

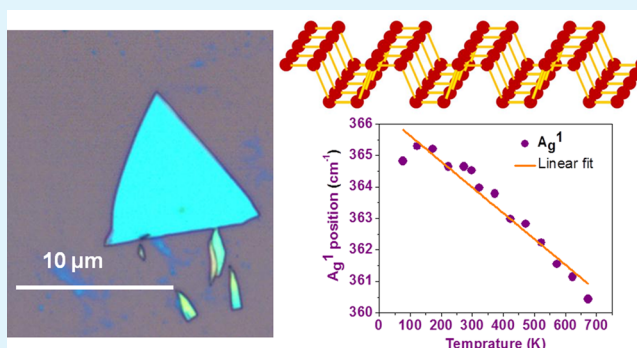
Temperature Dependent Phonon Shifts in Few-Layer Black Phosphorus

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ABSTRACT: Atomically thin two-dimensional (2D) sheets of black phosphorus have attracted much attention due to their potential for future nanoelectronic and photonics device applications. Present investigations deal with the temperature dependent phonon shifts in a few-layer black phosphorus nanosheet sample prepared using micromechanical exfoliation on a 300 nm SiO₂/Si substrate. The temperature dependent Raman spectroscopy experiments were carried out on a few-layer black phosphorus sample, which depicts softening of A_g¹, B_{2g}, and A_g² modes as temperature increases from 77 to 673 K. The calculated temperature coefficients for A_g¹, B_{2g}, and A_g² modes of the few-layer black phosphorus nanosheet sample were observed to be −0.01, −0.013, and −0.014 cm^{−1} K^{−1}, respectively. The temperature dependent softening modes of black phosphorus results were explained on the basis of a double resonance process which is more active in an atomically thin sample. This process can also be fundamentally pertinent in other promising and emerging 2D ultrathin layer and heterostructured materials.

KEYWORDS: black phosphorus, layered materials, Raman spectroscopy, phonon vibrations, thermal effect



1. INTRODUCTION

Atomically thin two-dimensional (2D) materials such as graphene^{1–5} and transition metal dichalcogenides (TMDCs) such as MoS₂,^{6–14} WS₂,^{8,15–17} MoSe₂,^{18–20} and WSe₂²¹ are attracting more interest for their application in nanoelectronics and photonics devices. However, these TMDC materials have demonstrated relatively slow performance, and because of the huge bandgap of Mo- and W-based compounds, they are more suited for applications in the visible range of the electromagnetic spectrum. A 2D material with a direct and tiny bandgap together with a high performance of device is needed to extend exposure range and wide application.

Bulk black phosphorus material is a highly stable phosphorus allotrope at ambient and room temperature^{22,23} which was first synthesized back in 1914 from white phosphorus materials under high pressure and high temperature conditions.²⁴ Similar to graphene, black phosphorene is made of a layered structure which is held together by weak interlayer forces with noteworthy van der Waals character. Inside a single layer, each P atom is covalently bonded with three neighboring phosphorus atoms to form a wrinkled honeycomb structure.^{22–24} In particular as compared with the bulk counterpart, a single-layer black phosphorus sample has significantly more diverse electronic and optical properties due to its fundamental band gap and puckered layered structure. These useful properties originate from the bandgap of ~1.5 eV for a single-layer black phosphorus sample, while the bulk bandgap of black phosphorus material is ~0.3 eV.²⁵ Therefore, the band

gap of black phosphorus has been predicted to be tunable as a function of the number of layers.^{25,29–31} This property makes black phosphorus a potential semiconducting material, which is quite different from the single-layer graphene, which is a semimetal. As a semiconductor material, it can also be used to fabricate digital nanoelectronics and photonics devices. The atomically thin single-layer of black phosphorus is a *p*-type semiconducting material, and it has been reported to be flexible and capable of mechanical exfoliation.²⁹ This is well-suited for applications in near- and mid-infrared optoelectronic and spintronic devices.

