Tunable bright interlayer excitons in few-layer black phosphorus based van der Waals heterostructures

Yifeng Chen and Su Ying Quek

1 Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117542, Singapore
2 Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551, Singapore
E-mail: phyqsy@nus.edu.sg

Keywords: interlayer excitons, heterostructures, 2D materials, black phosphorus, optical properties, hexagonal boron nitride, germanium sulfide

Abstract
Few-layer black phosphorus (BP) is a direct band gap material with large exciton binding energies, and shows great promise in optoelectronic applications. Here, we study the excitons in BP-based heterostructures with encapsulation and spacer 2D layers, using first principles GW and Bethe–Salpeter equation (BSE) methods. The 2D layers chosen are germanium sulfide (GeS) and hexagonal boron nitride (hBN), representing respectively strong and weak hybridization with BP. Except for hBN-encapsulated BP, all systems host bright interlayer (or indirect) excitons. In contrast to 2D indirect gap heterostructures, the interlayer excitons here are much brighter. Strong hybridization between GeS and BP increases the effective mass and room temperature exciton lifetimes. In contrast, the hBN spacer layer decouples the BP monolayers in BP/hBN/BP, resulting in the lowest energy exciton being dark. Surprisingly, however, BP/hBN/BP hosts interlayer BP excitons that are even brighter than those in bilayer BP. This lowest energy bright exciton lies very close in energy to the dark state, resulting in an increased effective lifetime. Our work uncovers the interplay between interlayer interactions and the physics of interlayer excitons, and paves the way for the use of bottom-up materials design to optimize the dipole oscillator strengths and lifetimes of interlayer excitons for excitonic device applications.

1. Introduction
Layered two-dimensional (2D) materials possess novel excitonic properties due to reduced spatial dimensions and enhanced Coulomb interactions [1–3]. Depending on the application, the essential parameters important in the physics of excitons are the exciton binding energy, the spatial extent, the optical dipole oscillator strength and the radiative lifetime. Compared with semiconducting quantum wells, reduced screening in 2D leads to much larger exciton binding energies (BE) in 2D materials [4], which opens up opportunities for their observation and manipulation at room temperature. Stacking different 2D layered materials together forms so-called van der Waals heterostructures (vdWHs) [5, 6], enabling the bottom-up design of material properties without the need for explicit lattice matching. Recent experimental advancements have even enabled the control of stacking twist angle to within a few degrees [7, 8]. Just as in bulk quantum well structures [4], 2D vdWHs can also host interlayer (or indirect) excitons, where the electron and hole reside on different layers [9–12]. These excitons are of particular interest because they can be controlled by electric fields, and also because of their prolonged lifetime, paving the way for interesting applications such as excitonic devices, high temperature superfluidity, etc [13–17]. However, the larger spatial spread of the interlayer exciton also results in reduced oscillator strengths [18, 19], which are undesirable for light emitting diode and excitonic device applications. This is particularly notable in indirect band gap vdWHs (e.g. multilayer transition metal dichalcogenide (TMD) systems). The bottom-up process of forming vdWHs opens up opportunities to design 2D heterostructures that host strongly bound excitons with the optimal balance between lifetime and oscillator strength.
Studies on interlayer excitons in 2D vdWHs have mainly focused on gapped graphene and TMD systems [9–13, 20]. First principles density functional theory (DFT) together with the many-electron GW/Bethe–Salpeter Equation (BSE) method is the state-of-the-art approach for predicting excitonic properties of 2D materials [21–25]. Previous DFT+GW/BSE calculations on 2D vdWHs have studied the effects of electric fields [26] and interlayer distance [27] on excitons in bilayer TMD vdWHs.

Few-layer black phosphorus (BP) is a recent member of the family of 2D materials from group V [28–31]. Its tunable band gap size of 0.3–2.0 eV falls in the range between the band gaps of graphene and TMDs [22, 32, 33]. Importantly, few-layer BP is a direct band gap semiconductor for both mono layers TMDs [22, 32, 33]. Its tunable band gap size of 0.3–2.0 eV falls in the range between the band gaps of graphene and TMDs [22, 32, 33]. Importantly, few-layer BP is a direct band gap semiconductor for both mono layers TMDs [22, 32, 33].

