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Anomalous thickness dependence of photoluminescence quantum yield in black phosphorous

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Naoki Higashitarumizu (D^{1,2,9}, Shiekh Zia Uddin^{1,2,8,9}, Daniel Weinberg (D³, Nima Sefidmooye Azar⁴, I. K. M. Reaz Rahman^{1,2}, Vivian Wang (D^{1,2}, Kenneth B. Crozier^{4,5,6}, Eran Rabani^{2,3,7} & Ali Javey (D^{1,2})

Black phosphorus has emerged as a unique optoelectronic material, exhibiting tunable and high device performance from mid-infrared to visible wavelengths. Understanding the photophysics of this system is of interest to further advance device technologies based on it. Here we report the thickness dependence of the photoluminescence quantum yield at room temperature in black phosphorus while measuring the various radiative and non-radiative recombination rates. As the thickness decreases from bulk to ~4 nm, a drop in the photoluminescence quantum yield is initially observed due to enhanced surface carrier recombination, followed by an unexpectedly sharp increase in photoluminescence quantum yield with further thickness scaling, with an average value of ~30% for monolayers. This trend arises from the free-carrier to excitonic transition in black phosphorus thin films, and differs from the behaviour of conventional semiconductors, where photoluminescence quantum yield monotonically deteriorates with decreasing thickness. Furthermore, we find that the surface carrier recombination velocity of black phosphorus is two orders of magnitude lower than the lowest value reported in the literature for any semiconductor with or without passivation; this is due to the presence of self-terminated surface bonds in black phosphorus.

Black phosphorus (BP) is a single-elemental layered crystalline material that has emerged as a promising direct bandgap semiconductor for nanoelectronic, nanophotonic and optoelectronic applications from mid-infrared to visible wavelengths^{1–5}. Carrier recombination changes from a free-carrier to excitonic system when the BP thickness decreases to atomic thickness due to reduced Coulomb screening^{6,7}. The dominant optical transition in BP remains direct at all thicknesses due to the strong interlayer electronic state coupling^{8,9}. BP provides an ideal platform to demonstrate how the recombination mechanism evolves from excitonic to free-carrier in a semiconductor. However, the photophysics landscape of BP during this transition has not been fully explored. The photoluminescence (PL) quantum yield (QY) is a

¹Electrical Engineering and Computer Sciences, University of California, Berkeley, Berkeley, CA, USA. ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA. ³Department of Chemistry, University of California, Berkeley, Berkeley, CA, USA. ⁴School of Physics, University of Melbourne, Melbourne, Victoria, Australia. ⁵Department of Electrical and Electronic Engineering, University of Melbourne, Parkville, Victoria, Australia. ⁶Australian Research Council (ARC) Centre of Excellence for Transformative Meta-Optical Systems (TMOS), University of Melbourne, Parkville, Victoria, Australia. ⁷The Raymond and Beverly Sackler Center of Computational Molecular and Materials Science, Tel Aviv University, Tel Aviv, Israel. ⁸Present address: Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA, USA. ⁹These authors contributed equally: Naoki Higashitarumizu, Shiekh Zia Uddin. *Centrel and elecycle autore and the status and tere and the status address* and the status and the



Fig. 1 | **Excitonic to free-carrier transition in BP. a**, Normalized (Norm.) PL spectra of BP from monolayer (1 L) to bulk. **b**, Optical bandgap of BP versus thickness. **c**, Experimental (Exp.)²¹⁻²⁴ and theoretical^{9,22-27} excitonic binding energy at different thicknesses shows the excitonic (orange shading) to free-carrier (blue shading) transition. The solid line represents a theoretical result²². Thermal energy *kT* at room temperature is shown by the dashed line.