Interestingly the 2D form of black phosphorus layered material has shown good field effect transistor device performance with hall field effect mobility of 1000 and 600 cm² V^{−1} s^{−1} in the *x* and *y* directions within the plane at a temperature of 120 K.^{25–28} Further, the transistors fabricated using a 5 nm-thick black phosphorus nanosheet show a current ON/OFF ratio of ~10⁵ and a good current saturation nature at room temperature.^{25–28} Therefore, the black phosphorus layered material has great potential to fill up the gap between semimetal graphene and large-bandgap TMDC materials. There are exhaustive investigations on single-layer TMDC materials including their diverse properties, optical, magnetic, electronic, and mechanical, such as strain, thermal effects, and

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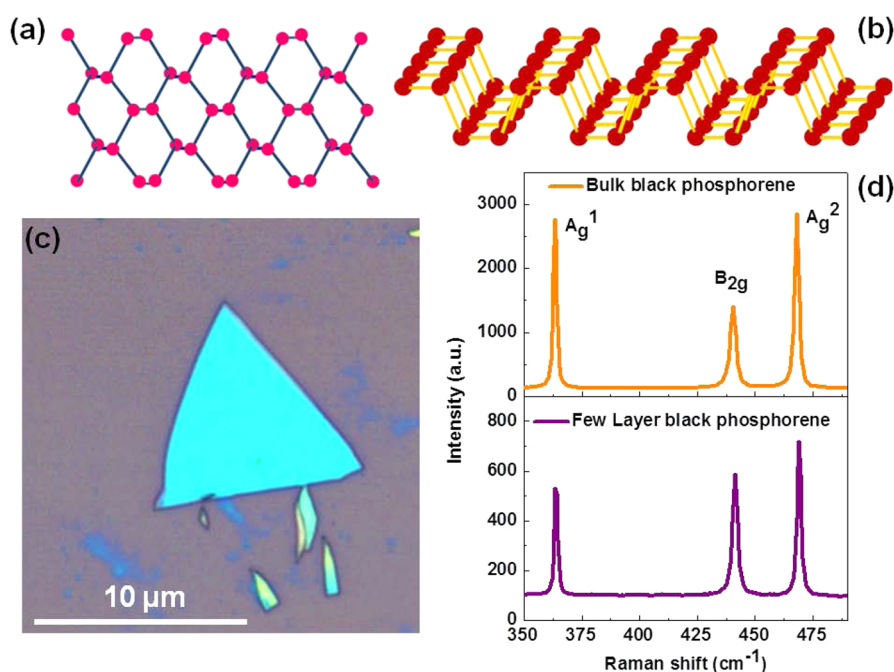


Figure 1. Typical perspective top view (a) and side view (b) of single-layer black phosphorus. (c) Typical optical microscope image of the few-layer black phosphorus nanosheet sample deposited on 300 nm SiO₂/Si using micromechanical exfoliation and (d) comparative Raman spectra of the pristine bulk and few-layer black phosphorus nanosheet sample recorded at room temperature using a 514.5 nm laser.

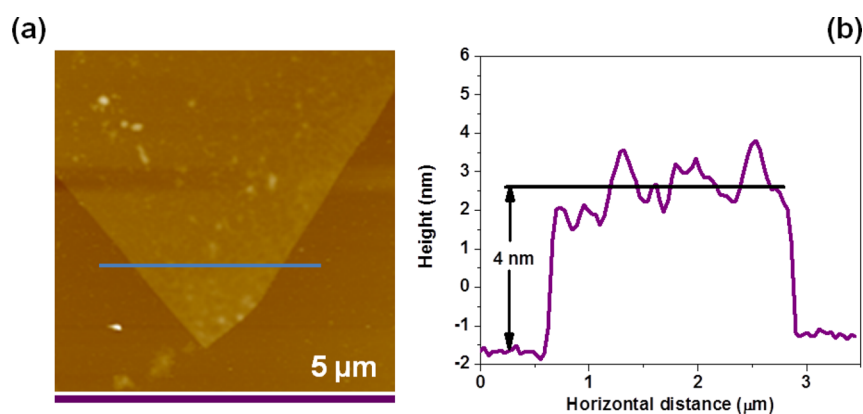


Figure 2. (a) Typical optical microscope image of the few-layer black phosphorus nanosheet sample deposited on 300 nm SiO₂/Si substrate and (b) the corresponding AFM height profile of the sample.

so on. However, the exploration of black phosphorus is just beginning. In the view of black phosphorus as a possible material for application in various nanoelectronics and optoelectronic and spintronic devices, it is essential to know the electron–phonon (e–p) interaction and temperature dependent vibrational properties of black phosphorus nanosheet sample. In field effect transistor devices, by applying the bias voltage and back gate voltage can result in the self-heating of the device which can affect the performance of black phosphorus based electronic device. The self-heating can thus lead to the changes in e–p interaction and vibrational properties of the black phosphorus materials. It is essential to make out the difference whether the changes in Raman mode positions due to the number of layers and other factors. The shape of the Raman mode, intensity, changes in the half width at half maxima (fwhm) as a function of number of layers and that of temperature will be quite different.^{5,19} Raman spectroscopy is nondestructive and a very powerful experimental technique to

investigate the properties of the materials such as number of atomic layers and thermal and mechanical properties of graphene⁵ and other TMDC layered materials.^{8,9} With change in the temperature of the black phosphorus nanosheet sample, the Raman-active modes are also affected as a result of e–p coupling.