Furthermore, the intrinsic anisotropic properties and relatively high carrier mobilities of BP are also promising for novel applications [21, 35–38]. In contrast to TMDs, graphene and many other 2D materials, the interaction between BP layers is not completely vanishing for novel applications [21, 35–38]. In contrast to TMDs, graphene and many other 2D materials, the interaction between BP layers is not completely vanishing for novel applications [21, 35–38]. In contrast to TMDs, graphene and many other 2D materials, the interaction between BP layers is not completely vanishing for novel applications [21, 35–38].

Our calculations were performed using Quantum ESPRESSO [41] and BerkeleyGW [42] software packages. Norm conserving pseudopotentials with a kinetic energy cutoff of 55 Ry were used, together with a vacuum height of at least 12 Å between periodic 2D slabs. A dielectric matrix cutoff of 15 Ry was used in the one-shot G0W0 calculations. Monkhorst-Pack k-mesh densities of at least 14 × 10 × 1 and 56 × 40 × 1 for a 1 × 1 BP primitive cell were used in the GW and BSE calculations, respectively. Further calculation details are available in the supplementary information (SI) (stacks.iop.org/TDM/5/045031/mmedia).

Following [43], we define the dimensionless optical oscillator strength per phosphorus atom as:

\[
S_\text{avg} = \frac{1}{N_i N_{\text{atom}}} \frac{2n}{\hbar \Omega_i} | \langle \mathbf{A} \cdot \langle \mathbf{v} | S \rangle \rangle |^2, \tag{1}
\]

where \( \mathbf{v} \) is the velocity operator, \( \Omega_i \) is the exciton frequency. BP has anisotropic optical properties, with the lowest lying bright excitons arising from light polarized in the armchair direction [22]. We therefore focus on the excitonic properties arising from light polarized in the armchair direction. Using Fermi’s Golden Rule [44, 45], we derive expressions for the radiative lifetimes of such excitons to be

\[
\tau_S^{-1} (T) = \gamma_S = \tau_S^{-1} (0) \left[ \frac{\sqrt{8}}{2} \sqrt{\frac{\Delta_S}{\hbar c T}} - \frac{\sqrt{8}}{4} \left( \frac{\Delta_S}{\hbar c T} \right)^2 \right]. \tag{2}
\]

Here, \( \Delta_S = E_S^2 (0) / 2M_S c^2 \) is the maximum kinetic energy, where \( M_S = m_e^2 + m_h^2 \) is the exciton mass (the electron and hole effective masses were fitted from DFT-PBE bands near \( \Gamma \) along the armchair direction). Note that the second term in (2) is much smaller than the first term, so that the lifetime has a \( \sim \sqrt{T} \) dependence on temperature, similar to that in one-dimensional materials [44]. The lifetime at 0 K, \( \tau_S (0) \), is defined as

\[
\tau_S^{-1} (0) = \gamma_S (0) = \frac{4\pi e^2 E_S (0) m_e^2}{\hbar^2 c A_{\text{uc}}}, \tag{3}
\]

where \( A_{\text{uc}} \) is the area of the unit cell, and \( \mu_e^2 = (\hbar^2 / m_e^2) E_S^2 (0) \) \( \langle | (G \rho_c) | \Psi_S (0) \rangle \rangle \rangle / N_k \rangle \) is the square of the dipole matrix element. The expression for \( \tau_S (0) \) is similar to that in a 2D isotropic material, but larger by a factor of 2 [45]. Details of the derivation are presented in the SI.

We define an effective radiative lifetime by averaging the decay rates over the lowest energy bright and dark excitons:

\[
\langle \tau_{\text{eff}} \rangle^{-1} = \frac{\sum \tau_S^{-1} e^{-E_S (0) / k_B T}}{\sum e^{-E_S (0) / k_B T}}. \tag{4}
\]
3. Results

3.1. Monolayer BP and GeS

Monolayer (ML) BP has a puckered orthorhombic geometry with armchair and zigzag directions as shown in figure 1(a). Our GW band gap and exciton binding energy (table 1) are in good agreement with previous theoretical and experimental results [22, 46, 47]. We also compute a large oscillator strength of 0.068 and an intrinsic radiative lifetime of 2.0 ps at room temperature (RT; 300 K).