direct probe of material photophysics and a key metric of optoelectronic performance that determines the maximum device efficiency. Here we study the room temperature PL QY in a wide range of BP thicknesses from the monolayer limit to the bulk. At the same defect density level, we find that a larger exciton binding energy leads to more light emission, and that monolayer BP (that is, phosphorene) has the highest PL QY. In the free-carrier regime, together with a low Auger recombination rate in BP owing to a large electron-hole effective mass ratio $(m_{e}^{*}/m_{h}^{*})^{10,11}$, we also observe that the surface recombination velocity (SRV) in as-exfoliated BP is two orders of magnitude lower than in passivated silicon, the most electrically inactive surface known to the modern semiconductor industry¹². This low SRV is observed despite the oxidized surface of BP. Although the PL OY in bulk BP is limited to a few percent due to Auger recombination, we demonstrated one order of enhancement of the internal PL QY by the Purcell effect with an optimized optical cavity structure. Generally, BP has been considered to be unstable in air due to oxide formation^{13–17}, but the present results indicate that the surface oxidation has no effect on the optical performance in relatively thick BP due to a self-limited oxide formation.

Excitonic to free-carrier transition in black phosphorus

Our samples were prepared as follows. BP was mechanically exfoliated in a nitrogen environment from bulk crystals onto SiO₂/Si substrates to produce bulk to monolayer flakes. Optical contrast was used to identify flakes likely to have the desired thickness, later confirmed by atomic force microscopy^{18,19}. Micro PL spectra were measured at room temperature in a nitrogen environment (more details in Methods). PL spectra shown in Fig. 1a exhibit a thickness-dependent optical bandgap ranging from -1.7 eV for a monolayer to -0.3 eV for bulk BP. The full-width at half-maximum (FWHM) varies with thickness, as has been reported previously^{19,20}. Compared to the purely excitonic emission from monolayer BP, the PL FWHM can be broadened during the excitonic to free-carrier transition due to the coexistence of the excitonic and free-carrier systems. Along with the excitonic to free-carrier transition, multiple factors contribute to the peak width in the real system, such as interactions with the substrate, defects and impurities. The optical bandgap changes sharply with thickness for BP flakes with thicknesses up to six layers, beyond which the bandgap asymptotically approaches 0.32 eV (Fig. 1b). A similar dichotomy is also present in the exciton binding energy curated from the experimental²¹⁻²⁴ and theoretical^{9,22-27} results in the literature (Fig. 1c). For thicknesses from a monolayer to five layers, the exciton binding energy is larger than the average room temperature thermal energy so that the photogenerated carriers will be excitons. Above five layers, the binding energy falls below the thermal energy, so photogenerated electron–hole pairs will thermalize and relax as free carriers.

Radiative excitonic recombination

We first explore radiative excitonic recombination in BP. Figure 2a shows PL spectra of monolaver BP at different generation rates. The PL peak positions for one-layer to five-layer BP are independent of generation rate, indicating the absence of photodegradation (Fig. 2b). The calibrated PL QY of BP decreases drastically as we go from a monolayer to five layers at a generation rate of 3.6×10^{26} cm⁻³ s⁻¹ (Fig. 2c). The PL QY at different generation rates from a monolayer to five layers is shown in Fig. 2d. The monolayer has an average internal PL QY of ~30%. The large exciton binding energy in monolayers means that we have strongly bound excitons, leading to a brighter emission. To a first order approximation, the exciton radiative recombination rate Γ_x in a two-dimensional semiconductor can be written as $\Gamma_{\chi} \propto E_{\chi} E_{h}^{2}$, where $E_{\rm x}$ is the exciton transition energy and $E_{\rm b}$ is the exciton binding energy $(details in Supplementary Information)^{28}$. Both E_x and E_b increase with decreasing layer number, resulting in a nonlinearly enhanced radiative recombination rate. The calculated radiative recombination rate using the experimental exciton transition energy and theoretical exciton binding energy is shown in Fig. 2c, which displays a similar trend as the PL QY dependence on thickness. Note that the present model is correct only in the lowest order of approximation, which ignores the non-radiative recombination rate, as well as other complexities such as the permittivity and effective mass changing with binding energy; further analysis will be more complicated due to a band structure change and the possible introduction of defects during experiments. We also do not observe the signature of any of the exciton-exciton annihilation that plagues other excitonic materials²⁹, as illustrated in Fig. 2d. Both facts are reminiscent of transition-metal dichalcogenide monolayers, where strongly bound direct excitons can recombine completely radiatively despite the presence of a large native defect density $^{6,30-33}$. Even though special care was taken to minimize the oxidation of the BP monolayer as detailed in Methods, some oxidation is expected given the high reactivity, thus resulting in the formation of defects. To investigate the effect of these defects on the recombination processes, low-temperature PL measurements were performed (Supplementary Fig. 1). At 3.6 K, there was no emission peak observed between 0.8 and 1.6 eV, indicating the absence of recombination processes induced by mid-gap states. A clear shoulder arising from trions was observed in the main emission peak (inset in Supplementary Fig. 1A), consistent with previous reports³⁴. Specifically, emission peaks of 1.70 eV and 1.76 eV are observed for trions and neutral excitons, respectively. Trions are known to predominantly undergo non-radiative recombination at room temperature, thus limiting the maximum measured PL QY⁶. The PL QY drastically decreases at all pumping densities as BP thickness increases (Fig. 2d). Such a decrease in PL QY with thickness is also observed in semiconducting transition-metal dichalcogenides and generally has been attributed to the dominance of the indirect transition when the thickness is increased beyond the monolayer³⁵. However, BP remains a direct bandgap material regardless of thickness, with a relatively large energy difference between the direct and indirect bandgap^{22,36,37}; therefore, the observed PL QY decrease with thickness arises from an increase in screening and a decrease in exciton binding energies^{26,38}, as well as the dramatic change of exciton transition energy. As all of these layers are sourced from the same bulk material, our results show that