Predominantly, a temperature dependent Raman spectroscopy investigation on few-layer black phosphorus samples is important to understand the fine structure and properties of the material, such as thermal expansion, thermal conductivity, and nature of the atomic bonds. To date there is only one report³² on the temperature dependence of the Raman spectra of 5L black phosphorus sample but which is also only limited to temperature range from +20 to –160 °C. Here, we demonstrate a proof-of-concept for change in large shift in Raman peak position for few-layer black phosphorus nanosheet sample with wide temperature range from 77 to 673 K.

2. RESULTS AND DISCUSSION

Figure 1a and b show the typical perspective top and side view of the single-layer black phosphorus nanosheet. The black phosphorus nanosheet samples were exfoliated onto 300 nm SiO₂/Si substrate by using mechanical exfoliation using scotch tape similar to single-layer graphene⁵ and inorganic layered TMDC materials.^{6,9,33} Figure 1c shows the typical optical microscope image of the few layer black phosphorus nanosheet sample. The number of layers present in the sample was identified by using the optical microscope with specific color contrast.^{26,34} During the present investigations several samples of black phosphorus nanosheet deposited on various 300 nm SiO₂/Si substrates with similar color contrast were identified and characterized. The thicknesses of the black phosphorus nanosheet samples were further determined by using atomic force microscopy (AFM). Figure 2a and b shows the typical AFM image and height profile which confirms the height of the nanosheet were ~ 4 nm indicating the few layer nature of the black phosphorus nanosheet sample. The single-layer black phosphorus nanosheet samples were observed to be difficult to locate on the 300 nm SiO₂/Si substrate as compared with the few layer sample. It is possible that the single-layer and bilayer black phosphorus sample has very strong interlayer coupling as compared with that of few layer black phosphorus samples. Figure 1d shows the typical comparative Raman spectra of the pristine bulk and few layer black phosphorus samples recorded at room temperature using 514.5 nm laser. A typical bulk sample of black phosphorus consists of one out-of-plane mode (A_g^1) and two in-plane modes (A_g^2 and B_{2g}). The Raman spectra of the black phosphorus sample^{26,34} show well-defined layer dependence, with the A_g^2 mode upshifted when the number of layers decreased as observed for MoS₂.⁹ In the present investigations for the bulk black phosphorus sample the A_g^2 mode appears at ~ 467.9 which shifts to 469.5 cm⁻¹ for a few layer thin sample. The other Raman modes namely A_g^1 appear at ~ 363.3 cm⁻¹ and B_{2g} (440.4 cm⁻¹) which does not depict much changes as a function of number of layers as reported in the literature.³⁴ It has been also reported that the A_g^2 and A_g^1 Raman modes shifts toward each other with increasing thickness due to the double resonance scattering which can be the spectral fingerprint of identifying the single- and few-layer nature of the black phosphorus sample.²⁶ The single-layer or bilayer of the black phosphorus nanosheet sample was reported to be more sensitive to the ambient conditions such as water and oxygen as similar to the graphene and other TMDC materials.³⁵

The present investigations mainly deal with the temperature dependent Raman spectroscopy investigations of few-layer black phosphorus sample. Figure 3a–c shows the low and high resolution transmission electron microscopy (TEM) images of the few-layer black phosphorus nanosheet sample prepared using micromechanical exfoliation from bulk black phosphorus crystal transferred directly onto the Quanta foil TEM grid. The typical high resolution TEM image shows the high crystalline quality of the as transferred black phosphorus nanosheet sample onto the TEM grid. Figure 3d shows the typical selected area electron diffraction pattern of the few-layer black phosphorus sample. Figure 4 shows the Raman spectra of the few-layer black phosphorus nanosheet sample as a function of temperature variation from 77 to 623 K. Figure 5 shows the Raman spectra peak position as a function of temperature for (a) A_g^2 , (b) B_{2g} , and (c) A_g^1 modes. It is clearly observed that

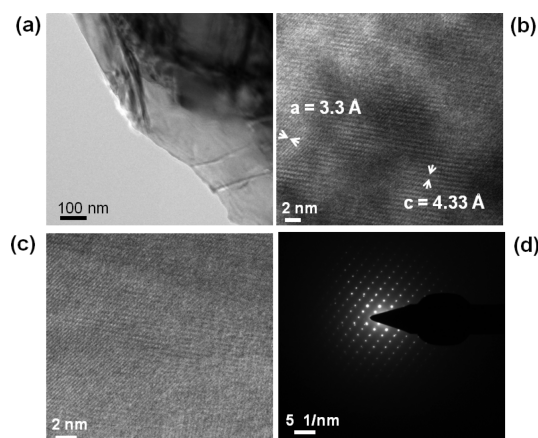


Figure 3. (a) TEM image and (b, c) HRTEM images of the few-layer black phosphorus nanosheet sample. (d) Corresponding SAED pattern of the black phosphorus nanosheet sample.