Few-layer GeS is a readily available material that does not degrade in ambient conditions [48]. GeS is a group IV monochalcogenide layer with a similar atomic structure to BP (figure 1) and a relatively small lattice mismatch with BP. Like BP, it has anisotropic optical properties, with low energy optical excitations along the armchair direction (figure S2). Compared to ML BP, the exciton oscillator strength is weaker (0.039) and the RT lifetime is longer (4.5 ps). This longer RT lifetime is partly due to a larger effective mass (table 1).

3.2. Bilayer BP/GeS and BP/hBN

For the relaxed AB stacked BP/GeS bilayer structure, the strain on BP (GeS) is $-2.4\%$ ($3.8\%$) along armchair and $3.9\%$ ($-7.2\%$) along zigzag directions. The puckered structure of GeS implies that the interaction between GeS and BP will resemble that between BP layers themselves. Indeed, the DFT projected density of states (PDOS) in figure 2(a) shows significant hybridization between BP and GeS in the BP/GeS bilayer (BL). We note that while it is not clear whether the $-7.2\%$ strain for GeS in the zigzag direction can be achieved in experiment, this does not change the conclusions in the manuscript significantly, because we are focusing on the low energy excitations along the armchair direction in BP.

In contrast to GeS, ML hBN has an optical band gap larger than 5.5 eV and does not hybridize significantly with BP (figure 2(b)). We note that for the bilayer BP/hBN supercell, we have interfaced a $1 \times 3$ supercell of BP with a $1 \times 4$ supercell of an orthorhombic hBN primitive cell, similar to [49, 50]. We note that BP can sustain a relatively large strain along the armchair

---

Table 1. Properties of low energy bright intralayer excitons. The GW band gap is given as well. The exciton binding energy (BE) is the difference in energy between the GW gap and the exciton energy. Mass units are in free electron mass $m_0$. Energy units are in eV.

| Intralayer exciton | ML BP | BL BP/hBN | TL hBN/BP/hBN | Ideal ML GeS |
|--------------------|-------|-----------|---------------|--------------|
| GW gap@Γ          | 2.10  | 1.86      | 2.03          | 3.40         |
| Exciton energy     | 1.29  | 1.14      | 1.34          | 2.35         |
| Exciton BE         | 0.81  | 0.72      | 0.69          | 1.05         |
| Oscillator strength $f^{\text{exc}}_S$ | 0.068 | 0.049     | 0.047         | 0.039$^*$    |
| τ_S(0) (ps)        | 0.026 | 0.034     | 0.036         | 0.048        |
| Effective mass (electron/hole) | 0.141/0.131 | 0.150/0.142 | 0.190/0.193 | 0.838/0.616 |
| τ_S(300K) (ps)     | 1.998 | 2.963     | 3.039         | 4.489        |

* Number of atoms in a single GeS primitive cell is counted as 4.
direction at low energy cost [51], and the relaxed structure has $-6.2\%$ ($+0.3\%$) strain on BP along the armchair (zigzag) direction.

The optical absorption spectra for BL BP/GeS and BL BP/hBN are anisotropic (figure S4), and the spectra for light polarized in the armchair direction of BP are shown in figures 2(c) and (d). The lowest energy bright excitons are both 1s excitons, but the exciton in BP/GeS is a mixed interlayer exciton [27], whereas that in BP/hBN is an intralayer one localized on BP (figures 2(e) and (f)). The contrasting nature of the exciton wavefunctions is consistent with the significant hybridization between BP and GeS, and the clear Type I alignment in BP/hBN.

