Observation of $A_g^1$ Raman mode splitting in few layers black phosphorus encapsulated with hexagonal boron nitride

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Abstract

We investigate the impact of the encapsulation with hexagonal boron nitride (h-BN) on the Raman spectrum of few layer black phosphorus. The encapsulation results in a significant reduction of the line width of the Raman modes of black phosphorus, due to a reduced phonon scattering rate. We observe a so far elusive peak in the Raman spectra $\sim 4 \text{cm}^{-1}$ above the $A_g^1$ mode in trilayer and thicker flakes, which had not been observed experimentally. The newly observed mode originates from the strong black phosphorus inter-layer interaction, which induces a hardening of the surface atoms vibration with respect to the corresponding modes of the inner layers. The observation of this mode suggests a significant impact of h-BN encapsulation on the properties of black phosphorus and can serve as an indicator of the quality of its surface.
Black phosphorus (BP), the most stable allotropic form of phosphorus, has been synthesized more than a century ago\textsuperscript{1}. Its recent rediscovery\textsuperscript{2} is related to the possibility of exfoliating thin layers, adding BP to the rapidly emerging family of two-dimensional (2D) materials. Its unique physical properties\textsuperscript{3,4} make it attractive for the next generation of electronic\textsuperscript{5–8}, optoelectronic\textsuperscript{9,10} and thermo-electronic applications\textsuperscript{11–13}. Similarly to other layered semiconductors, such as transition metal dichalcogenides (TMDs) or graphene, the physical properties of BP can be tuned by varying the number of layers\textsuperscript{14}. What distinguishes BP from other 2D semiconductors is the simultaneous presence of strong in-plane anisotropy, and a relatively strong inter-layer coupling.

In single layer BP the atoms form a puckered honeycomb lattice, giving rise to a strong in plane anisotropy of the optical\textsuperscript{15,16}, electrical\textsuperscript{7,17} and thermal\textsuperscript{11–13} properties. Each phosphorus atom forms covalent bonds with its three closest neighbors leaving a pair of lone electrons with elongated orbitals perpendicular to the plane\textsuperscript{18,19}. This results in a significant overlap of the electronic wave function between the layers\textsuperscript{19}. The inter-layer coupling is therefore much stronger than in the case of other layered semiconductors such as TMDs, hexagonal boron nitride (h-BN) or few layer graphene\textsuperscript{3,20,21}. Due to the strength of the inter-layer coupling, the band gap can be tuned over a wide range of energies from 0.3 eV for a bulk crystal up to more than 2 eV for monolayer black phosphorus\textsuperscript{22–28}. In contrast to most TMDs, the gap is always direct even for bulk crystals\textsuperscript{26,29}. The lattice dynamics are also influenced by the strong inter-layer interaction. In contrast to weakly coupled TMDs or few layer graphene\textsuperscript{21,30,31}, in BP the vibrational modes are either unaffected or soften (red shift) with an increasing number of layers\textsuperscript{19,21}. This trend is opposite to the predictions of the classical model of coupled harmonic oscillators\textsuperscript{32}, indicating that the inter-layer interaction in BP is of a different nature than the weak van der Waals forces\textsuperscript{18,19}. Moreover the strong inter-layer interaction is predicted to manifest in different out of plane vibration frequencies of surface and inner layers\textsuperscript{19}.

Despite the interesting electronic properties, there are a number of technological challenges to overcome if BP is to be used in applications. Notably, BP is highly sensitive to the ambient conditions. The lone electron pairs are responsible for the rapid degradation of BP in air\textsuperscript{20,33–35}. The surface readily reacts with oxygen and moisture, leading to the formation of oxygen defects\textsuperscript{33,34,36–44} (which can modify the doping level of BP), and ultimately to the formation of oxide and phosphoric acid\textsuperscript{44}. This reactivity is one of the main
hindrances for the production of functional devices. Encapsulation in different materials such as PMMA, epitaxial organic monolayers, h-BN, and Al₂O₃ has been used in an attempt to stabilize BP. Few layer h-BN is particularly promising for encapsulation, as h-BN encapsulated BP becomes resistant to oxidation and exhibits excellent electrical properties. However, very little is known about the optical properties of encapsulated BP. Since encapsulation is an inevitable step in the production of stable BP based devices, it is crucial to fully understand its impact on the electronic and optical properties of BP.

