



Staggered band offset induced high performance opto-electronic devices: Atomically thin vertically stacked GaSe-SnS₂ van der Waals p-n heterostructures

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ABSTRACT

Atomically thin vertically stacked 2D vdW heterostructures have recently emerged as a new kind of device with intriguing novel phenomena for both academic and industrial interests. However, the lack of p-type materials remains a challenging issue to create useful devices for the realization of practical applications. Here, we demonstrate the first vertically stacked few-layered p-type GaSe and n-type SnS₂ vdW heterostructure for high-performance optoelectronic applications. It is found that the phototransistors based on a few-layered GaSe/SnS₂ p-n junction show superior performance with the responsivity, EQE and specific detectivity as high as $\sim 35 \text{ AW}^{-1}$, 62%, and $8.2 \times 10^{13} \text{ J}$, respectively, which exceed all the reported values derived from 2D materials. Also, the GaSe/SnS₂ p-n junction can serve as a photovoltaic cell with a high power conversion efficiency of about $\sim 2.84\%$. Moreover, the heterostructures can be deposited on flexible PET substrates with excellent performance. Through a detailed study, the underlying mechanism responsible for the high performance can be attributed to the unique type II band alignment and excellent quality of the interface. The heterojunctions presented in this work demonstrate a new illustration for the stacking of 2D materials, which is very useful for the development of next-generation novel optoelectronic devices.

1. Introduction

Recently, several two-dimensional (2D) crystals with superior performance have been discovered and sparked broad interest on the stacking of 2D materials through van der Waals (vdW) heterostructures, making them feasible to create a wide range of heterojunctions in a new frontier of modern semiconductor industry [1–4]. In this regard, unlike conventional heterostructures, 2D heterostructures are emerging as an ideal platform for their potential applications in atomically thin electronics, optoelectronics, and light-harvesting [5–9]. Relatively, various distinct frameworks of heterojunctions, created by lateral and vertical stacking of several 2D crystals have stimulated intensive research for new kinds of 2D heterostructures [10–11]. Usually, heterojunctions applied in the optoelectronic devices require anisotype, i.e., p-n heterojunctions, which consist of two semiconductors with dissimilar types of charge carriers. However, even though vertically stacked p-n heterostructures based on 2D materials have been studied in several published works due to their great potential applications, the reported

performance remains a large room for improvement [12–15]. Especially, carrier transport in the vertical heterostructures based on p and n-type materials with sharp and clean interfaces has become promising and remains challenging, which is desirable for the realization of unprecedented functional device applications by the interlayer coupling [16–20]. These heterostructures have fascinated considerable scrutiny and opened up a new pavement for exploring novel optoelectronic device applications, such as high-mobility field-effect transistors (FETs), tunable p-n junction photo-diodes, LEDs, solar cells and sensors.

Until now, various 2D vdW heterostructures, including WSe₂/MoS₂, WS₂/MoS₂, p/n-MoS₂ and MoS₂/black phosphorus, have been reported recently for novel optoelectronics applications [21–22]. Among them, the new 2D materials-based optoelectronic devices, particularly of an anisotype heterojunction, possess a wide combination of various 2D materials and exhibit novel functional properties with remarkable strong light-matter interactions for future prospectives [23–24]. For example, a switchable bidirectional charge transport has been developed, instead of the unidirectional charge transport in a traditional p-n

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heterojunction [25]. Recently, the generations of photocurrent and electroluminescence from a vertical p-n junction between p-WSe₂/n-MoS₂ have been reported [26]. Also, the electrostatic-gating-induced lateral p-n junction between WSe₂/black phosphorus has been realized for photodetectors, solar cells, and light-emitting diodes (LEDs) [27]. Notably, the tuning of Fermi levels at the vertical junction depends on the Thomas-Fermi screening of the bottom constituent nanoflakes of a vertical heterojunction, which only works well for few-layered heterojunction [28–30]. Among the recent advances, gallium selenide (GaSe), an III-VI 2D layered semiconductor, has the planar tetra-layer (TL) structure in the unit cell, and consists of four covalent bonds in a series of Se-Ga-Ga-Se, a bandgap energy (E_g) of ~ 2.1 eV and an intrinsic p-type nature [31–32]. The advantage of GaSe is that it has a direct bandgap in the form of bulk and few-layered thickness (< 7 layers) compared to other TMDs [33]. Tin disulphide (SnS₂) is an n-type CdI₂-type crystal structure with a bandgap $E_g \sim 2.3$ eV, which has attracted great attention, for its abundance on earth and green optoelectronics. SnS₂ remains an indirect bandgap even when scaling down to monolayer from bulk counterpart [34]. Its intrinsic bandgap in the range of 1 to 3 eV is significant for optoelectronics, i.e., photodetectors, photovoltaic and flexible devices [35]. Considering all of these distinct features, it is foreseeable that p-GaSe/n-SnS₂ 2D vdW heterostructure will possess many intriguing properties and make a promising building block for the development of optoelectronic devices with the functionalities of great significance.

In this paper, we introduced this new 2D vdW vertically stacked p-GaSe/n-SnS₂ heterojunctions formed by high-quality single crystals. In addition to the electrical characteristics, photodetector and photovoltaic behaviours of the junction were investigated. It is found that, the GaSe/SnS₂ p-n junction exhibits a high photoresponsivity (~ 35 A/W at $\lambda = 633$ nm, $V_g = 30$ V), external quantum efficiency ($\sim 62\%$) and specific detectivity ($\sim 8.2 \times 10^{13}$ J). These excellent performances are much better than those of recently published 2D vdW p-n heterojunctions configured with other few-layered materials. Impressively, the GaSe/SnS₂ p-n heterojunction can serve as a photovoltaic cell with a high power conversion efficiency of about $\sim 2.84\%$. Moreover, taking a step further, the optoelectronic characteristics of these heterojunction devices on a flexible PET substrate were scrutinized with and without bending, showing good endurance and retention. These observations indicate that atomically thin vertically stacked 2D p-GaSe/n-SnS₂ vdW heterostructures can be featured as an excellent candidate for the feasibility of various functionalities.