### 3.3. Encapsulated monolayer BP

The optical absorption spectra for ML BP encapsulated with GeS and hBN MLs are shown in figures 3(a) and (b), respectively, for light polarized in the armchair direction (zigzag direction: figure S5). These systems all have direct band gaps (figure S6), with GW quasiparticle (QP) gaps that are smaller than those in ML BP, because of increased screening from the encapsulation layers, as well as wavefunction hybridization in the case of GeS/BP/GeS. (We note that the GW gap in hBN/BP/hBN is larger than that in BL BP/hBN (table 1), because of the interaction between $p_z$ orbitals in BP and hBN [50]). The lowest energy absorption peaks both correspond to 1s excitons, but that in GeS/BP/GeS is a mixed interlayer exciton (figure 3(a) inset) while that in hBN/BP/hBN is an intralayer exciton on BP. Figure 3(c) compares the exciton BE in different systems (showing excitons with oscillator strengths that are at least 5% of the maximum oscillator strength in the respective systems).

We first focus on comparing the BE for excitons in trilayer (TL) hBN/BP/hBN, BL BP/hBN and in ML BP. Although no interlayer excitons are present here, these systems are relevant because of the use of hBN for encapsulation of BP [52–55]. hBN does not change the exciton spectrum significantly. However, similar to the QP gap, the BE are shifted to smaller values due to elec-
Electronic screening from the hBN layers (the exciton BE is a measure of the electron-hole interaction strength, and it depends crucially on quantum confinement and environmental screening effects [25]). As the exciton energy is given by the difference between the QP gap and the exciton BE, there is negligible change in the exciton energy (table 1). Interestingly, we see that just one layer of hBN is sufficient to reduce the BE of the 1s exciton by 19%, whereas adding another hBN ML on the other side of BP has relatively little additional effect on the exciton BE. These results point toward non-trivial screening from the atomically thin 2D hBN monolayer, despite its large QP gap. The RT intrinsic radiative lifetime of the 1s exciton increases slightly from ~2 ps in ML BP to ~3 ps in BL BP/hBN and TL hBN/BP/hBN (table 1).

In contrast to hBN-encapsulated BP, there are significant changes to the exciton levels in GeS/BP systems in figure 3(c), compared to ML BP. There are a larger number of bound excitons with oscillator strengths at least 5% of the maximum oscillator strength for each system. LX refers to a lower intensity exciton with energy below the 1s peak.
significantly smaller than those in BP. Besides increased screening from GeS, the smaller BE arise from hybridization between GeS and BP, giving a larger spatial spread of the interlayer excitons, which reduces the effective electron-hole interaction. For GeS/BP/GeS, the levels LX1 and LX2 in figure 3(c) have weaker oscillator strengths and result in a low energy shoulder in the optical absorption spectra (figure 3(a)). The binding energy of the brightest exciton (figure 3(a) inset) is 0.20 eV, ~4 times smaller than that in ML BP, but still an order of magnitude larger than those in bulk semiconductor quantum wells [4]. Interestingly, compared to the 1s exciton in ML BP, the RT lifetime of this bright interlayer 1s exciton is 28.92 ps, almost 15 times longer (table 2), while its oscillator strength is only 5 times smaller. The enhanced lifetime at RT arises from the larger effective mass of the exciton (table 2; see equation (2)), which in turn results from a combination of lattice strain and hybridization with GeS, the latter having larger effective masses. Our results suggest that GeS can function as an electronically active encapsulation layer and also point to the possibility of using hybridization and lattice strain to increase the exciton effective mass, and thereby increase the RT exciton lifetime without compromising the oscillator strength.

### 3.4. Bilayer BP with GeS and hBN spacers

Experimental advancements in the synthesis of 2D layered heterostructures, enabling control over both the stacking sequence and stacking angle [7, 8], imply that bottom-up design of 2D layered heterostructures can be used to tailor the properties of interlayer excitons. In particular, it is interesting to ask how a spacer of 2D layers between two BP MLs would change the excitonic properties. Would these systems host interlayer excitons involving the BP layers? How would the oscillator strength, lifetime and BE of these excitons depend on the thickness and nature of the interlayers? We present here the optical properties of ABA-stacked TL BP/GeS/BP (figure 1(d)), ABAB-stacked BP/3L-GeS/BP (figure 4(e)), and TL BP/hBN/BP (figure 1(e)) with AA stacking between the BP layers. TL BP/hBN/BP with AB stacking between the BP layers have similar results (see SI). All these systems have direct band gaps (figure S8).