In this work we present a systematic study of few layer BP encapsulated in h-BN using Raman spectroscopy. This method has previously been applied in multiple studies of non-encapsulated BP. We find that encapsulation with h-BN leads to significant and unexpected narrowing of the Raman lines, accompanied by the appearance of a so far elusive Raman mode. This Raman peak appears slightly above the A₁g mode and is most pronounced in the trilayer. We interpret this observation as a consequence of the different vibrational frequency of atoms in the layer at the surface resulting from the covalent nature of interlayer bondings. This effect was predicted theoretically but has not been observed experimentally so far. Our findings indicate that Raman spectroscopy provides a measure of the BP crystalline quality. Since the photoluminescence emission vanishes in h-BN/BP/h-BN heterostructures, Raman spectroscopy is the only readily available optical technique that can be used for samples characterization/selection before further processing. Moreover, the observed surface mode gives a direct handle to the condition of the surface i.e. its oxidation state and opens the way for the investigation of the interaction of the encapsulating material with the surface of BP.

For our investigation, several flakes of BP with different number of layers were encapsulated in hexagonal boron nitride. A schematic illustration of such a structure is shown in Fig. 1(a). Thin flakes of BP are prepared by micro-mechanical exfoliation of a single crystalline BP on silicon substrates covered with 300 nm-thick SiO₂. Bottom and top hexagonal boron nitride (h-BN) sheets are prepared on another silicon substrate and a PMMA thin film, respectively. The top h-BN sheet is then applied to pick up the BP flake from the silicon substrate. The formed h-BN/BP structure is then transferred to the top surface of the bottom h-BN sheet to form h-BN/BP/h-BN heterostructure. Due to the sensitivity of BP flakes to air, the exfoliation and transfer processes are performed in a glove box filled with highly pure nitrogen gas to protect the BP flakes from oxidation and degradation.
The heterostructure is then stabilized by annealing at 250 – 350°C in Ar atmosphere for 15 hours. Annealing improves the contact between h-BN and BP, removing small bubbles and adsorbants that might be trapped between the heterolayers during the fabrication process, and it reduces charge trap density. Raman measurements were performed under ambient conditions at room temperature using 630 µW of a 532 nm laser. The light was focused down to a spot approximately 1 µm in diameter using a 100× objective (N.A.=0.9). The spectral resolution of the setup was 0.5 cm⁻¹. Flakes were mapped over the areas of several µm with approximately 1 µm step. We did not observe any degradation of the samples during the measurements over a period of a few weeks.

The unit cell of BP contains 4 atoms, which results in 12 vibrational modes at the Γ point of the Brillouin zone. Six of the vibrational modes are Raman active in bulk and few layer BP (few layers and bulk BP share the same character table since they are described by the same point group $D_{2h}$): three acoustic modes ($B_{3g}^1$, $B_{1g}$, $B_{3g}^2$) and three optical modes ($A_{1g}$, $B_{2g}$, $A_{2g}^2$). Here we focus our Raman investigation on the three most intense optical vibrational modes, presented schematically in Fig. 1(b).

Fig. 2 shows optical images of two BP flakes together with representative Raman spectra acquired at different positions on the flake. In the optical image we can distinguish regions with different thickness (interference effects lead to a different color depending on the number of layers). For flake 1 the optical image was taken before encapsulation. We stress that all Raman data are taken on h-BN encapsulated flakes. Raman peaks related to $A_{1g}$, $A_{2g}$ and $B_{2g}$ vibrational modes are observed for all flakes. While the Raman spectrum of the $B_{2g}$ mode does not change significantly from place to place (see supplementary information), the shape of the $A_{1g}$ and $A_{2g}$ Raman peaks clearly depends on the flakes thickness. Moreover, for some places on the sample additional peaks above $A_{1g}$ and $A_{2g}$ are clearly visible. While the peak on the high energy side of $A_{2g}$ mode was observed previously, to the best of our knowledge this is the first experimental observation of an additional Raman mode a few wave numbers above $A_{2g}$.