2. Results

Fig. 1a shows the schematic illustration of the atomic configuration of vertically stacked p-GaSe/n-SnS₂ vdW heterostructure. The schematics of the individual layer of GaSe and SnS₂ are shown in Figure S1 in the Supporting Information. Fig. 1b presents an optical microscope (OM) image of a GaSe/SnS₂ vertical heterojunction device with a clear enhanced colour contrast between the layer interface. The devices were fabricated by micromechanical cleavage technique and explained in the experimental section. Fig. 1c reveals the single-crystal X-ray diffraction (XRD) of GaSe and SnS₂ crystals grown by chemical vapor transport (CVT) method, which is identical to the previously reported diffraction patterns [36–37]. Fig. 1d shows the Raman spectra of an GaSe/SnS₂ heterostructure, which includes the Raman modes from the constituent layers (Figure S2 in the Supporting Information). The peak positions at ~ 208 nm (E_g) and ~ 316 (A_{1g}^2) can be assigned to the Raman active modes for 2D SnS₂ [38,39], and the Raman spectra of a GaSe crystals exhibit 4 peaks at ~ 137 nm (A_{1g}^1), 216 nm (E_{2g}^1), ~ 250 nm (E_{2g}^2), and ~ 305 nm (A_{1g}^2), which are also consistent with previous reports [40–41].

Fig. 2a shows an OM image of a vertical p-n heterojunction diode with the deposition of metallic electrodes for the electric and optoelectronic measurements. Briefly, a thin SnS₂ flake (~ 10.5 nm) were

transferred on a Si/SiO₂ substrate, followed by transferring a GaSe flake (~ 25.5 nm) on top of the SnS₂ flake as shown in Fig. 2a. Throughout this work, a pair of Cr/Au (5/100 nm) electrodes were used as the source and drain electrodes in all of the devices, which were fabricated with a shadow mask using the thermal evaporation technique. Before the measurement of GaSe/SnS₂ heterojunction FETs, we have first analysed separately the electrical characteristic of few-layered SnS₂ and GaSe FETs to confirm the conductive nature of the channel materials. Figures S3 a and b show the V_g -dependent characteristics of SnS₂ and GaSe while sweeping the V_g from -60 V to $+60$ V, respectively. The plots show that the current increases with increasing positive gate voltage for SnS₂-FET, indicating an n-type semiconductor behaviour. On the contrary, the current increases with decreasing negative gate voltage in GaSe-FET, consistent with the p-type characteristics. The Hall-effect measurement of the bulk SnS₂ and GaSe crystal evidence its n- and p-type nature, respectively, as shown in Figure S4. Figure S5 illustrates the schematic representation of the GaSe/SnS₂ p-n heterojunction device layout with the back gate electrode. Meanwhile, the I_{sa} - V_{sd} characteristics of the fabricated GaSe/SnS₂ FETs exhibit a clear current rectification behaviour as shown in Fig. 2b. The saturated current of the heterojunction was observed in reverse bias following the Shockley diode equation of $I = I_s (\exp(V_{ds}/nV_t) - 1)$, where I_s is the saturation current in the reverse bias regime, n is the ideality factor of the fabricated device, and V_t and V_{ds} are the thermal and bias voltages, respectively. Next, we probed the V_g -dependent output characteristics of the heterojunction by sweeping V_g from 0 to -70 V as shown in Fig. 2c. Interestingly, the applied negative V_g enhances the current in forward bias and maintains the saturated current in reverse bias. The fabricated heterojunction has a rectification ratio of $\sim 10^2$ at $V_g = -30$ V (Fig. 2d). These strong current-rectifying characteristics indicate that an excellent vdW p-n heterojunction spans between p-GaSe and n-SnS₂ layers.

As excellent rectification features were realized, the optoelectronic characteristics of our fabricated p-GaSe/n-SnS₂ heterojunction as a photodetector were examined. We measured the photoresponse of the p-GaSe/n-SnS₂ heterojunction, by using a 633 nm laser with different intensities of 0 (in the dark), 0.328, 1.6, 3.1 and 32.6 mW/cm² to illuminate the device as shown in Fig. 3a. The photocurrent (I_{photo}) was calculated by subtracting the dark current (I_{dark}) from the light-induced current (I_{light}), i.e., $I_{photo} = I_{light} - I_{dark}$. As seen in Fig. 3a, the I_{photo} in reverse bias is gradually enhanced with increasing illumination intensity, which shows that I_{photo} has a strong dependence on the incident power. The probable reason for the enhancement of the reverse current under illumination is due to the obvious photovoltaic effect. Next, we evaluated the performance of photodiode by calculating photoresponsivity (R) and external quantum efficiency (EQE) as follows. Fig. 3b exhibits the laser intensity-dependent R , defined as the ratio of the generated photocurrent to the total incident photon energy, i.e., $R = I_{ph}/(P_\lambda S)$ where P_λ and S are the incident light power and the illuminated area, respectively. The photoresponsivity of the p-n junction could reach $R \sim 24.8$ AW⁻¹ at 633 nm of 0.326 mW/cm² illumination, which is the highest photoresponsivity achieved compared with other reported 2D p-n junctions. Additionally, note that R can be climbed to about ~ 35 AW⁻¹ by simply changing the gate voltage ($V_g = 30$ V) as shown in Figure S6 in the Supporting Information.