| Interlayer exciton | AA-BL BP | AB-BL BP/GeS | GeS | TL GeS/BP/GeS | TL BP/GeS/GeS/GeS | TL BP/GeS/GeS/GeS | BP/3L-GeS/GeS | BP/hBN/BP | BP/hBN/BP |
|--------------------|----------|-------------|-----|--------------|-------------------|-------------------|--------------|------------|----------|
| GW gap@Γ (eV)     | 1.27     | 1.91        | 1.54 | 1.43         | 1.57              | 1.65              | 1.65         | 1.65       |
| Exciton energy     | 0.73     | 1.27        | 1.34 | 0.95         | 1.24              | 1.23              | 1.41         |
| Oscillator strength $f^\text{S}_{\text{S}}$ | 0.030 | 0.034 | 0.014 | 0.014 | 0.0074 | 0.032 | 0.011 |
| τ(0) (ps)          | 0.029    | 0.054       | 0.131 | 0.064       | 0.122             | 0.026             | 0.079        |
| Effective mass (electron/hole) | 0.095/0.089 | 0.669/0.253 | 2.198/0.401 | 0.217/0.243 | 0.336/0.434 | 0.171/0.171 | 0.144/0.132 |
| τ(300K) (ps)       | 3.113    | 7.470       | 28.92 | 8.375 | 15.93 (65.6) | 2.257 (17.3) | 5.422 |

Compared to BP MLs, the low energy excitons in BL BPs all have strong interlayer character and the exciton BE are reduced to ~0.5 eV (tables 2 and S1, also see figure S7). AA- and AB-stacked BP bilayers have similar optical properties (tables 2 and S1; figure S7). First, we consider the effect of GeS spacers. There is significant hybridization between GeS and BP wavefunctions, but the VBM and CBM wavefunctions of TL BP/GeS/BP are predominantly of BP character (figure 4(a)). Compared to AA-BL BP, the direct band gap in BP/GeS/BP is larger (1.54 eV versus 1.27 eV), and the exciton BE is slightly reduced from 0.54 eV in AA-BL BP to 0.48 eV in BP/GeS/BP (figure 4(g), table 2). More significant changes are observed in the oscillator strengths and lifetimes. The oscillator strength of the lowest lying 1s exciton is reduced by ~50%, while the zero temperature lifetime is doubled. Insertion of GeS increases the exciton effective mass, which leads to a larger increase in the RT lifetime of the exciton, from 3.1 ps in AA-BL BP to 8.4 ps in BP/GeS/BP. The interlayer nature of this 1s exciton is clearly seen in figure 4(d).

Even when the GeS thickness is increased to three layers, the BP/3L-GeS/BP system still hosts bound interlayer excitons (figure 4(e)) involving the two BP layers, with a larger exciton BE of 0.37 eV and a reasonably large oscillator strength (only three times smaller than the 1s exciton in AB-BL BP, and four times smaller than that in AA-BL BP). The RT lifetime of this 1s exciton is 15.93 ps, five times that in AA-BL BP. We note that taking into account the darker exciton close in energy to this 1s exciton (LX; figure 4(b)), the effective exciton lifetime is significantly longer—65.6 ps. These results indicate that GeS spacer layers allow one to tune the properties of interlayer excitons, enhancing their lifetimes while still maintaining significant oscillator strength and exciton BEs.

BP/hBN/BP systems also host bright interlayer excitons (figure 4(f)). Similar interlayer excitons were also observed in TMD heterostructures with hBN interlayers [13]. The hBN layer decouples the two BP layers. As a result, the GW band gap is larger than that of bilayer BP, and the VBM and VBM-1 bands are reordered, changing the low energy exciton spectrum considerably (figures 4(c) and (g)). The reordering of
bands makes the optical transition between VBM and CBM optically forbidden (DX), while the transitions from VBM-1 to CBM (IX₁) and VBM to CBM +1 (IX₂) become bright (figures 4(c) and (g)), in contrast to bilayer BP (see figure S9 for the Γ-point wavefunctions) [25]. DX, IX₁ and IX₂ all have 1s character. From the exciton wavefunction distribution (figure 4(f)), we see that IX₁ has a larger intralayer character, with 65% of the electron wavefunction residing in the same layer as the hole, while IX₂ has a larger interlayer character. Because of this distinction, we expect that the relative energies of IX₁ and IX₂ can be tuned by an external vertical electric field [27]. Surprisingly, the oscillator strength of IX₁ is in fact slightly larger than that of the 1s exciton in AA-BL BP (table 2). With the larger oscillator strength and similar exciton effective mass, the RT lifetime of the IX₁ exciton is slightly shorter than those of the 1s excitons in BL BP. However, the low energy dark exciton DX serves to increase the effective RT lifetime to 17.3 ps.