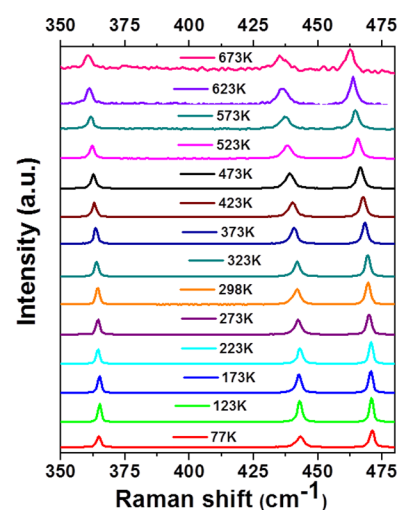


Figure 4. Raman spectra of the few-layer black phosphorus nanosheet sample in a temperature range of 77 to 673 K.

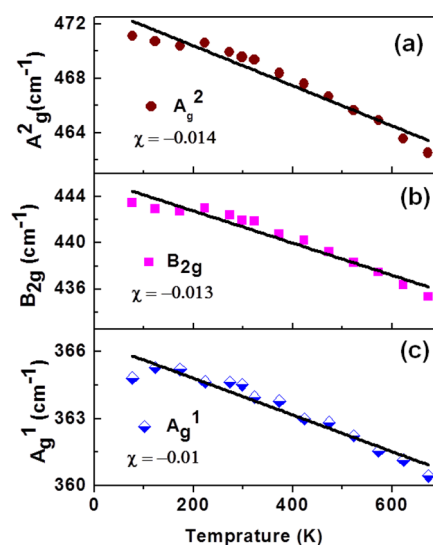


Figure 5. Temperature dependence Raman mode variation as a function of temperature for the few-layer black phosphorus nanosheet sample (a) A_g^2 , (b) B_{2g} , and (c) A_g^1 .

the Raman modes of the few-layer Black phosphorus sample change linearly as a function of temperature. It is well-known that Raman spectroscopy is a four-phonon process which is dominant over thermal expansion as well as the phonon process on Raman mode line shift with change in temperature. The changes in the Raman mode frequencies $\Delta\omega$, with temperature variation from 77 to 623 K were observed to be 4.39 cm^{-1} for A_g^1 , 8.14 cm^{-1} for B_{2g} , and 8.63 for A_g^2 modes, respectively. A few data point dispersion for the Raman peak positions can be expected and is well-understood due to the slight variation in the laser spot on the few-layer black phosphorus nanosheet sample or the local Raman stage vibration and low excitation power on the black phosphorus nanosheet sample surface followed by the extra attenuation from the cold-hot cell window during the experiments.⁵ Measurement of the temperature dependence of the Raman spectra on the few layer black phosphorus nanosheet sample was repeated on several other identical samples, and the results were found to be similar in nature. The observed data of the peak positions obtained from Lorentzian fittings for A_g^1 , B_{2g} , and A_g^2 modes versus temperature were fitted using the Grüneisen model³⁶

$$\omega(T) = \omega_0 + \chi T \quad (1)$$

where ω_0 is the peak position of the black phosphorus nanosheet sample vibration modes at zero kelvin temperature and χ is the first-order temperature coefficient of the same mode. The plot of the Raman mode position as a function of temperature (Figure 5) gives a slope of a fitted straight line which directly depicts the temperature coefficient χ . The temperature coefficients of the frequencies of the A_g^1 , B_{2g} , and A_g^2 modes are observed to be -0.01 , -0.013 , and $-0.014\text{ cm}^{-1}\text{ K}^{-1}$, respectively (Table 1). It is noteworthy that the