The EQE (%) is defined as $hcR/e\lambda$, where h is Planck's constant, c is the velocity of the light, R is photoresponsivity of the device, e is the electron charge, and λ is the laser wavelength. Fig. 3c represents the EQE of the p-GaSe/n-SnS₂ junction, which could reach $\sim 62\%$ measured at 633 nm, $V_{ds} = 10$ V, and $V_g = 0$ V. Another critical parameter to determine the photodetection performance of a fabricated p-n junction is specific detectivity (D^*). The D^* is quantified by $D^* = A^{1/2} / NEP = R_\lambda A^{1/2} / (2eI_{dark})^{1/2}$, where R_λ , A , e and I_{dark} are the photoresponsivity, illuminated area, elementary charge, and dark current, respectively. Fig. 3d shows the D^* versus illuminated laser power. Based on the measured parameter, the obtained $D^* \sim 8.2 \times 10^{13}$ J for

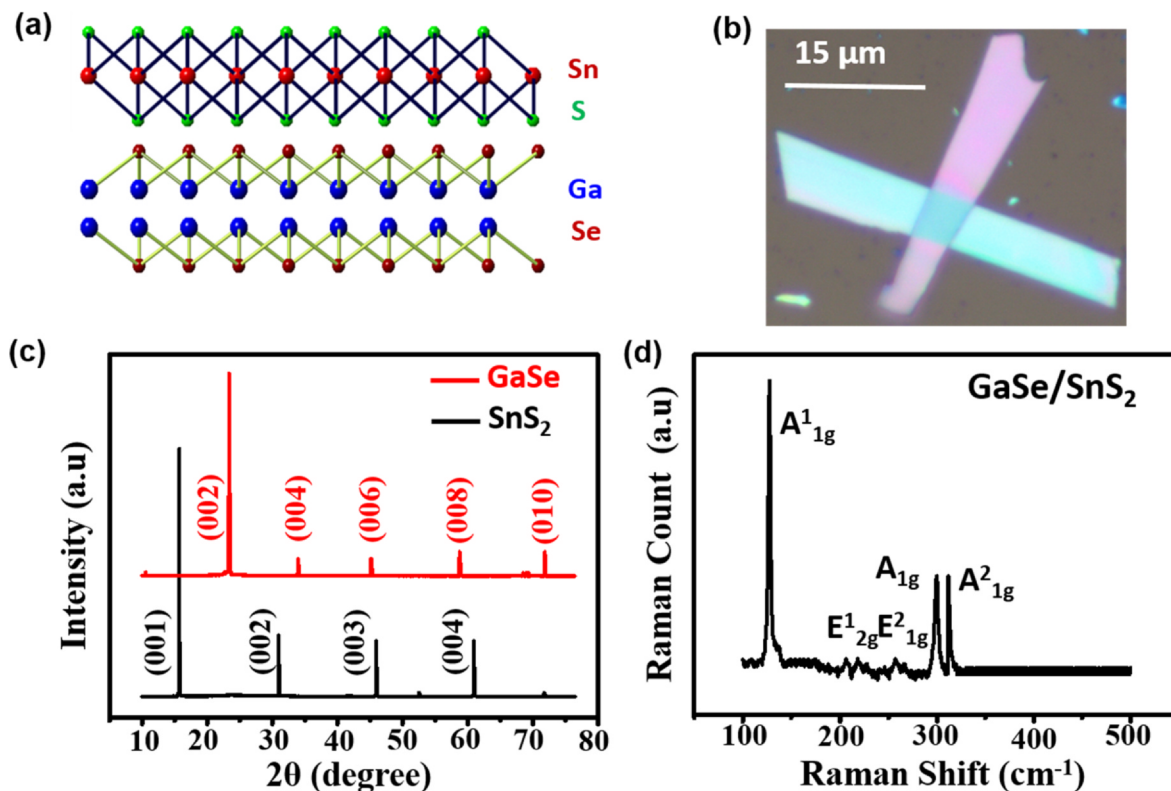


Fig. 1. (a) Schematic of the vertically stacked GaSe/SnS₂ heterostructure. (b) Optical microscope image of fabricated GaSe/SnS₂ heterostructure. (c) X-ray diffraction pattern of GaSe and SnS₂ single crystals. (d) Raman Spectra of GaSe/SnS₂ heterostructure.

the fabricated p-n heterojunction is higher than commercial silicon photodiodes ($\sim 10^{13}$ J) [42] and InGaAs ($\sim 10^{12}$ J to $\sim 10^{13}$ J) [43].

Owing to the low dark current under reverse bias condition, excellent photoresponse performance was achieved. Furthermore, the time-resolved photoresponse was carried out to exhibit the response time (τ) of the GaSe/SnS₂ heterojunction photodiode. The $I_{\text{light}} - t$ plot was measured with a continuation of on/off illumination using 633 nm laser. Fig. 3 (e-f) show the device response to one on/off illumination ($P = 0.326 \text{ mWcm}^{-2}$), that exhibits a steep increase of photocurrent (I_{light}) underneath illumination and an instant drop after switched off. It is found that the rising time and falling time of the device are estimated to be ~ 9 ms and ~ 8 ms, respectively. Table 1 summarizes and compares the selected figures of merit between the GaSe/SnS₂ p-n junction and several other reported 2D layered p-n heterostructures. Based on the time-resolved measurement, The calculated frequency bandwidth of the device is ~ 12.8 Hz. If the response time (9 ms) is faster, the calculated bandwidth will be wider, because the response time can be also used to express as frequency response, which is the frequency when the photodetector output decreases by 3 dB. It is roughly approximated by $f_{3\text{dB}} \approx 0.35/\tau_r$, where τ_r is the response time [49].