Figure 4. Optical properties of BP bilayers with GeS and hBN spacer layers in between. (a)–(c) Optical absorption spectra for (a) TL BP/GeS/BP, (b) BP/3L-GeS/BP, (c) TL BP/hBN/BP. The stacking in these systems is ABA, ABABA in (a) and (b), respectively, while the BP layers are AA-stacked in (c). Thus, the AA-stacked bilayer BP spectra is shown for comparison. The vertical lines correspond to the GW QP gap energies. Insets show the GW band structures, with the optical transitions labeled. DX stands for dark exciton. (d)–(f) Wavefunctions of the excitons as labeled in (a)–(c), showing the distribution of electrons with the hole fixed in the middle of the bottom BP layer. (g) Comparison of exciton BE of bound excitons with oscillator strengths that are at least 5% of the maximum oscillator strength for each system. Black lines in BP/hBN/BP refer to dark excitons below IX₂.
4. Conclusion

There is an obvious trade-off between strong optical oscillator strength of interlayer excitons and their prolonged lifetime. While in type-II TMD heterostructures, interlayer exciton lifetime up to nanoseconds at low temperature have been observed [9], their oscillator strength is rather low [18, 19]. Here, we show that bright interlayer excitons exist in BP-based heterostructures with a reasonable balance between the oscillator strength and lifetimes. Compared to bulk quantum wells, the BE of these excitons are much larger due to reduced screening and quantum confinement. We further show that non-trivial interlayer interactions between BP and other 2D materials can be used to tune excitonic properties from the bottom up—such tuning is not possible in traditional TMD materials with only vdW interactions. Specifically, for BP interfaced with monochalcogenides, hybridization and strain increase the RT lifetime significantly (BP/GeS systems; tables 1 and 2). On the other hand, the weak coupling between BHBN result in additional low energy excitons with very small oscillator strengths in BP/hBN/BP, enhancing the effective lifetimes (table 2). These tunable interlayer interactions, as well as layer material and thickness, can be used to optimize the exciton properties in BP-based heterostructures for various optoelectronic and excitonic device applications, motivating bottom-up experimental efforts toward this direction.

Acknowledgments

We acknowledge support from Grant NRF-NRFF2013-07 from the National Research Foundation, Singapore. Computations were performed on the NUS Graphene Research Centre cluster and National Supercomputing Centre Singapore (NSCC) under project ID: 11000446. We acknowledge support from the Singapore National Research Foundation, Prime Minister’s Office, under its medium-sized centre program.

ORCID iDs

Yifeng Chen  https://orcid.org/0000-0003-4216-8242
Su Ying Quek  https://orcid.org/0000-0003-4223-2953