Table 1. Extracted Temperature Coefficient and Frequency Difference for Few-Layer Black Phosphorus Samples in the Temperature Range 77–673 K

few-layer black phosphorus	χ ($\text{cm}^{-1}\text{ K}^{-1}$)	$\Delta\omega$
A_g^1	-0.008	4.39
B_{2g}	-0.013	8.14
A_g^2	-0.014	8.63

temperature coefficient of the few-layer black phosphorus for the A_g^1 and A_g^2 modes was observed to be nearly same as reported earlier for a 5L phosphorene sample.³² Interestingly the temperature coefficients for A_g^1 , B_{2g} , and A_g^2 are also similar in nature to those reported earlier for single-layer and few-layer MoS_2 by Lanzillo et al.,³⁷ Sahoo et al.,³⁸ and Najmaei et al.³⁹ Further, the temperature coefficients for A_g^2 and B_{2g} modes are observed to be similar in nature to that reported for single-layer graphene^{5,40–45} and MoS_2 ^{37–39} and one order larger in nature than that reported for single- and few-layer WS_2 ,^{46–48} MoSe_2 ,¹⁹ and WSe_2 ¹⁹ nanosheets. With the chosen temperature range, the shift in the Raman mode is observed to be larger, this indicates that the phonon frequencies of the few-layer black phosphorus nanosheet sample are much more sensitive to the temperature than that of observed for graphene^{5,40–45} and other 2D inorganic layered materials such as MoS_2 ,^{37–39} WS_2 ,^{46–48} MoSe_2 ,¹⁹ WSe_2 ,¹⁹ and WTe_2 .⁵⁰ This might be due to the fact that the black phosphorus nanosheet sample has better mechanical flexibility, which basically originates from its unique puckered crystal structure.^{26,32,49} We also believe that the two in-plane modes A_g^2 and B_{2g} in the atomically thin black

phosphorus nanosheet sample restrict the motion of P atoms in a plane of sheet. It is interesting and noteworthy to report that the increase of fwhm for all the Raman modes with increasing temperature for few layer black phosphorus nanosheet samples. The significance of increasing the fwhm sensitively for black phosphorus nanosheet samples with temperature is due to the contribution of anharmonic terms. The observed softening of the A_g^1 , B_{2g} , and A_g^2 modes of Raman spectra is due to the phonon–phonon interaction which involves a phonon decaying into the lower-energy phonons and electron–phonon interaction which results from a phonon generating an electron–hole (e–p) pair. The variation in the Raman spectra peak position as a function of temperature is also a contribution of the anharmonicity and the thermal expansion, which is negative in sign, or due to the volume contribution. This phenomenon is stronger at the few-layer atomically thin black phosphorus nanosheet sample as it is attributed to a double resonance effect.

3. CONCLUSIONS

In conclusion, we have systematically investigated the temperature dependent Raman spectroscopy of a few-layer black phosphorus nanosheet sample within a wide temperature range, 77–623 K. All of the three Raman modes of the black phosphorus sample soften as a function of increasing temperature. The calculated temperature coefficients of the frequencies of the A_g^1 , B_{2g} , and A_g^2 Raman modes are observed to be -0.01 , -0.013 , and $-0.014\text{ cm}^{-1}\text{ K}^{-1}$, respectively. Our results are explained on the basis of the double resonance process which is more active in the atomically thin black phosphorus nanosheet sample. Further, our work can motivate researchers to implement this technique to investigate the temperature coefficients of other emerging 2D materials to understand e–p interactions and the underlying physics.

4. EXPERIMENTAL METHODS

Preparation of Few-Layer Black Phosphorus. Bulk black phosphorus crystals were purchased from Smart Elements GmbH Ferrogasse 4/I A-U80 Wien, Germany (purity 99.998%). Few-layer black phosphorene nanosheets were deposited at room temperature in ambient conditions by mechanically exfoliating bulk black phosphorene crystal onto precleaned 300 nm SiO_2/Si as described earlier for other TMDCs.^{9–12}

Optical Microscope. Nikon LV150NL Trinocular upright optical microscope with an imager M1m was used to locate the few-layer of black phosphorene nanosheets deposited on 300 nm SiO_2/Si substrates using specific color contrast. The color images were acquired with LED illumination and using bright field imaging modes with MTI plan EPI 150 X objectives and a 10X eyepiece. Auto exposure times were used during the image recording, which varied in the range 10–500 ms.

Atomic Force Microscopy. The AFM tapping mode images were recorded using an ICON system (Bruker, Santa Barbara Ca). For the correct AFM height profile measurements, few-layer black phosphorus nanosheet samples deposited on 300 nm SiO_2/Si were annealed at 200 °C in Ar + H_2 ambient for 1 h.