In addition to the electrical and photodetection characteristics of the junction discussed above, we explored the application of this junction as a photovoltaic cell. Fig. 4 represents the current density-voltage (J-V) characteristics device under AM 1.5G illumination. Under illumination, the open-circuit voltage (Voc) of 0.51 V, a short-circuit current density (Jsc) of 26.5 mA cm⁻², and a fill factor (FF) of 0.42 were obtained, which leads to the power conversion efficiency (PCE) of 2.84% [19]. However, heterojunction formed between two different semiconductors having different energy bandgaps. The electric field formed due to the potential energy barrier between two dissimilar materials (p-GaSe/n-SnS₂) at the interface is capable of separating the electrons and holes generated by absorption of light within the materials. Furthermore, being direct-bandgap at few-layer thickness, it allow high radiative efficiency. The strong absorption in atomically thin

layers with sharp, clean interfaces allows the highest watt-per-gram utilization of the active material. Owing to their excellent electron-transport properties, high carrier mobility, direct bandgap and type II band alignment, shows its great potential to be used for low-cost, flexible, and highly efficient photovoltaic devices.

Moreover, to examine the further applicability, we deposit GaSe/SnS₂ 2D vdW p-n heterojunctions on a high degree of flexible PET substrate, by the similar process as on silicon platforms as shown in Fig. 5a. Interestingly, the device of conducting p-n heterojunction channel can stick well onto the surface of the PET, revealing the potential capability of the device's flexibility. Subsequent thermal deposition of metal electrodes at both ends ensure mechanical flexibility. The power-dependent photocurrents recorded in each flat and bent states are shown in Fig. 5b and S7a in the Supporting Information, respectively, showing an equivalent performance compared with devices deposited on SiO₂/Si substrates.

The photocurrent increases with increasing laser power, yielding the highest photoresponsivity of $\sim 3.8 \text{ AW}^{-1}$ at a power density of 0.326 mWcm^{-2} as shown in Fig. 5c. To differentiate the p-GaSe/n-SnS₂ device performance on PET with flat and bending (a radius of ~ 2.5 cm), we observed that the responsivity within the bending state is reduced slightly compared with flat state, i.e., the responsivity is slightly reduced to $\sim 3.2 \text{ AW}^{-1}$ under the same measured condition as shown in Fig. 5d and S7c in the Supporting Information. The responsivity was calculated under different bending radius as shown in Figure S8 in the Supporting Information, demonstrating bending durability. The reduced responsivity within the bending state is reasonable due to the possible mechanism that the erected tension in the bending state may additionally reduce the responsivity as a result of the variation of the band structure in the p-GaSe/n-SnS₂ channel and its relative optical properties [50–52]. These investigations reveal a promising potential of thin layered 2D vdW p-n heterojunctions for flexible and wearable optoelectronic applications.

