentially with increasing sample thickness and becomes almost oxygen independent over six layers with values similar to that of pristine BP. Instead, oxidation alters excitation probability of excitons in few-layer BP via a direct/indirect bandgap transition.

## 1. Introduction

Few-layer black phosphorus (FLBP) has emerged as a promising 2D material in optical and optoelectronic applications due to its excellent electronic and optical properties including layer-dependent bandgap, prominent charge-carrier mobility, high current on/off ratios, tunable intraband optical conductivity, etc [1–3]. On the one hand, BP-based photodetectors, electroluminescent devices, spectrometers, photovoltaics are being continuously investigated and upgraded for better device performance [2–8]. On the other hand, issues of rapid carrier recombination rate and low ambient stability result in optical performance penalty in 2D BP and are waiting to be overcome [9–11].

It is critical to decrypt the excitonic effects that dominate optical response of 2D BP owing to significantly reduced dielectric screening and enhanced quantum confinement in low dimensional systems [12]. Excitons in 2D BP exhibit strong optical anisotropy where absorption spectrum, optical permittivity, polarizability vary significantly along different light polarization directions, which can be ascribed to the anisotropic band structure, exciton states and inherent geometries formed in 2D BP [12–14].

Exciton binding energy (EBE) describes the strength of electron–hole ( $e-h$ ) interaction within excitons and directly determines the carrier recombination rate thereby playing an important role in BP optoelectronic research [9, 15–17]. It is defined as the energy difference between quasiparticle bandgap and optical bandgap [15]. In 2D BP, EBE decreases exponentially with increasing layer numbers, leading to a high optical conductivity for thin samples [12, 13].

The chemical instability of BP primarily originates from surface oxidation. It has been proven both experimentally and theoretically that oxidation occurs at the top BP layer only, which performs as a passivation layer preventing further  $O_2$  penetration into sublayers [18–21]. Besides, the passivation role of the oxide layer can be further enhanced by introducing a coating layer like octadecyltrichlorosilane [22]. In single layer BP, surface oxidation significantly accelerates exciton–exciton annihilation due to introduction of surface defect sites [17]. Furthermore, with the increasing  $O_2$  coverage, EBE increases drastically up to 3 eV at which recombination almost occurs immediately, leading to optoelectronic performance deterioration [23, 24]. Despite of the above limits, black phosphorus oxides (BPOs) are still an excellent candidate for electronic and optical applications:

high-transconductance field effect transistors, with long-time air resistivity up to 28 days, and tunable photoluminescence (PL) device, controlled by degree of oxidation, have been achieved on BPOs [22, 25, 26]. However, the influence of surface oxidation on excitonic effect of multilayer BP is still unclear; also, interconnection between EBE and dielectric constant, effective mass has rarely been mentioned. Considering the practicability of FLBP and the self-termination feature of BP oxidation, it is of practical significance to investigate the excitonic effects in few-layer black phosphorus oxides (FLBPOs).

In this work, the excitonic effect in FLBPOs has been investigated via density functional theory (DFT) combined with effective mass approximation (EMA). DFT calculations were carried out using CASTEP for geometric optimization, band structure calculation, density of states (DOS) analysis, optical properties calculation [27]. Generalized gradient approximation (GGA) with exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE) in the norm-conserving pseudopotentials were implemented [28–30]. Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional and ultrasoft pseudopotentials were also used for band structure computation for the purpose of bandgap comparison [31, 32]. EBE was estimated using EMA for anisotropic 2D films with a Hamiltonian of:

$$H = -\frac{\hbar^2}{2\mu_x} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu_y} \frac{\partial^2}{\partial y^2} + V_{eh}(r) \quad (1)$$

where  $\mu_{x(y)} = \left(1/m_{x(y)}^e + 1/m_{x(y)}^h\right)^{-1}$  is the exciton effective mass [33–35].  $m_{x(y)}^e$ ,  $m_{x(y)}^h$  represents the effective mass of electron, hole along  $x(y)$  direction. The electron–hole ( $e$ – $h$ ) in-plane interaction  $V_{eh}(r)$  is described by the Keldysh equation:

$$V_{eh}(r) = -\frac{e^2}{4(\varepsilon_1 + \varepsilon_2)\varepsilon_0 r_0} \left[ H_0\left(\frac{r}{r_0}\right) - Y_0\left(\frac{r}{r_0}\right) \right] \quad (2)$$

where  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\varepsilon_0$ ,  $r_0$ ,  $H_0$ ,  $Y_0$  correspond to relative dielectric constant of upper layers, relative dielectric constant of bottom layers, vacuum permittivity, screening length, Struve function, Bessel function of the 2nd kind, respectively. EBE is equivalent to the system ground state energy. This approach has been widely applied for 2D system computation in which dielectric constant and exciton effective mass are determinants [13, 36–38]. Calculation details have been provided in supplementary material. Different degree of oxidation and layer numbers have been considered during EBE prediction in this work. It is found that influence of  $O_2$  coverage on EBE becomes trivial with increasing layer numbers. In the meanwhile, bandgap types, i.e. direct or indirect, determine excitonic effect in FLBPOs rather than EBE. Our research provides further insight into the optoelectronic characteristics of BPOs.

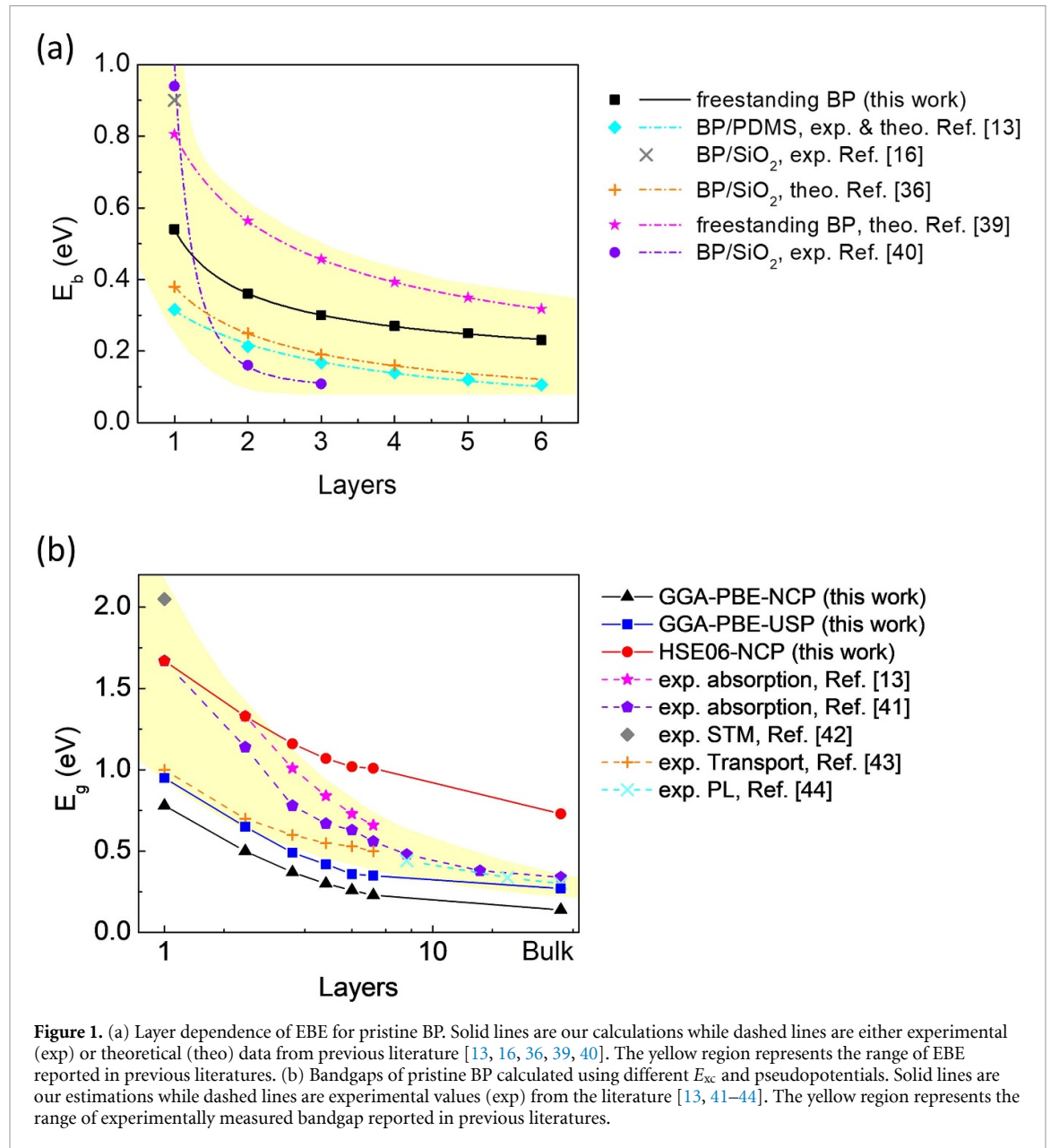
## 2. Results and discussion

EBE of pristine BP from single layer to six layers have been calculated as shown in figure 1(a). EBE decreases exponentially with increasing BP layers as:

$$E_b = \frac{A}{B+N^\alpha} \quad (3)$$