To reliably extract the position, width and intensity of the Raman modes we fit the Raman peaks with either a single or double Lorentzian line shape as presented in Fig. 2. The error bars presented in Fig. 3 and 4 represent the standard deviations of the distributions of the peak positions and line widths obtained on all the positions of the investigated flakes. To understand the evolution of the Raman peaks we estimate the number of layers involved.
A precise determination of the BP thickness is not straightforward since the layers are encapsulated by h-BN, making AFM measurements difficult to interpret. Therefore, we use the relative shift of the $A^2_g$–$B_{2g}$ as the indicator of layer thickness\textsuperscript{21} (detailed discussion of this approach is presented in the supplementary information). Having determined the number of layers, we can follow the evolution of the $A^2_g$ and $A^1_g$ Raman peaks as a function of the flake thickness. Figure 3 shows representative Raman spectra for 2–7 layers measured on flake 2 and flake 3 (only flake 2 had a bilayer region). A strong characteristic Raman
line \( \simeq 4 \text{ cm}^{-1} \) above the \( A_g^2 \) mode is observed especially for bilayer BP. The intensity of this line systematically decreases with an increasing number of BP layers. This additional Raman mode has been already reported in the literature\cite{44, 51}. It is related to the doubling of the number of atoms in the bilayer unit cell, which allows the Davydov conversion of two out-of-phase IR-active mode \( B_{2u} \) modes to a Raman allowed mode with energy very close to that of the \( A_g^2 \) mode. This infrared converted mode is particularly robust since the high energy peak can still be distinguished even in the case of 5 layers. This is most probably related to the reduced line width of our Raman peaks after encapsulation of the BP with hexagonal boron nitride.
FIG. 3. (a) Evolution of $A_1^g$ and $A_2^g$ peaks as a function of the number of layers (grey) and together with Lorentzian fits (red). The spectra are normalized by the $A_1^g$ peak intensity and the $A_2^g$ peak has been rescaled for clarity for the bilayer spectrum. All spectra have been measured on flake 3, with the exception of the 2L spectrum measured on flake 2. (b) Averaged (over all spectra measured at different places) dependence of $A_1^g$ inner and surface mode energy as a function of the number of layers (red squares) together with the predictions of Ref. 19 (open diamonds).

The main result of this work is the first experimental observation of an additional, easily distinguishable Raman mode, which appears as a peak shifted by $\sim 4 \text{ cm}^{-1}$ on the high wave number side with respect to the $A_1^g$ mode for three layer and thicker BP. The intensity of this peak is highest for the trilayer, and it decreases rapidly with increasing number of layers. A similar behavior of the Raman modes (splitting and rapid decrease of the intensity with the number of layers) has been observed in other layered materials. It has been
attributed to Davydov splitting, induced by van der Waals interaction between the layers, which gives rise to an additional force felt by atoms vibrating out of phase in neighboring layers. However, the nature of the inter-layer interaction is fundamentally different in BP. Theoretical calculations predict a hybridization of the lone electron pairs in adjacent layers, which leads to a large charge density in the region between the neighboring layers. The inter-layer interactions in black phosphorus are thus of quasi-covalent character. The Davydov-related splitting should result in a different number of peaks depending on the number of interacting BP layers. In contrast, we always observe only two peaks with relative intensities monotonically changing as a function of the number of layers. Moreover, the splitting observed here is much larger than the full width half maximum of the $A_{1g}^1$ mode of previous studies (see also Fig. 3) for non-encapsulated BP. Therefore, if the splitting of the $A_{1g}^1$ mode was due to the out of phase vibration of adjacent layers, it should have been easily observed in the previous works, which is not the case. Based on these arguments and on the good qualitative agreement between the observed splitting and the theoretical predictions (see Fig. 3(b)), we attribute the additional peak to the splitting of the $A_{1g}^1$ mode into surface and inner modes, which can be observed in our samples due to their superior quality. A particularly important role in this respect is played by the protection of surface layers from oxidation and by the narrowing of the Raman lines induced by the h-BN capping layers, as will be discussed further.