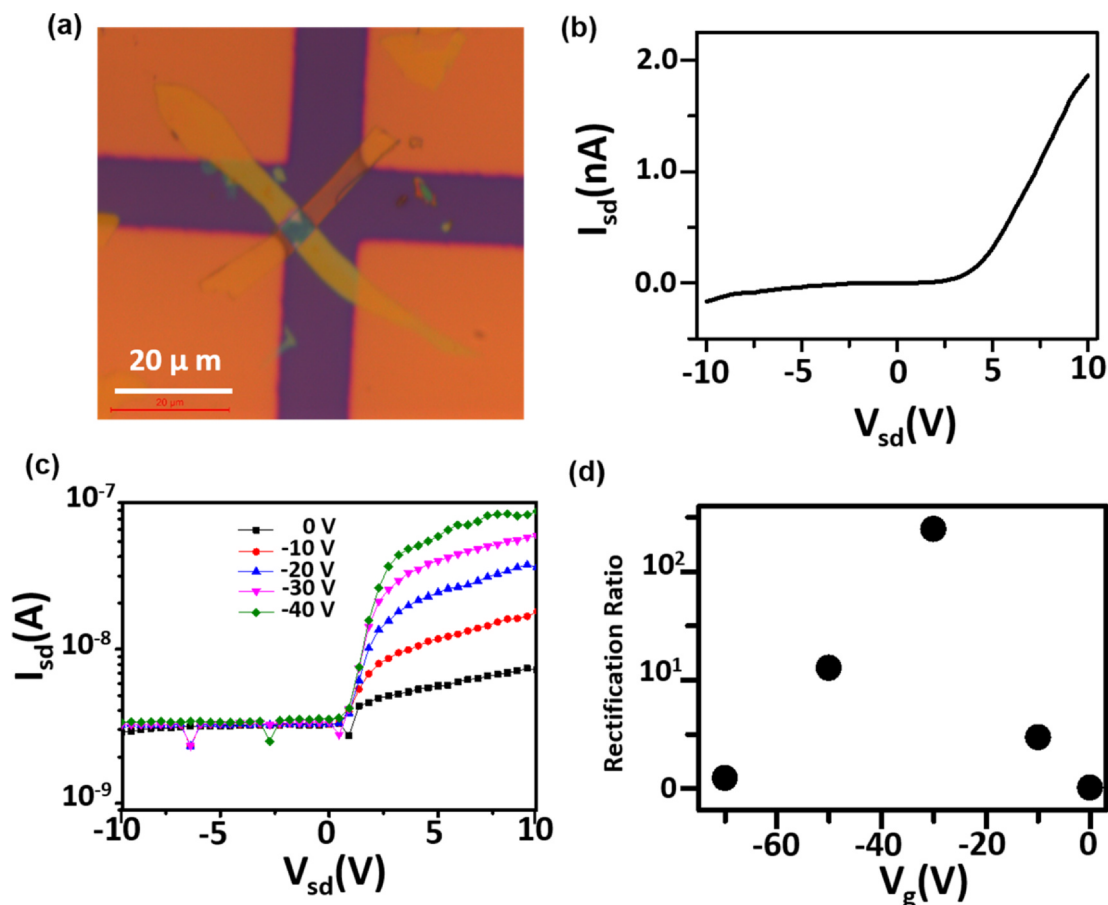


Fig. 2. (a) Optical microscope image of vertically stacked GaSe/SnS₂ heterostructure device. (b) I_{sd} - V_{sd} characteristics of p-n junction diode. (c) Gate tunable I-V characteristics. (d) Rectification ratio as a function of back-gate voltage (V_g).

3. Discussion

To find out the underlying mechanisms responsible for the high performance of GaSe/SnS₂ 2D vdW p-n heterojunctions as observed above, we first look for the possibility of the unique band alignment. Fig. 6a and 6b show the schematic of the relative energy alignment of the conduction/valance bands of the constituent 2D materials before and after contact, respectively. The work functions (Φ) of GaSe and SnS₂ are 5.25 and 5.2 eV, respectively, adopted from literature reports [30,37,53–54]. The band alignment of the heterojunction belongs to type II as depicted in Fig. 6a and b. To obtain further evidence for supporting the type-II band alignment of GaSe/SnS₂ heterojunction, we have performed photoluminescence measurement. The PL spectra show two distinct peak positions, corresponding to two different layers. We have also performed PL spectra for each isolated GaSe and SnS₂ layers as shown in Figure S9 in the Supporting Information. Both of GaSe and SnS₂ layers show a strong PL intensity at their respective exciton position (2.11 eV and 2.28 eV, respectively), [29,40] which indicates the excellent crystallinity of the as-synthesized 2D single crystals. Quite interestingly, the PL intensity is significantly quenched for the heterostructure sample. Accordingly, the observation of the reduced PL intensity from GaSe/SnS₂ heterostructures reveals that an efficient charge transfer takes place in this heterojunction due to the type II band alignment. After photoexcitation, electrons transfer to the SnS₂ layer, while holes will like to stay in the GaSe layer.

Next, we explain the charge transport mechanism under varying the gate voltage in the junction region of p-GaSe/n-SnS₂ with the help of the band alignment as shown in Fig. 6. The advantage of ultrathin materials in vertical heterostructures allows the penetration of the electric field from the back gate through the entire stack, thereby

enabling gate tunability of the heterointerface. This unique feature is not feasible in the heterojunction formed by bulky semiconductors due to Thomson-Fermi screening [26–28]. In this work, the fabricated p-n junction consists of the bottom few-layered flakes of SnS₂ (~10.5 nm) on a SiO₂/Si substrate and the top flakes of GaSe (~25.2 nm). The heterojunction formed by a few-layered GaSe/SnS₂/SiO₂/Si allows tuning the Fermi level of the bottom few-layered SnS₂ by the gate field and also affecting the top GaSe layer. In the equilibrium condition, no current passes through the GaSe/SnS₂ junction. Under forward bias condition, the height of the developed built-in potential of the junction is reduced, which allows the transfer of electrons from n-SnS₂ to p-GaSe over the lower barrier due to the gate field as shown in Figure S10 in the Supporting Information. Consequently, fewer electrons transport over the junction from n-SnS₂ to p-GaSe as evidenced experimentally shown in Figure S6 in the Supporting Information. On the other hand, under reverse bias, the built-in potential at the interface of the p-n junction is enhanced, which prohibits electrons moving from SnS₂ to GaSe. As a result, a significant reverse current is observed because electrons now can easily transfer from GaSe to SnS₂.

The high photoresponsivity (R) of the vdW GaSe/SnS₂ p-n junction can be attributed to the following reasons. (1) Because of the type II band alignment and the existence of a strong built-in potential in the p-n heterojunction, the photogenerated electron-hole pairs can be efficiently separated and it leads to the increased lifetime of photo-generated carriers. (2) The high carrier mobilities of SnS₂ (~4.6 V⁻¹ cm² S⁻¹) [50] and GaSe (~0.6 V⁻¹ cm² S⁻¹) [55] also play an important role. (3) Intrinsic characteristics of good quality of both p-GaSe and n-SnS₂ single crystals contain much less scattering from foreign atomic dopants. (4) The few-layered thickness of the bottom layer (~10.5 nm thin SnS₂) provides a better screening effect against the Coulomb