where  $N$  is the number of layers and  $A$ ,  $B$ ,  $\alpha$  are fitting variables related to effective polarizability of 2D layers [13, 39]. This is consistent with previous experimental and theoretical results [13, 16, 36, 39, 40]. Experimental values measured from PL spectrum vary from 0.9 eV to 0.3 eV for single layer BP due to different substrate screening effect [13, 16, 40]. There are also discrepancies in theoretical values, which might be attributed to substrate screening as well as different choices of exchange-correlation functionals ( $E_{xc}$ ) [13, 36, 39]. As can be found in figure 1(b),  $E_{xc}$  prominently influences DFT-calculated bandgaps that differ to experimental values as well [13, 41–44]. Since EBE is equivalent to energy difference between quasiparticle bandgap and optical bandgap, huge electronic bandgaps usually lead to huge EBE [15]. In the EMA used here, however, EBE calculation involves effective mass instead of electrical bandgap as can be seen from equation (1). Considering the trivial difference in effective mass calculated using both functionals, as shown in table S2 (available online at [stacks.iop.org/2DM/9/015007/mmedia](https://stacks.iop.org/2DM/9/015007/mmedia)), PBE functional is used for EBE calculation in this work. Despite of difference in EBE magnitudes, our results locate in a reasonable range. Moreover, the predicted layer dependent trend is identical to the one in previous literature.