Ab initio calculations show that strong and highly directional interlayer interactions arising from the electronic hybridization of the lone electron-pairs lead to anomalous surface phenomenon where the surface layer is stiffer than the inner ones. Thus, the atoms at the surface of BP vibrate with higher frequency than those inside. The predicted splitting between the inner and surface modes appears for 3 and more layers exactly as observed in our data. The splitting is predicted to be $\approx 1\, \text{cm}^{-1}$ for $B_{2g}$ and $\approx 6\, \text{cm}^{-1}$ for $A_{1g}^1$. The predicted splitting of the $B_{2g}$ mode is smaller than the Raman line width, so only the splitting of the $A_{1g}^1$ mode is observed experimentally. Our data are in good qualitative agreement with the theoretical predictions, as demonstrated by Fig. 3 (b), with the experimental shift of the high energy peak slightly smaller than theoretically predicted ($\approx 1$–$2\, \text{cm}^{-1}$). The smaller energy of both the surface mode and the $A_{1g}^1$ mode of bilayers as compared to theoretical predictions may originate from interactions of the surface layers with the capping h-BN (the calculations were performed for BP suspended in vacuum). Due to the lone
electron pairs of BP, a significant interaction with encapsulating layers can be expected for BP. Theoretical calculations predict a significant redistribution of the carriers across BP/BN and BP/graphene interfaces and BP/Al₂O₃ interface, which can affect the electronic properties of BP, as demonstrated by the expected increase of the BP bandgap in the case of graphene-encapsulated Br. Moreover, in BP encapsulated with h-BN the photoluminescence is quenched. These results suggest that the encapsulation with h-BN affects the electronic properties of BP. Therefore, small discrepancies between the theory and our measurements of the A₁g splitting might be a hallmark of the interaction between the outer layers of BP and h-BN.

The surface origin of the high energy Raman mode can also explain why it is not observed in uncapped BP. It is well established that the Raman signal is quenched in oxidized BP. Since the oxidation proceeds layer by layer the signal from the surface layers will be quenched while the signal from the inner layers remains strong. Encapsulation stabilizes the surface preserving the Raman modes associated with the vibration of surface atoms. Nevertheless, with increasing thickness the bulk response becomes dominant (due to the volume) and the Raman mode from the surface is not observed (its amplitude is less than 2–3 times the noise level) for more than 6–7 layers.

The h-BN encapsulation affects also the line width of the A₁g, A₂g and B₂g peaks, as shown in Fig. 4. All Raman lines measured on encapsulated samples are narrower, as demonstrated by the comparison of our data (averaged over all the spectra acquired on 4 flakes) with the literature data. We can see that the FWHM of A₂g and B₂g modes measured on bare BP is ~1 cm⁻¹ larger than that we measured on our encapsulated samples. We observe a similar effect for the inner A₁g mode, which in the case of our encapsulated samples is ~0.5 cm⁻¹ narrower.

The reduction of FWHM is most probably related to the reduction of the phonon boundary and impurity scattering rate, due to the better quality of BP protected by boron nitride. It is interesting to note that in non encapsulated BP, the broadening of the peaks does not change significantly with time (over several days) under ambient conditions. This suggests that the broadening is mainly related to the layers adjacent to the oxidized layers. Since the oxidation occurs layer by layer there is always one layer next to the oxidized layer, which explains why the FWHM remains constant despite the continued degradation of the uncapped BP. The boron nitride encapsulation performed in nitrogen atmosphere
FIG. 4. Comparison of the Raman mode FWHM of BP encapsulated with hexagonal boron nitride (red) and bare flakes (black) taken after Ref. [51].

prevents the initial degradation of the first layer and adsorption processes, thereby reducing the Raman line width with respect to uncapped black phosphorus.