b

PL peak (eV)

1.8

1.5

1.2

0.9

51 0.6 10¹⁶ 10¹⁸ 10¹⁹ 10¹⁵ 10¹⁷ 10²⁰ Generation rate (cm⁻² s⁻¹) d 100 11 10 PL QY (%) 1 21 0.1 0.01 0.001 10²³ 10²⁴ 10²² 10^{2} 10^{2} 10^{2} 10²¹ Generation rate (cm ⁻³ s⁻¹)

Fig. 2 | **Excitonic recombination in thin BP. a**, PL spectra of monolayer BP at different generation rates, shown by depth of the purple colour. **b**, PL peak position as a function of generation rate and thickness. **c**, Measured PL QY at a generation rate of \sim 3.6 × 10²⁶ cm⁻³ s⁻¹ for different thicknesses, along with the calculated radiative rate normalized by that of the monolayer. **d**, PL QY as a

function of generation rate for different thicknesses. The error bars δQY in **c** and **d** are based on the uncertainties in the laser power measurement (δP) and measured PL signal (δN): $\delta QY = QY \sqrt{(\delta P/P)^2 + (\delta N/N)^2}$, where *P* and *N* are measured laser power and PL counts, respectively.

for the same level of defect density, increasing binding energies can lead to increasing radiative recombination.

Radiative free-carrier recombination

Before we investigate radiative free-carrier recombination in BP, we first discuss carrier recombination in conventional free-carrier semiconductors. Non-equilibrium populations of electrons and holes relax in a conventional semiconductor mainly through four different pathways: Shockley–Read–Hall (SRH)^{39,40}, surface^{41,42}, bimolecular radiative⁴³ and Auger^{44,45} recombination. The generation rate *G* in the steady state is balanced by the rates of all the recombination channels; for the case of a semiconductor with low background doping, where the electron and hole concentrations are at the same level,

$$G = \left(A + \frac{2S}{d}\right)\frac{n^2 - n_i^2}{n} + B\left(n^2 - n_i^2\right) + 2Cn\left(n^2 - n_i^2\right)$$
(1)

where *n* is the carrier concentration; n_i is the intrinsic carrier concentration; *d* is the semiconductor thickness; and *A*, *B*, *C* and *S* are the SRH, radiative and Auger recombination coefficients, and SRV, respectively. The PL QY is calculated according to a standard *ABC* recombination model (where *A*, *B* and *C* are the coefficients) as

$$QY = \frac{B\left(n^2 - n_i^2\right)}{G}.$$
 (2)

Defect-mediated non-radiative SRH recombination and surface recombination dominate at low generation rates and lower the QY⁴⁶. Non-radiative Auger recombination dominates and lowers the QY at high generation rates⁴⁷. The surface recombination rate depends inversely on the semiconductor thickness⁴⁸.