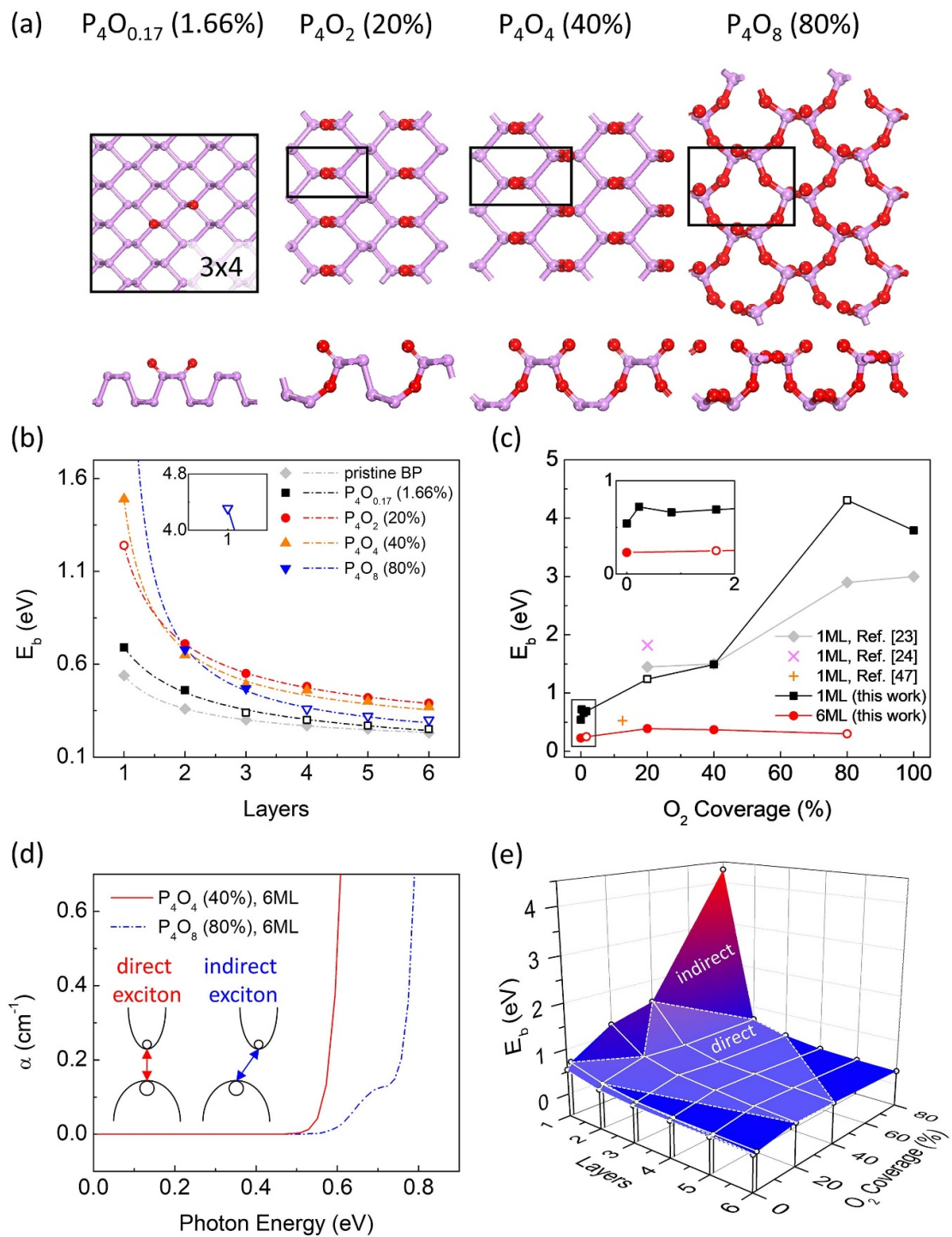
EBE of FLBPOs with regard to layer numbers at different degree of oxidation is shown in figure 2(b) where corresponding crystal structures of single layer BPOs are exhibited in figure 2(a). Unit cells used for DFT computation are labelled in each structure. Only top BP layer is oxidized in the structural models, in consistent with previous experimental observations [18–20, 22]. The bottom BP layer remains intact considering the bottom layer would be protected against air exposure by substrates in practical cases. Construction of oxide structures are detailed in supplementary material. Exponential decay trend described in equation (3) for pristine BP reappears in its oxides, accompanied by bandgap shrink as shown in figure S3. Fitting curves are represented by dashed lines. At low degree of oxidation (1.66%, black squares), EBE is close to that of pristine BP (grey rhombuses). A highest EBE of 0.69 eV is found in single layer, which is 0.15 eV higher than that of pristine BP (0.54 eV). With the increase of layer numbers up to six, EBE drops down to 0.25 eV equivalent to that of pristine BP. In comparison, at high degree of oxidation (20% ~ 80%), EBE significantly deviates from



pristine BP in single layer circumstance. A high EBE of 4.31 eV is observed in single layer P<sub>4</sub>O<sub>8</sub> (80% oxidation), suggesting a strong electron–hole ( $e$ – $h$ ) interaction in excitons, giving rise to instant exciton recombination and short exciton radiative lifetime in the system, unfavourable for optoelectronic use [45]. Nevertheless, introducing extra BP layers drastically reduces EBE by an order of magnitude. When there are six layers in total, EBE in BPOs becomes slightly larger than that in pristine BP, suggesting similar exciton radiative lifetime between them. Besides, EBE at different O<sub>2</sub> coverages exhibits the sharpest decrease from single layer to double layers, indicating that the 2nd layer introduces a qualitative change. It is worth mentioning that there are multiple BPO configurations as previously reported [18, 19, 23]. EBE calculated on another P<sub>4</sub>O<sub>0.17</sub> structure also satisfies the exponential decay trend as can be found in the

supplementary material. Another common concern is the influence of water vapours. It has been demonstrated that H<sub>2</sub>O will first facilitate surface oxidation on BP then react with BPOs to form phosphoric acid [46]. The 1st step plays a critical role while the 2nd step can be perfectly inhibited via a capping layer [22, 25]. Therefore, from the perspective of practical use, influence of H<sub>2</sub>O on BP only involves acceleration in surface oxidation rather than introduction of new functional groups.