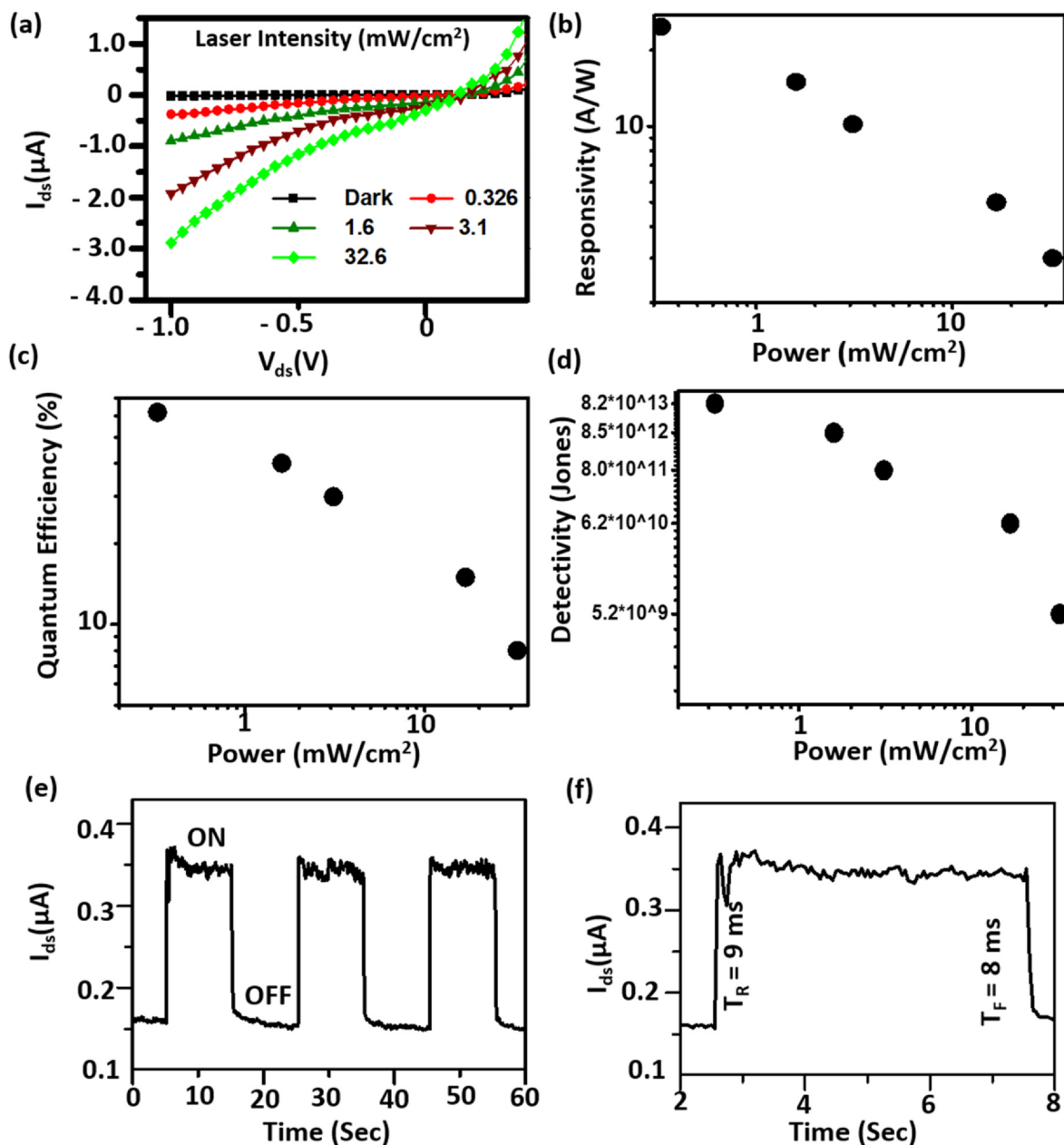


Fig. 3. Photoresponse study of vertically stacked p-GaSe/n-SnS₂ heterostructure device on SiO₂/Si substrate. (a) Photoconductivity spectra of vertically stacked GaSe/SnS₂ photodiode at dark and various illuminated power intensities (Dark, 0.326, 1.6, 3.1, and 32.6 mW/cm²). (b) The plot of responsivity versus power intensity. (c) The plot of quantum efficiency versus power intensity. (d) The plot of detectivity versus power intensity. (e,f) The time-dependent photoresponse characteristics of the device.

Table 1
Summary of performance metrics of 2D vdW crystal based p-n heterostructure.

Materials	Responsivity (A/W)	Detectivity	Response time	Ref.
Monolayer MoS ₂ /WSe ₂	0.011	—	—	[44]
Few-layered MoS ₂ /WSe ₂	0.125	—	—	[20]
Few-layered MoS ₂ /WSe ₂	1.42	—	—	[45]
Few-layered MoS ₂ /BP	3.54	—	—	[46]
Few-layered MoS ₂ /WSe ₂	5.07	3.0 × 10 ¹⁰	—	[47]
Few-layered GaTe/MoS ₂	21.83	8.4 × 10 ¹³	~7 ms	[48]
Few-layered GaSe/SnS ₂ on SiO ₂ /Si	24.8	8.2 × 10 ¹³	~8 ms	Present work
	35.2 (V _g = 30 V)	—	—	Present Work
Few-layered GaSe/SnS ₂ on PET	3.8 (planar state)	—	—	Presentwork
	3.2 (bent state)(bent state)	—	—	Presentwork

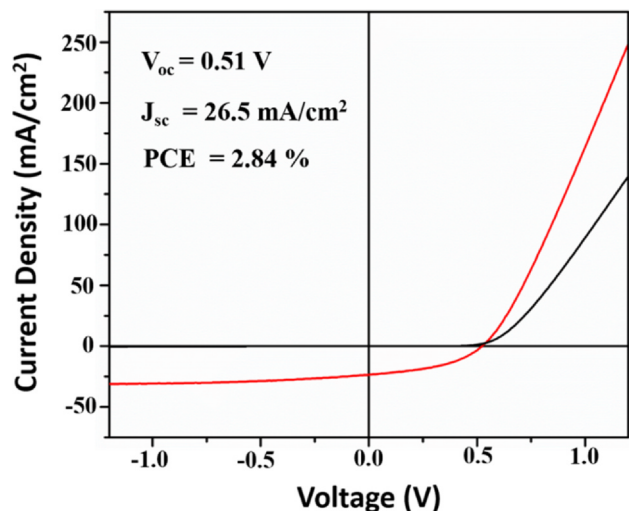


Fig. 4. *J-V* characteristics of p-GaSe/n-SnS₂ heterostructure measured with and without the illumination of AM 1.5 G solar simulator.

scattering [56].