References

[1] Mak K F and Shan J 2016 Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides Nat. Photon. 10 216–26.
[2] Xiao J, Zhao M, Wang Y and Zhang X 2017 Excitons in atomically thin 2D semiconductors and their applications Nanophotonics 6 1309–28
[3] Lin C, Grassi R, Low T and Helmy A S 2016 Multilayer black phosphorus as a versatile mid-infrared–electro-optic material Nano Lett. 16 8683–9
[4] Bayer M, Timofeev V B, Faller F, Gutfrood T and Forchel A 1996 Direct and indirect excitons in coupled GaAs/AlAs/GaAs double quantum wells separated by AlAs barriers Phys. Rev. B 54 8799–808
[5] Novoselov K S, Mishchenko A, Carvalho A and Neto A H C 2016 2D materials and van der Waals heterostructures Science 353 aac9439
[6] Liu Y, Weiss N O, Duan X D, Cheng H C, Huang Y and Duan X F 2016 Van der Waals heterostructures and devices Nat. Rev. Mater. 1 16042
[7] Tan Z et al 2016 Building large-domain twisted bilayer graphene with van Hove Singularity ACS Nano 10 6725–30
[8] Cao Y et al 2018 Unconventional superconductivity in magic-angle graphene superlattices Nature 556 43
[9] Rivera P et al 2015 Observation of long-lived interlayer excitons in monolayer MoSe2/WSe2 heterostructures Nat. Commun. 6 6242
[10] Liu X M, Watanabe K, Taniguchi T, Halperin B I and Kim P 2017 Quantum Hall drag of exciton condensate in graphene Nat. Phys. 13 746–50
[11] Li H A, Taniguchi T, Watanabe K, Hone J and Dean C R 2017 Excitonic superfluid phase in double bilayer graphene Nat. Phys. 13 731–4
[12] Kogar A et al 2017 Signatures of exciton condensation in a transition metal dichalcogenide Science 358 1314–7
[13] Fang H et al 2014 Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides Proc. Natl. Acad. Sci. USA 111 6198–202
[14] Rigos A F, Hill H M, Li Y L, Chernikov A and Heinz T F 2015 Probing interlayer interactions in transition metal dichalcogenide heterostructures by optical spectroscopy: MoS2/WS2 and MoSe2/WSe2 Nano Lett. 15 5033–8
[15] Latini S, Winther K T, Olsen T and Thygesen K S 2017 Interlayer excitons and band alignment in MoS2/hBN/WSe2 van der Waals heterostructures Nano Lett. 17 938–45
[16] Berman O L, Gumbs G and Kezerashvili R Y 2017 Bose-Einstein condensation and superfluidity of dipolar excitons in a phosphorene double layer Phys. Rev. B 96 014305
[17] Fogler M M, Butov L V and Novoselov K S 2014 High-temperature superfluidity with indirect excitons in van der Waals heterostructures Nat. Commun. 5 4555
[18] Komsa H-P and Krasheninnikov A V 2013 Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles Phys. Rev. B 88 085318
[19] Ross J S et al 2017 Interlayer exciton optoelectronics in a 2D heterostructure p–n junction Nano Lett. 17 638–43
[20] Wang Z, Chiu Y H, Honz K, Mak K F and Shan J 2018 Electrical tuning of interlayer exciton gases in WSe2 bilayers Nano Lett. 18 1317–22
[21] Tran V, Fei R X and Yang L 2015 Quasiparticle energies, excitons, and optical spectra of few-layer black phosphorus 2D Mater. 2014014
[22] Tran V, Soklaski R and Liang Y F and Yang L 2014 Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus Phys. Rev. B 89 235319
[23] Qiu D Y, da Jornada F H and Louie S G 2013 Optical spectrum of MoS2: many-body effects and diversity of exciton states Phys. Rev. Lett. 111 216805
[24] Qiu D Y, da Jornada F H and Louie S G 2016 Screening and many-body effects in two-dimensional crystals: monolayer MoS2 Phys. Rev. B 93 235335
[25] Qiu D Y, da Jornada F H and Louie S G 2017 Environmental screening effects in 2D materials: renormalization of the bandgap, electronic structure, and optical spectra, of few-layer black phosphorus Nano Lett. 17 4709–12
[26] Gao S, Yang L and Spataru C D 2017 Interlayer coupling and gate-tunable excitons in transition metal dichalcogenide heterostructures Nano Lett. 17 7809–13
[27] Dellmann T and Thygesen K S 2018 Interlayer excitons with large optical amplitudes in layered van der Waals materials Nano Lett. 18 2986–9
[28] Li L K et al 2014 Black phosphorus field-effect transistors Nat. Nanotechnol. 9 372–7