To better understand EBE dependence on degree of oxidation, EBE has been replotted with regard to O<sub>2</sub> coverages as exhibited in figure 2(c). The inset is a zoom-in image of the rectangular region corresponding to low O<sub>2</sub> coverages. For single layer (1ML) BPOs, an increasing tendency in EBE can be observed with increasing degree of oxidation, in agreement with previous literature (orange cross, pink cross and



**Figure 2.** (a) Crystal structure of single layer BPOs. (b) Layer dependence of EBE at different O<sub>2</sub> coverages. Inset is EBE of single layer  $P_4O_8$ . (c) O<sub>2</sub> coverage dependence of EBE at one layer and six layers. Inset is a zoom-in image of squared region. Gray rhombus, pink cross and orange cross are literature values [23, 24, 47] (ML means monolayer). (d) DFT-calculated absorption coefficient of six layers  $P_4O_4$  and  $P_4O_8$  as a function of photon energy. Inset is an illustration of direct/indirect excitons. (e) 3D map of EBE with regard to O<sub>2</sub> coverages and layer numbers. In (b) and (c), open and closed circles correspond to indirect and direct bandgaps, respectively.

grey rhombuses in the graph) [23, 24, 47]. Again, discrepancy in absolute EBE values between literature data and ours can be attributed to different  $E_{xc}$  choices, nevertheless overall trend in changes of EBE is identical. For six-layer (6ML) BPOs at different O<sub>2</sub> coverages, EBE is calculated to be 0.46 eV (1.66%), 0.51 eV (20%), 0.53 eV (40%), 0.53 eV

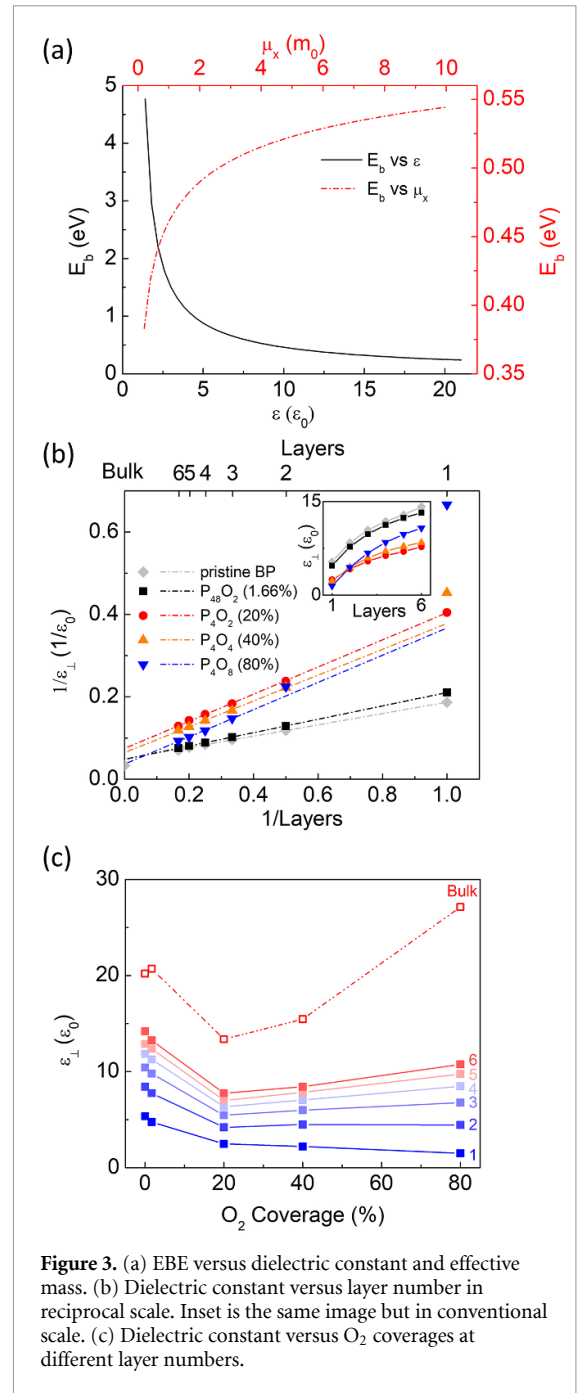
(80%), respectively, comparable to that of pristine BP and no longer exhibits oxygen dependence.