4. Conclusion

In summary, we have successfully demonstrated the fabrication of vertically stacked few-layered vdW p-GaSe/n-SnS₂ heterostructures, which enables a gate tunable electronic and optoelectronic characteristics. The electrical characteristics of the junction exhibit excellent

current rectification behaviour. We show that the rectifier behavior of the heterojunction provides a useful route to manipulate the performance of phototransistor. The GaSe/SnS₂ p-n junction can serve as an excellent photodetector with a responsivity of about ~35 A/W, an external quantum efficiency as high as 62%, and a selective detectivity of 8.2×10^{13} J, which is even higher than commercial Si/InGaAs photodetectors. Furthermore, we demonstrate the application of this junction as a photovoltaic cell and the measured power conversion efficiency is about ~2.84%. Moreover, we also demonstrate this new type of heterojunction on flexible PET substrates with excellent performance. All these findings demonstrate that GaSe/SnS₂ vdW p-n junctions have attractive potential applications in both electronic and optoelectronic devices. Therefore, our work shown here provides a new illustration for the vertically stacked 2D vdW heterostructures with various novel properties, which is very useful for the development of not-yet realized devices.

5. Experimental section

5.1. Material synthesis

A technique called chemical vapor transport (CVT) is used for synthesizing single-crystalline p-type GaSe and n-type SnS₂ semiconductors. Using iodine as the transport agent, GaSe single crystals were synthesized. In a quartz tube, 99.999% pure Ga powder and Se pellets were introduced with pure Iodine (5.8 mg of 1 per cm³). At a temperature gradient of ~100 °C, the quartz tube was vacuumed up to 1150 °C for 1.5 weeks and cooled to 1050 °C at a rate of 10 °C/h followed by another cool down to 800 °C at a rate of 2 °C/h for 2 days and subsequently quenched in air. In our previous reports, growth methods

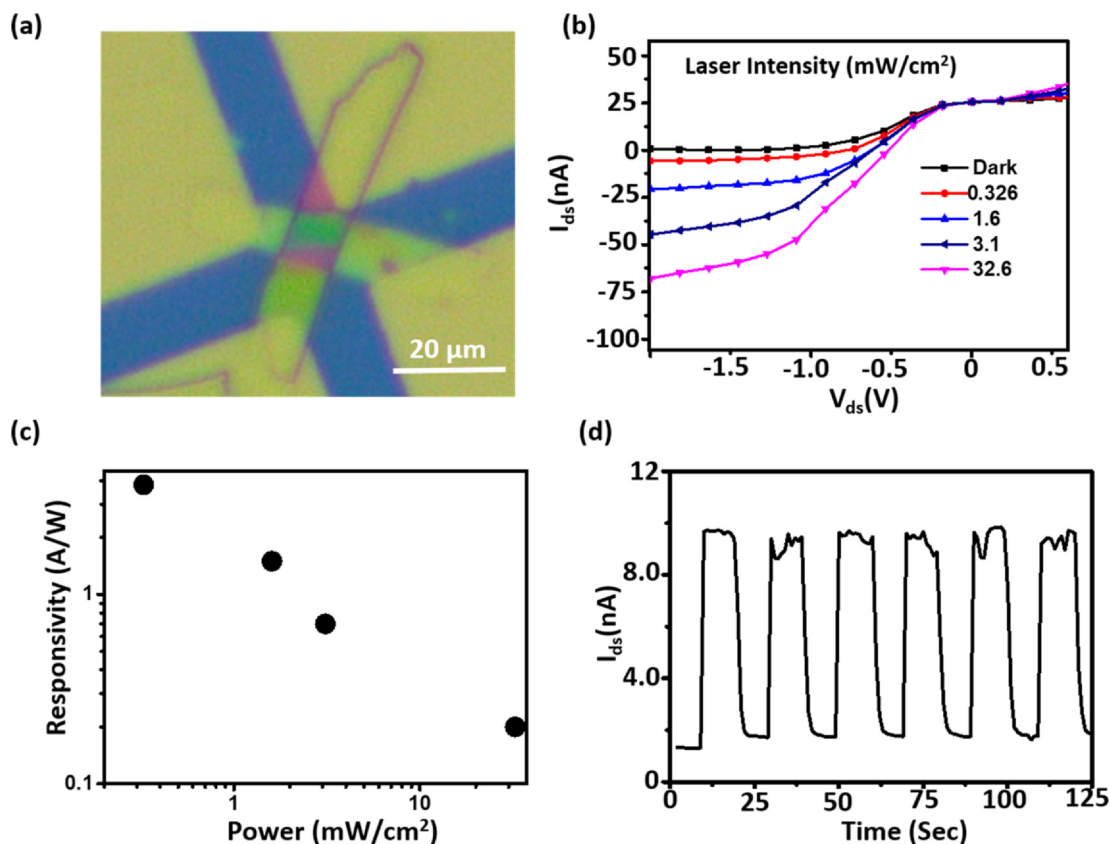


Fig. 5. Optoelectronic performance of van der Waals heterostructure deposited on flexible PET substrate. (a) Optical microscope image of vertically stacked GaSe/SnS₂ heterostructure on PET substrate. (b) Photoconductivity spectra of vertically stacked GaSe/SnS₂ photodiode on PET, performed at flat state with various illuminated power intensities (Dark, 0.326, 1.6, 3.1, and 32.6 mW/cm²). (c) The plot of responsivity versus power intensity. (d) The photoswitching measurement of the device on a flexible PET substrate.