Raman Spectroscopy. The Raman spectra of the few-layer black phosphorene nanosheet sample prepared using micromechanical exfoliation were used to investigate the temperature dependent Raman spectroscopy with a (LabRAM HR) using Ar laser (514.5 nm) in the back scattering geometry. The detector was a Synapse CCD detector with thermoelectric cooling to $-70\text{ }^\circ\text{C}$. A 50X objective was used to focus the laser beam and to collect the Raman signal. The laser power on the sample was $\sim 2\text{ mW}$ for 514.5 nm, to avoid the possible heating effect by the laser on black phosphorus nanosheet

surface. The size of the laser spot was $\sim 1 \mu\text{m}$. All the Raman spectra were collected under the identical experimental conditions. The band positions and widths of the Raman spectra were obtained by fitting them with a Lorentzian function.

HR-TEM. HR-TEM images were acquired using FEI TECNAI TF-30 (FEG) instrument.

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Notes

The author declares no competing financial interest.

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REFERENCES

- (1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- (2) Schwierz, F. Graphene Transistors. *Nat. Nanotechnol.* **2010**, *5*, 487–496.
- (3) Avouris, P.; Chen, Z.; Perebeinos, V. Carbon Based Electronics. *Nat. Nanotechnol.* **2007**, *2*, 605–615.
- (4) Ghosh, A.; Late, D. J.; Panchakarla, L. S.; Govindaraj, A.; Rao, C. N. R. NO₂ and Humidity Sensing Characteristics of Few-Layer Graphenes. *J. Exp. Nanosci.* **2009**, *4*, 313–322.
- (5) Late, D. J.; Maitra, U.; Panchakarla, L. S.; Waghmare, U. V.; Rao, C. N. R. Temperature Effects on the Raman Spectra of Graphenes: Dependence On the Number of Layers and Doping. *J. Phys.: Condens. Matter* **2011**, *23*, 055303.
- (6) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single Layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- (7) Jariwala, D.; Sangwan, V. K.; Late, D. J.; Johns, J. E.; Dravid, V. P.; Marks, T. J.; Lauhon, L. J.; Hersam, M. C. Band-Like Transport in High Mobility Unencapsulated Single-Layer MoS₂ Transistors. *Appl. Phys. Lett.* **2013**, *102*, 173107.
- (8) Matte, H. S. S. R.; Gomathi, A.; Manna, A. K.; Late, D. J.; Datta, R.; Pati, S. K.; Rao, C. N. R. MoS₂ and WS₂ Analogues of Graphene. *Angew. Chem. Inter. Ed.* **2010**, *49*, 4059–4062.
- (9) Late, D. J.; Liu, B.; Matte, H. S. S. R.; Rao, C. N. R.; Dravid, V. P. Rapid Characterization of Ultrathin Layers of Chalcogenides on SiO₂/Si Substrates. *Adv. Fun. Mater.* **2012**, *22*, 1894–1905.
- (10) Ghatak, S.; Pal, A. N.; Ghosh, A. Nature of Electronic States in Atomically Thin MoS₂ Field-Effect Transistors. *ACS Nano* **2011**, *5*, 7707–7712.
- (11) Late, D. J.; Liu, B.; Matte, H. S. S. R.; Dravid, V. P.; Rao, C. N. R. Hysteresis in Single-Layer MoS₂ Field Effect Transistors. *ACS Nano* **2012**, *6*, 5635–5641.
- (12) Late, D. J.; Huang, Y.; Liu, B.; Luo, J.; Acharya, J.; Shirodkar, S. N.; Luo, J.; Yan, A.; Charles, D.; Waghmare, U. V.; Dravid, V. P.; Rao, C. N. R. Sensing Behavior of Atomically Thin-Layered MoS₂ Transistors. *ACS Nano* **2013**, *7*, 4879–4891.
- (13) Kashid, R. V.; Late, D. J.; Chou, S. S.; Huang, Y.; De, M.; Joag, D. S.; More, M. A.; Dravid, V. P. Enhanced Field-Emission Behavior of Layered MoS₂ Sheets. *Small* **2013**, *9*, 2730–2734.
- (14) Late, D. J.; Shaikh, P. A.; Khare, R.; Kashid, R. V.; Chaudhary, M.; More, M. A.; Ogale, S. B. Pulsed Laser Deposited MoS₂ Thin Films on W and Si: Field Emission and Photoresponse Studies. *ACS Appl. Mater. Interfaces* **2014**, *6*, 15881–15888.
- (15) Rout, C. S.; Joshi, P. D.; Kashid, R. V.; Joag, D. S.; More, M. A.; Simbeck, A. J.; Washington, M.; Nayak, S. K.; Late, D. J. Superior Field Emission Properties of Layered WS₂-RGO Nanocomposites. *Sci. Rep.* **2013**, *3*, 3282.