To summarize, Raman spectroscopy has been used to investigate the vibrational properties of few-layer BP flakes encapsulated with hexagonal boron nitride as a function of the
number of layers. A previously unobserved observed splitting of the $A_g$ Raman mode has been demonstrated for trilayer and thicker flakes. The origin of the splitting is attributed to different vibration frequency of the inner and surface layers. This effect results from the strong inter-layer interaction present in BP. The encapsulation of BP is crucial for the observed splitting since h-BN prevents surface layer oxidation. The positive impact of encapsulation on the BP layers quality is confirmed by the narrow lines of the Raman peaks.

**AUTHOR CONTRIBUTIONS**

DKM and PP coordinated the project. GL and YW fabricated the samples under NW supervision. JMU, DW, A. Suchocki and LK performed Raman spectroscopy measurements. JMU, MB, A. Surrente, LK, DKM and PP analyzed the data and discussed the results. JMU, MB, AS, LK, DKM, and PP wrote the manuscript with input of all other co-authors.

**CONFLICTS OF INTEREST**

There are no conflicts of interest to declare.

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1 P. Bridgman, *Journal of the American Chemical Society*, 1914, **36**, 1344–1363.
2 X. Ling, H. Wang, S. Huang, F. Xia and M. S. Dresselhaus, *Proceedings of the National Academy of Sciences*, 2015, 112, 4523–4530.

3 A. Carvalho, M. Wang, X. Zhu, A. S. Rodin, H. Su and A. H. C. Neto, *Nature Reviews Materials*, 2016, 1, 16061.

4 H. Liu, Y. Du, Y. Deng and D. Y. Peide, *Chemical Society Reviews*, 2015, 44, 2732–2743.

5 J. Na, Y. T. Lee, J. A. Lim, D. K. Hwang, G.-T. Kim, W. K. Choi and Y.-W. Song, *ACS Nano*, 2014, 8, 11753–11762.

6 X. Luo, Y. Rahbarighagh, J. C. Hwang, H. Liu, Y. Du and D. Y. Peide, *IEEE Electron Device Letters*, 2014, 35, 1314–1316.

7 L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen and Y. Zhang, *Nature Nanotechnology*, 2014, 9, 372–377.

8 H. Liu, A. T. Neal, Z. Zhu, X. Xu, D. Tomanek, P. D. Ye and Z. Luo, *ACS Nano*, 2014, 8, 4033–4041.

9 M. Engel, M. Steiner and P. Avouris, *Nano Letters*, 2014, 14, 6414–6417.

10 N. Youngblood, C. Chen, S. J. Koester and M. Li, *Nature Photonics*, 2015, 9, 247–252.

11 R. Fei, A. Faghaninia, R. Soklaski, J.-A. Yan, C. Lo and L. Yang, *Nano Letters*, 2014, 14, 6393–6399.

12 Z. Luo, J. Maassen, Y. Deng, Y. Du, R. P. Garrelts, M. S. Lundstrom, P. D. Ye and X. Xu, *Nature Communications*, 2015, 6, 8572.

13 H. Jang, J. D. Wood, C. R. Ryder, M. C. Hersam and D. G. Cahill, *Advanced Materials*, 2015, 27, 8017–8022.

14 V. Tran, R. Soklaski, Y. Liang and L. Yang, *Physical Review B*, 2014, 89, 235319.

15 J. Qiao, X. Kong, Z.-X. Hu, F. Yang and W. Ji, *Nature Communications*, 2014, 5, 4475.

16 X. Wang, A. M. Jones, K. L. Seyler, V. Tran, Y. Jia, H. Zhao, H. Wang, L. Yang, X. Xu and F. Xia, *Nature Nanotechnology*, 2015, 10, 517–521.