In addition to changes in EBE magnitudes, excitation probability also plays a critical role in excitonic effect in FLBPOs. Two exciton types dominate the absorption probability as illustrated in figure 2(d). Direct excitons are excited by direct

transition without momentum loss while indirect excitons involve indirect transition accompanied with momentum change via phonon absorption or emission. Corresponding excitation probability is proportional to absorption coefficient ( $\alpha$ ) [48]. Therefore, DFT-calculated absorption coefficient is plotted in figure 2(d) as a function of photon energy. Six-layer  $P_4O_4$  and  $P_4O_8$  are selected for plotting because both structures have a bandgap of 0.53 eV with the former one direct whereas the latter indirect. It is obvious that absorption coefficient, therefore excitation probability, in direct bandgap system is much higher than indirect system. Exciton types are labelled in figures 2(b) and (c), with solid and hollow symbols representing direct and indirect excitons, respectively. For a better visualization, 3D surface map of EBE with regard to layer numbers and  $O_2$  coverages is plotted in figure 2(e) where direct bandgap region is marked individually. The 3D map further corroborates EBE independence on  $O_2$  coverages at high layer numbers. A continuous direct bandgap area exists at  $O_2$  coverages between 20% and 40%. Outside the region excitonic effect impairs due to low excitation probability. Indirect bandgaps appear randomly among different wave numbers irrelevant to  $O_2$  coverages as can be seen from figure S4. There is no layer dependence in bandgap type as well: indirect bandgaps occur or eliminate either at single layer or at multilayers. However, based on PDOS shown in figure S5, global bandgaps in FLBPOs, either direct or indirect, are commonly contributed from sublayer P–P bonds instead of P–O or P=O bonds on the oxide layer. It is worth mentioning that bandgap types might be altered by substrates. Overall, excitonic effect in multilayer BPOs is less sensitive to EBE whereas more dominated by O-induced bandgap transitions.

Determinants of EBE, i.e. 2D dielectric constant and exciton effective mass, are discussed in the following paragraphs. Figure 3(a) shows EBE as a function of those two factors. It can be easily found that EBE is negatively related to dielectric constant (black solid line) yet positively related to effective mass (red dashed line). More importantly, EBE is more sensitive to dielectric constant than to effective mass. The value shrinks by an order of magnitude with the change of dielectric constant (vertical scale on the left), while mildly increases as effective mass grows (vertical scale on the right). Layer dependence of dielectric constant is plotted in figure 3(b) in reciprocal scale while the normal scale image is shown in the inset. A linear dependence can be observed through the image for all  $O_2$  coverages. Relative dielectric constant ( $\varepsilon_r$ ) is related to polarizability ( $P$ ) by:

$$\frac{1}{\varepsilon_r} = 1 - \frac{P}{\varepsilon_0 V_{\text{cell}}} \quad (4)$$



**Figure 3.** (a) EBE versus dielectric constant and effective mass. (b) Dielectric constant versus layer number in reciprocal scale. Inset is the same image but in conventional scale. (c) Dielectric constant versus  $O_2$  coverages at different layer numbers.

where  $V_{\text{cell}}$  is the effective 2D cell volume without vacuum space [49]. In the meanwhile, polarizability is proportional to layer numbers ( $N$ ) by:

$$P(N) = NV_{\text{bulk}} \frac{\varepsilon_0}{2} \left( 1 - \frac{1}{\varepsilon_{\text{bulk}}} \right) + b \quad (5)$$

where  $V_{\text{bulk}}$ ,  $\varepsilon_{\text{bulk}}$ ,  $b$  correspond to volume of the bulk unit cell with two layers, bulk dielectric constant, constant related to surface polarizability, respectively [49].  $V_{\text{cell}}$  can be approximated by:

$$V_{\text{cell}} \approx \frac{N}{2} V_{\text{bulk}} \quad (6)$$

for multilayers. Therefore, equation (4) can be rewritten to a linear function between  $1/\varepsilon_r$  and  $1/N$  as:

$$\frac{1}{\varepsilon_r} = \frac{1}{\varepsilon_{\text{bulk}}} + k \frac{1}{N} \quad (7)$$