- (16) Braga, D.; Lezama, I. G.; Berger, H.; Morpurgo, A. F. Quantitative Determination of the Band Gap of WS₂ with Ambipolar Ionic Liquid Gated Transistors. *Nano Lett.* **2012**, *12*, 5218–5223.
- (17) Georgiou, T.; Jalil, R.; Belle, B. D.; Britnell, L.; Gorbachev, R. V.; Morozov, S. V.; Kim, Y. J.; Gholinia, A.; Haigh, S. J.; Makarovskiy, O.; Eaves, L.; Ponomarenko, L. A.; Geim, A. K.; Novoselov, K. S.; Mishchenko, A. Vertical Field Effect Transistor Based on Graphene-WS₂ Heterostructures for Flexible and Transparent Electronics. *Nat. Nanotechnol.* **2013**, *8*, 100–103.
- (18) Larentis, S.; Fallahzad, B.; Tutuc, E. Field Effect Transistors and Intrinsic Mobility in Ultra Thin MoSe₂ Layers. *Appl. Phys. Lett.* **2012**, *101*, 223104.
- (19) Late, D. J.; Shirodkar, S. N.; Waghmare, U. V.; Dravid, V. P.; Rao, C. N. R. Thermal Expansion, Anharmonicity and Temperature-Dependent Raman Spectra of Single- and Few-Layer MoSe₂ and WSe₂. *ChemPhysChem* **2014**, *15*, 1592–1598.
- (20) Late, D. J.; Doneux, T.; Bougouma, M. Single Layer MoSe₂ Based NH₃ Sensor. *Appl. Phys. Lett.* **2014**, *105*, 233103.
- (21) Allain, A.; Kis, A. Electron and Hole Mobilities in Single-Layer WSe₂. *ACS Nano* **2014**, *8*, 7180–7185.
- (22) Warschauer, D. Electrical and Optical Properties of Crystalline Black Phosphorus. *J. Appl. Phys.* **1963**, *34*, 1853.
- (23) Nishii, T.; Maruyama, Y.; Inabe, T.; Shirovani, I. Synthesis and Characterization of Black Phosphorus Intercalation Compounds. *Synth. Met.* **1987**, *18*, 559–564.
- (24) Bridgman, P. M. Two New Modifications of Phosphorus. *J. Am. Chem. Soc.* **1914**, *36*, 1344–1363.
- (25) Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y. Black Phosphorus Field Effect Transistors. *Nat. Nanotechnol.* **2014**, *9*, 372–377.
- (26) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tomanek, D.; Ye, P. D. Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility. *ACS Nano* **2014**, *8*, 4033–4041.
- (27) Na, J.; Lee, Y. T.; Lim, J. A.; Hwang, D. K.; Kim, G.; Choi, W. K.; Song, Y. Few Layer Black Phosphorus Field-Effect Transistors with Reduced Current Fluctuation. *ACS Nano* **2014**, *8*, 11753–11765.
- (28) Buscema, M.; Groenendijk, D. J.; Steele, G. A.; Zant, H. S. J.; Castellanos-Gomez, A. Photovoltaic Effect in Few Layer Black Phosphorus P-N Junctions Defined by Local Electrostatic Gating. *Nat. Commun.* **2014**, *5*, 4651–4658.
- (29) Buscema, M.; Groenendijk, D. J.; Blanter, S. I.; Steele, G. A.; Zant, H. S. J.; Castellanos-Gomez, A. Fast and Broadband Photoresponse of Few-Layer Black Phosphorus Field-Effect Transistors. *Nano Lett.* **2014**, *14*, 3347–3352.
- (30) Du, Y.; Ouyang, C.; Shi, S.; Lei, M. Ab initio Studies On Atomic and Electronic Structures of Black Phosphorus. *J. Appl. Phys.* **2010**, *107*, 093718.
- (31) Qiao, J.; Kong, X.; Hu, Z.; Yang, F.; Ji, W. High Mobility Transport Anisotropy and Linear Dichroism in Few Layer Black Phosphorus. *Nat. Commun.* **2014**, *5*, 4475.
- (32) Zhang, S.; Yang, J.; Xu, R.; Wang, F.; Li, W.; Ghufraan, M.; Zhang, Y.; Yu, Z.; Zhang, G.; Qin, Q.; Lu, Y. Extraordinary Photoluminescence and Strong Temperature/Angle-Dependent Raman Responses in Few-Layer Phosphorene. *ACS Nano* **2014**, *8*, 9590–9596.
- (33) Late, D. J.; Liu, B.; Luo, J.; Yan, A.; Matte, H. S. S. R.; Grayson, M.; Rao, C. N. R.; Dravid, V. P. GaS and GaSe Ultrathin Layer Transistors. *Adv. Mater.* **2012**, *24*, 3549–3554.
- (34) Lul, W.; Nan, H.; Hong, J.; Chen, Y.; Liang, Z.; Ni, Z.; Jin, C.; Zhang, Z. Plasma Assisted Fabrication of Monolayer Phosphorene and its Raman Characterization. *Nano Res.* **2014**, *7*, 853–859.
- (35) Castellanos-Gomez, A.; Vicarelli, L.; Prada, E.; Island, J. O.; Narasimha-Acharya, K. L.; Blanter, S. I.; Groenendijk, D. J.; Buscema,