17 F. Xia, H. Wang and Y. Jia, *Nature communications*, 2014, 5, 4458.

18 X. Luo, X. Lu, G. K. W. Koon, A. H. Castro Neto, B. Özyilmaz, Q. Xiong and S. Y. Quek, *Nano Letters*, 2015, 15, 3931–3938.

19 Z.-X. Hu, X. Kong, J. Qiao, B. Normand and W. Ji, *Nanoscale*, 2016, 8, 2740–2750.

20 A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. Alvarez et al., *2D Materials*, 2014, 1, 025001.
21 W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jin and Z. Zhang, *Nano Research*, 2014, 7, 853–859.

22 G. Zhang, S. Huang, A. Chaves, C. Song, V. O. Özenlik, T. Low and H. Yan, *Nature Communications*, 2017, 8, 14071.

23 H. Asahina and A. Morita, *Journal of Physics C: Solid State Physics*, 1984, 17, 1839.

24 J. Kim, S. S. Baik, S. H. Ryu, Y. Sohn, S. Park, B.-G. Park, J. Denlinger, Y. Yi, H. J. Choi and K. S. Kim, *Science*, 2015, 349, 723–726.

25 A. Morita, *Applied Physics A*, 1986, 39, 227–242.

26 L. Liang, J. Wang, W. Lin, B. G. Sumpter, V. Meunier and M. Pan, *Nano Letters*, 2014, 14, 6400–6406.

27 A. Surrente, A. Mitioglu, K. Galkowski, W. Tabis, D. Maude and P. Plochocka, *Physical Review B*, 2016, 93, 121405.

28 A. Surrente, A. Mitioglu, K. Galkowski, L. Klopotowski, W. Tabis, B. Vignolle, D. K. Maude and P. Plochocka, *Physical Review B*, 2016, 94, 075425.

29 L. Li, J. Kim, C. Jin, G. J. Ye, D. Y. Qiu, F. H. da Jornada, Z. Shi, L. Chen, Z. Zhang, F. Yang, K. Watanabe, T. Taniguchi, W. Ren, S. G. Louie, X. H. Chen, Y. Zhang and F. Wang, *Nature Nanotechnology*, 2017, 12, 21–25.

30 Q. Song, Q. Tan, X. Zhang, J. Wu, B. Sheng, Y. Wan, X. Wang, L. Dai and P. Tan, *Physical Review B*, 2016, 93, 115409.

31 A. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov, S. Roth et al., *Physical Review Letters*, 2006, 97, 187401.

32 T. Wieting and J. Verble, *Physical Review B*, 1972, 5, 1473.

33 S. P. Koenig, R. A. Doganov, H. Schmidt, A. Castro Neto and B. Özyilmaz, *Applied Physics Letters*, 2014, 104, 103106.

34 J. D. Wood, S. A. Wells, D. Jariwala, K.-S. Chen, E. Cho, V. K. Sangwan, X. Liu, L. J. Lauhon, T. J. Marks and M. C. Hersam, *Nano Letters*, 2014, 14, 6964–6970.

35 F. Alsaffar, S. Alodan, A. Alrasheed, A. Alhussain, N. Alrubaiq, A. Abbas and M. R. Amer, *Scientific Reports*, 2017, 7, 44540.

36 A. Ziletti, A. Carvalho, P. Trevisanutto, D. Campbell, D. Coker and A. C. Neto, *Physical Review B*, 2015, 91, 085407.
37 A. Ziletti, A. Carvalho, D. K. Campbell, D. F. Coker and A. C. Neto, Physical Review Letters, 2015, 114, 046801.

38 K. L. Utt, P. Rivero, M. Mehboudi, E. O. Harriss, M. F. Borunda, A. A. Pacheco SanJuan and S. Barraza-Lopez, ACS Central Science, 2015, 1, 320–327.