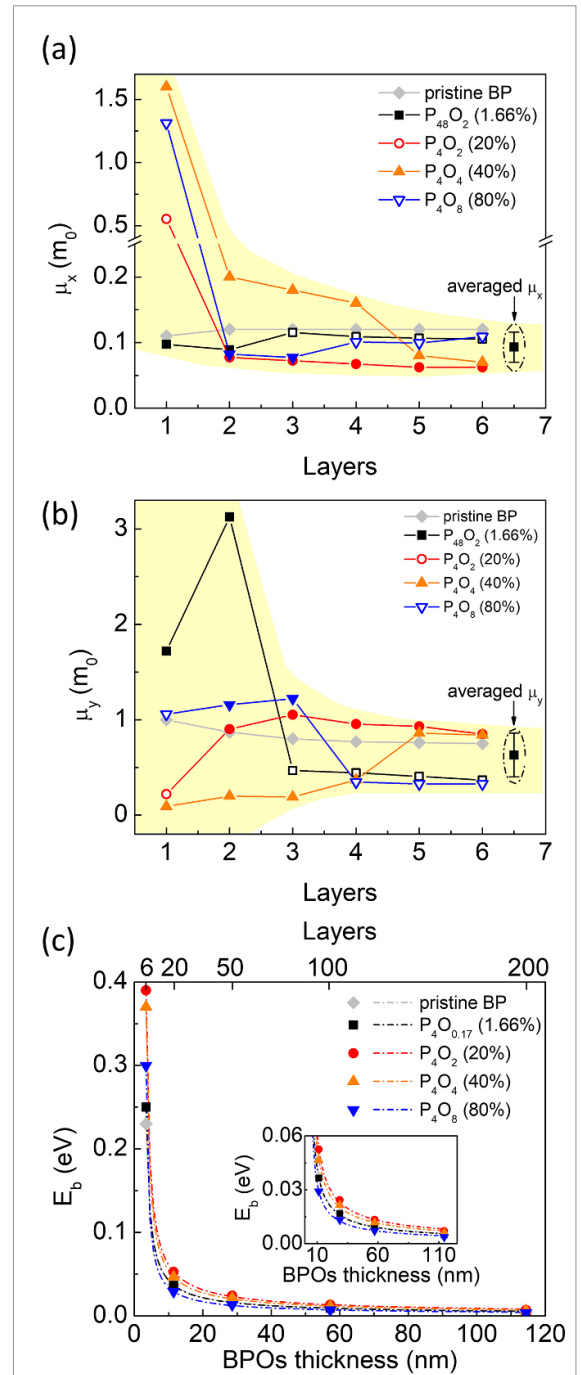
where  $k = -2b/\varepsilon_0$  is the linear constant for curve fitting. Fitting curves are represented by dashed lines in figure 3(b). According to equation (7), bulk dielectric constant can be estimated from vertical intercepts. Here, bulk structure represents an infinite thick BP covered by a single-layer BPOs. As-predicted bulk dielectric constants are 20.2, 20.7, 13.38, 15.46, 27.13 for pristine BP,  $\text{P}_4\text{O}_{0.17}$ ,  $\text{P}_4\text{O}_2$ ,  $\text{P}_4\text{O}_4$ ,  $\text{P}_4\text{O}_8$ , respectively, as plotted in figure 3(c) by hollow squares. The huge dielectric constants guarantee a relatively small EBE around 0.3 eV in FLBPOs. It should be mentioned that dielectric constant for  $\text{P}_4\text{O}_4$  and  $\text{P}_4\text{O}_8$  at single layer deviates from their fitting curves. This is because single layer  $\text{P}_4\text{O}_4$  or  $\text{P}_4\text{O}_8$  is much thicker than single layer pristine BP, as can be found from table S1. As a result, equation (6) will underrate effective cell volume ( $V_{\text{cell}}$ ) in single-layer case, leading to abovementioned mismatch. However, such a problem disappears in multilayer cases and as-calculated bulk dielectric constant is still trustworthy. Coverage dependence of dielectric constant is also exhibited in figure 3(c). At low  $\text{O}_2$  coverage (1.66%), dielectric constant is close to that of pristine BP. At high  $\text{O}_2$  coverage (20% ~ 80%), however, dielectric constant becomes sensitive to degree of oxidation. Larger bulk dielectric constant is achieved for higher  $\text{O}_2$  coverages.