M.; Steele, G. A.; Alvarez, J. V. Isolation and Characterization of Few Layer Black Phosphorus. *2D Mater.* **2014**, *1*, 025001.

(36) Zouboulis, E. S.; Grimsditch, M. Raman Scattering in Diamond up to 1900 K. *Phys. Rev. B* **1991**, *43*, 12490.

(37) Lanzillo, N. A.; Birdwell, A. G.; Amani, M.; Crowne, F. J.; Shah, P. B.; Najmaei, S.; Liu, Z.; Ajayan, P. M.; Lou, J.; Dubey, M.; Nayak, S. K.; Regan, T. P. O. Temperature Dependent Phonon Shifts in Monolayer MoS₂. *Appl. Phys. Lett.* **2013**, *103*, 093102.

(38) Sahoo, S.; Gaur, A. P. S.; Ahmadi, M.; Guinel, M. J. F.; Katiyar, R. S. Temperature Dependent Raman Studies and Thermal Conductivity of Few Layer MoS₂. *J. Phys. Chem. C* **2013**, *117*, 9042–9047.

(39) Najmaei, S.; Ajayan, P. M.; Lou, J. Quantitative Analysis of the Temperature Dependency in Raman Active Vibrational Modes of Molybdenum Disulfide Atomic Layers. *Nanoscale* **2013**, *5*, 9758–9763.

(40) Calizo, I.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N. Temperature Dependence of the Raman Spectra of Graphene and Graphene Multilayers. *Nano Lett.* **2007**, *7*, 2645–2649.

(41) Nika, D. L.; Balandin, A. A. Two Dimensional Phonon Transport in Graphene. *J. Phys.: Condens. Matter.* **2012**, *24*, 233.

(42) Chen, S.; Wu, Q.; Mishra, C.; Kang, J.; Zhang, H.; Cho, K.; Cai, W.; Balandin, A. A.; Ruoff, R. S. Thermal Conductivity of Isotopically Modified Graphene. *Nat. Mater.* **2012**, *11*, 203–207.

(43) Balandin, A. A. Thermal Properties of Graphene and Nanostructured Carbon Materials. *Nat. Mater.* **2011**, *10*, 569–581.

(44) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett.* **2008**, *8*, 902–907.

(45) Calizo, I.; Miao, F.; Bao, W.; Lau, C. N.; Balandin, A. A. Variable Temperature Raman Microscopy as a Nanometrology Tool For Graphene Layers and Graphene Based Devices. *Appl. Phys. Lett.* **2007**, *91*, 071913.

(46) Peimyoo, N.; Shang, J.; Yang, W.; Wang, Y.; Cong, C.; Yu, T. Thermal Conductivity Determination of Suspended Mono- and Bilayer WS₂ by Raman Spectroscopy. *Nano Res.* **2014**, DOI: 10.1007/s12274-014-0602-0.

(47) Thripuranthaka, M.; Kashid, R. V.; Rout, C. S.; Late, D. J. Temperature Dependent Raman spectroscopy of Chemically Derived Few Layer MoS₂ and WS₂ Nanosheets. *Appl. Phys. Lett.* **2014**, *104*, 081911.

(48) Thripuranthaka, M.; Late, D. J. Temperature Dependent Phonon Shifts in Single-Layer WS₂. *ACS Appl. Mater. Interfaces* **2014**, *6*, 1158–1163.

(49) Wei, Q.; Peng, X. Superior Mechanical Flexibility of Phosphorene and Few-Layer Black Phosphorus. *Appl. Phys. Lett.* **2014**, *104*, 251915.

(50) Jana, M. K.; Singh, A.; Late, D. J.; Rajamathi, C.; Biswas K.; Felser, C.; Waghmare, U. V.; Rao, C. N. R. A Combined Experimental and Theoretical Study of the Electronic and Vibrational Properties of Bulk and Few-Layer Td-WTe₂; Cornell University, 2015; arXiv:1502.04171.