Contrary to what occurs in the excitonic regime, the PL QY of BP increases when the thickness is increased in the free-carrier regime (Fig. 3a; Supplementary Fig. 2 for PL QY in a full thickness regime). An

efficiency drop was not observed for very thick BP at low generation rates, so the SRH process is negligible ($A \approx 0$) compared to the other recombination processes observed within our measurement range. We note a thickness-dependent QY decrease with decreasing generation rate, which indicates surface recombination ($S \neq 0$). Similar QY roll-off is observed for all thicknesses at high generation rates, indicating that the Auger process in thick BP is insensitive to the

thickness
$$\left(C \neq 0, \frac{\partial C}{\partial d} \approx 0\right)$$
. The radiative bimolecular recombination

coefficient *B* of BP was experimentally measured by employing the Shockley-van Roosbroeck relation (details in Supplementary Information and Supplementary Fig. 3) and is comparable to other reports in the literature¹⁰.

We next summarize carrier recombination pathways in BP (Fig. 3b). At the monolayer limit, excitonic recombination leads to bright luminescence. At intermediate thicknesses, QY is low due to surface recombination. At large thicknesses, only Auger recombination limits the QY. Auger recombination is typically pronounced in small-bandgap semiconductors^{49,50}; however, in BP, the observed Auger coefficient is also low compared to other semiconductors (Fig. 4a)^{10,11}. This originates from the relationship between the empirical ratio of the Auger lifetime (τ_a) to the radiative lifetime (τ_r) and the bandgap (E_g), which is given by

$$\frac{\tau_{\rm a}}{\tau_{\rm r}} \propto \exp\left(\frac{m_{\rm e}^*/m_{\rm h}^*}{1+m_{\rm e}^*/m_{\rm h}^*}\frac{E_{\rm g}}{kT}\right) \tag{3}$$

where m_e^* and m_h^* are the effective masses of electrons and holes, respectively⁵¹; *k* is Boltzmann's constant; and *T* is temperature. As electrons and holes have similar effective masses in BP, the effective mass ratio is much higher than that of other small-bandgap semiconductors and results in suppressed Auger recombination⁵². The effect of low Auger recombination is readily observed experimentally by comparing the electroluminescence and PL of BP with that of other small-bandgap semiconductors in the high-injection regime⁵³. Note that the



Fig. 3 | **Free-carrier recombination in BP. a**, Experimental (scatters) and calculated (solid lines) PL QY versus generation rate for BP of different thicknesses. The error bars are based on the uncertainties in the laser power measurement and measured PL signal: $\delta QY = QY \sqrt{(\delta P/P)^2 + (\delta N/N)^2}$. **b**, Dominant recombination pathways active in BP with excitonic and free-carrier systems.

expression for Auger lifetime given above is overly simplistic and does not capture everything, and further calculations that consider the total band structures are necessary⁵⁴, although the given expression is sufficient to understand the phenomenon of suppressed Auger recombination.