Layer dependence of exciton effective mass are shown in figures 4(a) and (b) where solid and hollow symbols correspond to direct and indirect excitons, respectively. At single layer, effective mass distributes dispersively in both directions. When reached six layers, however, effective mass almost converges regardless of  $\text{O}_2$  coverages. Averaged effective mass at six layers is  $0.093 \pm 0.023$  along armchair edge and  $0.63 \pm 0.23$  along zigzag edge, as marked in the image, indicating a huge anisotropy. More importantly, those values can be approximated as bulk effective mass considering its convergence feature.

Finally, we estimate EBE of bulk BPOs, e.g. 50 ~ 100 nm thick films, using EMA with a bulk screening length  $r_0$  of:

$$r_0 = \frac{d\varepsilon_{\text{bulk}}}{\varepsilon_1 + \varepsilon_2} \quad (8)$$

where  $d$ ,  $\varepsilon_{\text{bulk}}$ ,  $\varepsilon_1$ ,  $\varepsilon_2$  correspond to film thickness, bulk dielectric constant, capping layer dielectric constant, substrate dielectric constant, respectively [33]. Substituting equation (8) into equation (S3) in supplementary material enables computation of EBE. Bulk dielectric constant and effective mass are required and has been summarized in above context. Capping layer and substrate are treated as vacuum space. As-calculated EBE is plotted in figure 4(c) as a function of sample thickness (also layer numbers) at different  $\text{O}_2$  coverages. Points at six layers are collected from figure 2(b) as a reference. EBE



**Figure 4.** Exciton effective mass as a function of layer numbers along armchair (a) and zigzag (b) edges, respectively. (c) Predicted bulk EBE with regard to sample thickness. Dashed lines are fitting curves. Corresponding layer numbers are shown on the top scale. Inset is a zoom-in image of  $E_b$  for thick samples. Range of calculated effective mass is yellow highlighted. Open and closed symbols in (a) and (b) correspond to indirect and direct bandgaps, respectively.

in bulk scale (50 ~ 100 nm) converges to few milli electronvolts, which is close to that of free excitons experimentally measured in bulk BP [50]. However, it must be emphasized that EBE itself fails to guarantee excellent optoelectronic performances, bandgap types must take into consideration as abovementioned.

### 3. Conclusions

In conclusion, we investigated excitonic effect of FLBPOs. It is found that, first, EBE decreases exponentially with regard to layer numbers same as that in pristine BP. Second, EBE in single layer BPOs strongly depends on degree of oxidation. Oversized EBE above 3 eV is achieved at 80% and 100% O<sub>2</sub> coverages, indicating large  $e$ - $h$  interactions and giving rise to short exciton radiative lifetime. However, EBE in multilayer BPOs converges to pristine BP levels and varies trivially with O<sub>2</sub> coverage. Third, different layer numbers and O<sub>2</sub> coverages lead to different excitation probabilities by introducing direct/indirect bandgap transition. As a result, it is the bandgap type rather than EBE that determines excitonic effect in FLBPOs. Fourth, EBE is dominated by dielectric constant and exciton effective mass. The former exhibits linear dependence on layer numbers in reciprocal scale, while the latter converges at high layer numbers regardless of O<sub>2</sub> contents. Finally, EBE in bulk BPOs is estimated with values of few milli electronvolts similar to that of free excitons in bulk pristine BP.

### Supplementary material

Calculation details, construction of FLBPO structures, EBE of other BPO configurations, additional figures as mentioned in the text.

### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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### ORCID iDs

Longxing Chi  <https://orcid.org/0000-0003-4612-4941>

Ming-Hsien Lee  <https://orcid.org/0000-0003-3956-181X>

Ta-Ya Chu  <https://orcid.org/0000-0003-2114-5914>

Ye Tao  <https://orcid.org/0000-0002-0842-6650>

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