[29] Zhang S, Yan Z, Li Y, Chen Z and Zeng H 2015 Atomically thin arsenene and antimonene: semimetal–semiconductor and indirect–direct band-gap transitions Angew. Chem., Int. Ed. 54 3112–5
[30] Zhang S et al 2017 Antimonene oxides: emerging tunable direct bandgap semiconductor and novel topological insulator Nano Lett. 17 3434–40
[31] Zhang S et al 2018 Recent progress in 2D group-VA semiconductors: from theory to experiment Chem. Soc. Rev. 47 982–1021
[32] Das S, Zhang W, Demarteau M, Hoffmann A, Dubey M and Rooofo A 2014 Tunable transport gap in phosphorene Nano Lett. 14 5733–9
[33] Low T et al 2014 Tunable optical properties of multilayer black phosphorus thin films Phys. Rev. B 90 075434
[34] Carvalho A, Wang M, Zhu X, Rodin A S, Su H B and Neto A H C 2016 Phosphorene: from theory to applications Nat. Rev. Mater. 1 16061
[35] Wang X M et al 2015 Highly anisotropic and robust excitons in monolayer black phosphorus Nat. Nanotechnol. 10 517–21
[36] Yuan H T et al 2015 Polarization-sensitive broadband photodetector using a black phosphorus vertical p-n junction Nat. Nanotechnol. 10 707–13
[37] He J Q et al 2015 Exceptional and anisotropic transport properties of photocarriers in black phosphorus ACS Nano 9 6436–42
[38] Qiao J S, Kong X H, Hu Z X, Yang F and Ji W 2014 High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus Nat. Commun. 5 4475
[39] Luo X et al 2015 Large frequency change with thickness in interlayer breathing mode: significant interlayer interactions in few layer black phosphorus Nano Lett. 15 3931–8
[40] Shulenburger L, Raczewski A D, Zhu Z, Guan J and Tomanek D 2015 The nature of the inter layer interaction in bulk and few-layer phosphorus Nano Lett. 15 8170–5
[41] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software package for quantum simulations of materials J. Phys.: Condens. Matter 21 395502
[42] Deslippe J, Samsonidze G, Strubbe D A, Jain M, Cohen M L and Louie S G 2012 BerkeleyGW: a massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures Comput. Phys. Commun. 183 1269–89
[43] Choi S, Deslippe J, Capaz R B and Louie S G 2013 An explicit formula for optical oscillator strength of excitons in semiconducting single-walled carbon nanotubes: family behavior Nano Lett. 13 134–8
[44] Spataru C D, Ismail-Beigi S, Capaz R B and Louie S G 2005 Theory and ab initio calculation of radiative lifetime of excitons in semiconducting carbon nanotubes Phys. Rev. Lett. 95 247402
[45] Palumbo M, Bernardi M and Grossman J C 2015 Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides Nano Lett. 15 2794–800
[46] Liang L B, Wang J, Lin W Z, Sumpter B G, Meunier V and Pan M H 2014 Electronic bandgap and edge reconstruction in phosphorene materials Nano Lett. 14 164600–6
[47] Zhang G et al 2018 Determination of layer-dependent exciton binding energies in few-layer black phosphorus Sci. Adv. 4 eaap9977
[48] Hsueh H C, Li J X and Ho C H 2018 Polarization photoelectric conversion in layered GeS Adv. Opt. Mater. 6 1701194
[49] Cai Y Q, Zhang G and Zhang Y W 2015 Electronic properties of phosphorene/graphene and phosphorene/hexagonal boron nitride heterostructures J. Phys. Chem. C 119 13929–36
[50] Hu T and Hong J I 2015 Anisotropic effective mass, optical property, and enhanced band gap in BN/Phosphorene/BN heterostructures ACS Appl. Mater. Interfaces 7 23489–95
[51] Zhang Z, Zhao Y and Ouyang G 2017 Strain modulation of electronic properties of monolayer black phosphorus J. Phys. Chem. C 121 19296–304
[52] Avsar A et al 2015 Air-stable transport in graphene-contacted, fully encapsulated ultrathin black phosphorus-based field-effect transistors ACS Nano 9 4138–45
[53] Avsar A et al 2017 van der Waals bonded Co/h-BN contacts to ultrathin black phosphorus devices Nano Lett. 17 5361–7
[54] Chen X L et al 2015 High-quality sandwiched black phosphorus heterostructure and its quantum oscillations Nat. Commun. 6 7315
[55] Chen X et al 2017 Widely tunable black phosphorus mid-infrared photodetector Nat. Commun. 8 1672