The SRV and Auger coefficient are numerically fitted with the available data using the theoretical expression of QY (Fig. 3a and Supplementary Fig. 4). The experimental data for all thicknesses is reproducible by the theoretical model with two thickness-independent parameters, C and S, and no other combination of values leads to a fit (Supplementary Fig. 4). Relaxing the strict condition that C and S are thickness independent would lead to a better fit for intermediate thickness; however, even with such a strict condition, this simple ABC model with only two parameters captures the essential physics. Simulated QY values versus generation rate and thickness are shown in Supplementary Fig. 5 and capture the main features observed in the experiments (Supplementary Information for further details)⁵⁵. From the abovementioned experimental results, we observed an SRV of $(3 \pm 1) \times 10^{-3}$ cm s⁻¹ and an Auger coefficient of $(3 \pm 1) \times 10^{-44}$ cm⁶ s⁻¹ for BP (Supplementary Fig. 4 for calculation results). The Auger coefficient is consistent with other reports in the literature¹⁰ (Supplementary Table 1), while no previous work has reported the SRV for BP. The observed SRV is two orders of magnitude lower than that of passivated silicon¹², the most electrically inactive surface known to the modern semiconductor industry (Fig. 4b). In covalently bonded semiconductors, a large SRV is observed when dangling bonds at the surface introduce electronic energy levels inside the normally forbidden gap⁴¹. These levels are referred to as surface or interface states⁵⁶. Such states greatly enhance non-radiative electron-hole recombination at the surface by acting as stepping stones for transitions between the conduction and valence bands. Since each recombination event at the surface requires precisely one electron and one hole as well as an interface state, surface passivation in conventional semiconductors either reduces the number of surface states or the concentration of one carrier at the surface⁵⁷⁻⁵⁹. In BP, the surface is self-terminated, an inherent property of the crystal structure. Thus, the SRV in BP is expected to be substantially lower than that in conventional three-dimensional semiconductors whose surfaces are filled with dangling bonds.

An ideal sample of BP has no dangling bonds, although the BP surface is easily oxidized in air due to the lone pair electrons¹⁷, meaning that defects and native oxides can exist. We performed ab initio density functional theory calculations to locate the defect states in the band structure (Fig. 4c,d). Although simulations of very thick layers with an oxidized surface are desired, such computations are prohibitively expensive. Thus, we examine simulated band structures in four-layer

BP with bridging and terminal oxygen defects on the surface, as shown in Fig. 4c,d. The calculated densities of states show that these defects do not form electronic states within the bandgap and that a slight bandgap opening occurs with oxidation. These results support that a few-layer BP surface is naturally passivated and resistant to the formation of in-gap defect states from surface oxidation, which past work has shown to be the thermodynamically stable oxygen defects in monolayer BP^{16,60}.

Furthermore, we examined BP's optical stability against oxidation. Although thin BP layers below ~12 nm indicated PL QY degradation after air exposure for one week, relatively thick BP (>50 nm) shows no degradation in optical performance after air exposure for one week or even the harsh oxidation process of an oxygen plasma for 10 s (Supplementary Figs. 6 and 7). Previous studies have reported that BP oxidation occurs layer by layer, creating a steep interface between BP oxide (PO_x) and leaving intact BP layers underneath. The fact that PO_x formation is self-limiting has been employed previously for controlled exfoliation⁶¹. PO_x is also shown to have minimal charge transfer with BP and is suitable for passivation or as an interface layer for further dielectric deposition¹³⁻¹⁵. Considering the fact that PO_x has a much larger bandgap than BP (for example, 8.5 eV for the most stable phosphorene oxide, P_2O_5)¹⁶, a PO_x layer can also work as a cladding layer to effectively confine carriers in the BP active layer, similar to III-V compound semiconductors. Even with the localized PO, formation at the interface, the dangling bonds are only at the PO_x edge, and their density will be much lower than that of a covalently bonded semiconductor surface. BP generally has been regarded to be unstable in air due to oxide formation¹³⁻¹⁷; however, the present results indicate that the optical performance in relatively thick BP is feasible even if the surface is oxidized, suggesting its promising potential in practical optoelectronic applications such as mid-infrared photodetectors and light-emitting devices.

Photoluminescence quantum yield enhancement by optical cavities

The naturally passivated surface of bulk BP offers unique opportunities to integrate BP with external optical cavities without any deleterious effects on carrier recombination, which is a common issue for many semiconductors. We can use the Purcell factor enhancement by an optical cavity to maximize the internal PL QY. Although BP has a low SRV, the PL QY is still limited to a few percent due to the Auger recombination, especially in the high-generation-rate regime. The use of an optical cavity presents a means to enhance the internal QY in the emission layer⁶². Here a multilayer structure was fabricated using a BP layer sandwiched with insulators and mirrors (inset in Fig. 5a). The bottom half-cavity was prepared using Al₂O₃ and Au film before BP transfer. As a top insulator layer, a hexagonal boron nitride (h-BN) flake was transferred onto BP rather than depositing an oxide, to prevent the