39 T. Yang, B. Dong, J. Wang, Z. Zhang, J. Guan, K. Kuntz, S. C. Warren and D. Tománek, Physical Review B, 2015, 92, 125412.

40 J. O. Island, G. A. Steele, H. S. van der Zant and A. Castellanos-Gomez, 2D Materials, 2015, 2, 011002.

41 M. Edmonds, A. Tadich, A. Carvalho, A. Ziletti, K. ODonnell, S. Koenig, D. Coker, B. Ozyilmaz, A. C. Neto and M. Fuhrer, ACS Applied Materials & Interfaces, 2015, 7, 14557–14562.

42 R. A. Doganov, S. P. Koenig, Y. Yeo, K. Watanabe, T. Taniguchi and B. Özyilmaz, Applied Physics Letters, 2015, 106, 083505.

43 C. Han, Z. Hu, J. Zhang, F. Hu, D. Xiang, J. Wu, B. Lei, L. Wang, W. P. Hu and W. Chen, arXiv preprint arXiv:1603.02799, 2016.

44 A. Favron, E. Gaufres, F. Fossard, A.-L. Phaneuf-L’Heureux, N. Y.-W. Tang, P. L. Levesque, A. Loiseau, R. Leonelli, S. Francoeur and R. Martel, Nature Materials, 2015, 14, 826–832.

45 V. Tayari, N. Hemsworth, I. Fakih, A. Favron, E. Gaufres, G. Gervais, R. Martel and T. Szkopek, Nature Communications, 2015, 6, 7702.

46 Y. Zhao, Q. Zhou, Q. Li, X. Yao and J. Wang, Advanced Materials, 2017, 29, 1603990.

47 Y. Cao, A. Mishchenko, G. Yu, E. Khestanova, A. Rooney, E. Prestat, A. Kretinin, P. Blake, M. Shalom, C. Woods et al., Nano Letters, 2015, 15, 4914–4921.

48 X. Chen, Y. Wu, Z. Wu, Y. Han, S. Xu, L. Wang, W. Ye, T. Han, Y. He, Y. Cai et al., Nature Communications, 2015, 6, 7315.

49 G. Long, D. Maryenko, J. Shen, S. Xu, J. Hou, Z. Wu, W. K. Wong, T. Han, J. Lin, Y. Cai et al., Nano Letters, 2016, 16, 7768–7773.

50 A. Avsar, I. J. Vera-Marun, J. Y. Tan, K. Watanabe, T. Taniguchi, A. H. Castro Neto and B. Ozyilmaz, ACS Nano, 2015, 9, 4138–4145.

51 A.-L. Phaneuf-L’Heureux, A. Favron, J.-F. Germain, P. Lavoie, P. Desjardins, R. Leonelli, R. Martel and S. Francoeur, Nano Letters, 2016, 16, 7761–7767.

52 S. Sugai and I. Shirotani, Solid State Communications, 1985, 53, 753–755.
53 M. Staiger, R. Gillen, N. Scheuschner, O. Ochedowski, F. Kampmann, M. Schleberger, C. Thomsen and J. Maultzsch, *Physical Review B*, 2015, **91**, 195419.

54 K. Golasa, M. Grzeszczyk, M. R. Molas, M. Zinkiewicz, L. Bala, K. Nogajewski, M. Potemski, A. Wysmolek and A. Babiński, *Nanophotonics*, 2017, **6**, 1281–1288.

55 Y. Cai, G. Zhang and Y.-W. Zhang, *The Journal of Physical Chemistry C*, 2015, **119**, 13929–13936.

56 J. Sun, N. Lin, C. Tang, H. Ren and X. Zhao, *RSC Advances*, 2017, **7**, 13777–13783.

57 J. E. Padilha, A. Fazzio and A. J. R. da Silva, *Phys. Rev. Lett.*, 2015, **114**, 066803.

58 Q.-C. Sun, D. Mazumdar, L. Yadgarov, R. Rosentsveig, R. Tenne and J. L. Musfeldt, *Nano Letters*, 2013, **13**, 2803–2808.