Fig. 4 | **Comparison of SRV. a**, **b**, Auger coefficient (**a**) and SRV (**b**) of different semiconductors, organized by bandgap. Full lists of reported Auger coefficients and SRVs are shown in Supplementary Table 1. **c**, **d**, Schematic of crystal structure and density of states (DOS) for four-layer BP: intrinsic, with a terminal oxide atom, and with a bridging oxide atom.

introduction of defects in BP. Indium tin oxide (ITO) was selected as a top mirror, which partially reflects mid-infrared PL but is transparent against the excitation laser (638 nm). Figure 5a shows the Purcell factor in bulk BP in a cavity (PF_{cavity}) as a function of the Al_2O_3 and BP thicknesses, simulated by the finite-difference time domain (FDTD) method with fixed ITO and h-BN thicknesses of 50 nm and 30 nm, respectively. Compared to the Purcell factor for BP on 50 nm SiO₂/Si substrate ($PF_{SiO_2/Si}$), the enhancement factor of $PF_{cavity}/PF_{SiO_2/Si}$ is maximized when the BP thickness is below 50 nm (Fig. 5b). For 40 nm BP with a 500 nm bottom Al_2O_3 layer, the simulation result estimates one order Purcell factor enhancement compared to BP on SiO₂/Si. With the optimized cavity structure, a maximum PL QY of ~20% was demonstrated in -40 nm BP by the Purcell effect (Fig. 5c,d). The generation-rate-dependent PL QYs were fitted by the *ABC* model with a parameter of

radiative recombination rate, and with a fixed SRV and Auger recombination rate determined by PL QYs for different thicknesses (Fig. 3a). The radiative recombination rate in BP in an optical cavity was found to be one order higher than without the cavity (that is, BP on SiO₂/Si). As BP thickness increased to 130 nm, no PL enhancement was observed (Supplementary Fig. 8). These experimental results are consistent with the illustration based on FDTD simulation (Fig. 5b). Note that unlike the conventional materials used in state-of-the-art technologies such as heteroepitaxy or bonding, van der Waals materials can be readily added to almost any cavity structures.

Conclusions

In conclusion, we explored radiative recombination in BP when the nature of recombination varies from excitonic to free carrier. We found



Fig. 5 | **Enhanced PL QY by optical cavity. a**, FDTD simulation result of Purcell factor in bulk BP as a function of Al₂O₃ and BP thicknesses. ITO and h-BN thicknesses were fixed at 50 nm and 30 nm, respectively. The inset shows a schematic view of BP in an optical cavity, the ITO/h-BN/BP/Al₂O₃/Au structure. **b**, Simulated Purcell factor enhancement in an optical cavity (PF_{cavity}) compared with a 50 nm SiO₂/Si substrate (PF_{SiO₂/Si}). **c**, PL spectra from 40 ± 5 nm BP flakes}

that at the same defect density, more excitonic BP leads to a higher luminescence efficiency. We also measured the SRV of BP and found it to be two orders of magnitude lower than the lowest value reported in the literature for any semiconductor, to the best of our knowledge, a consequence of oxidation not creating defect levels inside the bandgap. This suggests exciting prospects for photonic devices in which BP is patterned, for example, to enhance light outcoupling and/or for integration with photonic circuits, with the ultra-low recombination velocity meaning that this patterning will not be detrimental to optoelectronic performance.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41565-023-01335-0.

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on a SiO₂/Si substrate and in a cavity at a generation rate of 1×10^{26} cm⁻³ s⁻¹. **d**, Experimental results of PL QY in 40 ± 5 nm BP in an optical cavity and on SiO₂/Si. Al₂O₃ thickness was fixed at 500 nm. The generation-rate-dependent PL QY values were fitted by the *ABC* model, for BP in an optical cavity (solid line) and on SiO₂/Si (dashed line). The error bars are based on the uncertainties in the laser power measurement and measured PL signal: $\delta QY = QY \sqrt{(\delta P/P)^2 + (\delta N/N)^2}$.

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Article

Methods

Device fabrication

BP (HQ Graphene) was mechanically exfoliated by Scotch tape and polydimethylsiloxane (Gel-pak) on 50 nm SiO₂/Si substrates; then the number of layers was identified with optical contrast microscopy and atomic force microscopy. To minimize the formation of natural oxide, both mechanical exfoliation and thickness measurements were performed in a nitrogen environment. After flake isolation, the samples were sealed in nitrogen and transferred to the optical measurement set-up. For the optical cavity, the bottom layers of Al_2O_3 and Au were fabricated on SiO₂/Si substrate by sputtering and electron-beam depositions, respectively. An h-BN flake (HQ Graphene) was mechanically exfoliated on another SiO₂/Si substrate, followed by ITO sputtering deposition. After exfoliating BP on the Al_2O_3 , the ITO and h-BN layers were dry transferred onto the BP flakes using polydimethylsiloxane.

Optical characterization

The calibrated PLQY was measured using PL instruments described in detail in previous studies^{1,6}. Different spectrometers were used for the different measurement wavelength ranges. For visible to near-infrared measurements, a home-built micro PL instrument was used with Si charge-coupled device and InGaAs detectors⁶. The excitation source was a laser with a wavelength of 514.5 nm. For longer wavelengths, a Fourier transform infrared spectrometer (iS50, Thermo Fisher) with a liquid-N₂-cooled HgCdTe detector was used¹. A 638 nm laser was used as the excitation source. All measurements, for bilayer or thicker BP flakes, were taken at room temperature in ambient lab conditions under nitrogen flow. For the monolayer, which is relatively air sensitive compared to thicker flakes, the sample was sealed in a home-built chamber with an optical window after the exfoliation in the glove box, excluding the introduction of oxygen, water and other contaminants to the monolayer. The sealed container with the monolayer inside was then promptly measured through the optical window. Even in the nitrogen atmosphere, monolayer quality can degrade if high-power or long-time laser exposure is performed. Note that the laser exposure time was minimized, and PL reproducibility was confirmed by sweeping the laser power up and down to ensure that there was no sample degradation under the continuous and repeated laser exposure. For the low-temperature PL measurements, the sample was cooled and measured using a closed-cycle optical cryostat (Cryostation s200, Montana Instruments). The excitation source was a laser with a wavelength of 532 nm, and PL spectra were measured with Si charge-coupled device and InGaAs detectors. To extract the PL QY for bulk BP, light incoupling and outcoupling efficiencies were calculated with FDTD simulations (FDTD Solutions, Lumerical), as shown in Supplementary Fig. 9. The simulation details are described in Supplementary Information.

Density functional theory calculations

Density functional theory calculations were carried out using the Quantum Espresso package⁶³⁻⁶⁵. Optimized geometries for pristine BP as well as BP with bridging and terminal oxygen defects were obtained for the monolayer through four-layer systems consisting of a $3 \times 3 \times 1$ supercell with over 2 nm of vacuum in the out-of-plane direction to avoid interactions with periodic replicas. We used the Perdew–Burke–Ernzerhof form of the general gradient approximation of the exchange–correlation energy⁶⁶ with Grimme-D2 (ref. ⁶⁷) dispersion corrections, which have been shown to sufficiently describe oxygen defects in BP systems⁶⁰. Using these geometries, band structures and densities of states were calculated at the same level of theory.

Data availability

All data generated or analysed during this study are included in this published Article. Source data are provided with this paper.

Code availability

All codes to analyse the band structures, densities of states and optical properties are available from the corresponding authors upon reasonable request.

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Author contributions

N.H., S.Z.U. and A.J. conceived the idea for the project and designed the experiments. N.H., S.Z.U., I.K.M.R.R. and V.W. prepared samples and performed optical measurements. N.H., S.Z.U. and A.J. analysed the data. S.Z.U. performed analytical modelling. D.W. and E.R. performed electronic band structure calculations. N.H., S.Z.U., N.S.A., V.W. and K.B.C. performed optical simulations. N.H., S.Z.U. and A.J. wrote the paper. All authors discussed the results and commented on the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Ali Javey.

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