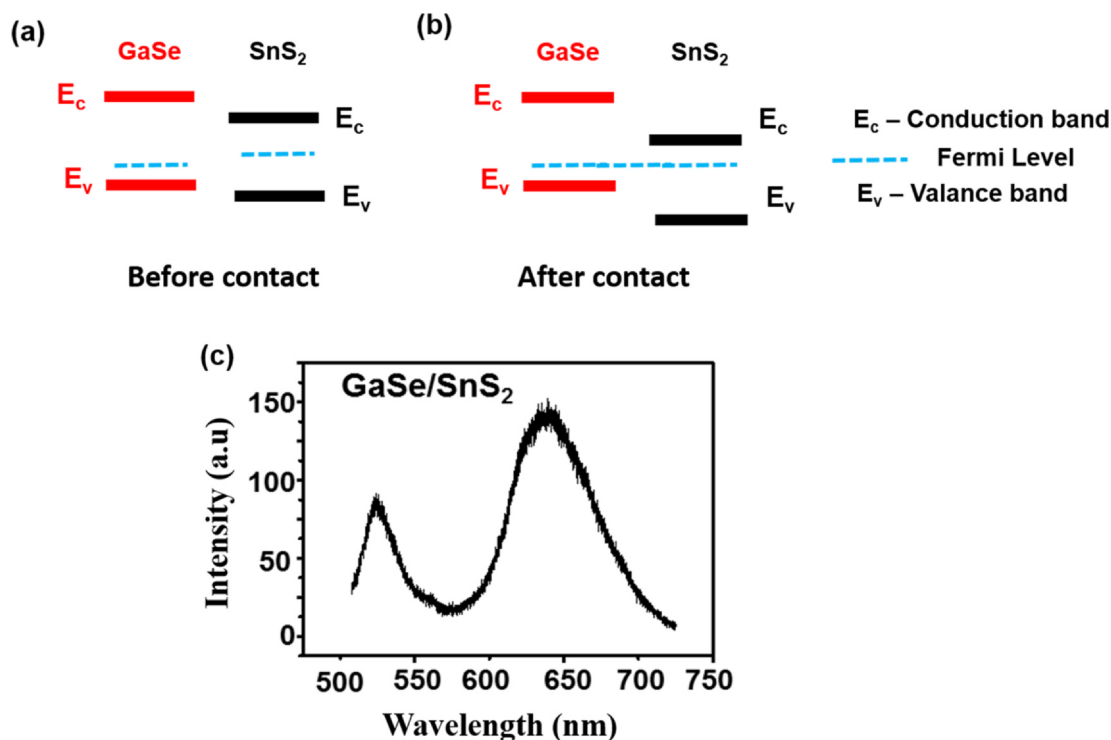


Fig. 6. Schematic of the band alignment of GaSe/SnS₂ heterostructure, which forms a type II heterojunction. (a) Before contact, (b) After contact and (c) Typical photoluminescence spectra of GaSe/SnS₂ heterostructure.

of SnS₂ were described [40].

5.2. Characterization

The X-ray diffractometry (SmartLab, Rigaku) with Cu K α radiation ($\lambda = 154059 \text{ \AA}$) and Bragg-Brentano geometry were used for investigating the crystal structures of all the grown crystals. The mechanical exfoliation method is used for preparing flakes of GaSe and SnS₂ with few-layer thickness and transferred to SiO₂ (300 nm)/Si substrate. Optical microscopy (Olympus, BX 51 M) equipped with a charge-coupled device (CCD) camera (Leica, DFC495) was used to observe the morphology of the exfoliated flakes. The confocal Raman spectrometer (Jobin Yvon, LabRAM HR800) with a 30 s exposure time and a 532 nm wavelength laser is used for individual measurement of Raman spectra of GaSe and SnS₂ flakes and at junction area.

5.3. Device Fabrication and Characterization

All the heterostructures after aligning shadow mask were fabricated and Cr/Au (5/100 nm) were evaporated as the source and drain electrodes. A laser diode (633 nm wavelength) and an electrical characterization system (Keithley 2636 source meter, Keithley Instruments) were used in measuring the optical and electrical characteristics of the devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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References

- [1] A.K. Geim, I.V. Grigorieva, *Nature* 499 (2013) 419.
- [2] D. Jariwala, T.J. Marks, M.C. Hersam, *Nat. Mater.* 16 (2017) 170.
- [3] V.W. Brar, A.R. Koltonow, J. Huang, *ACS Photon.* 4 (2017) 407.
- [4] J.Y. Lee, J.H. Shin, G.H. Lee, C.H. Lee, *Nanomaterials (Basel)* 6 (2016) 11.
- [5] W.J. Yu, Q.A. Vu, H. Oh, H.G. Nam, H. Zhou, S. Cha, J.Y. Kim, A. Carvalho, M. Jeong, H. Choi, A.H. Castro Neto, Y.H. Lee, X. Duan, *Nat. Commun.* 7 (2016) 13278.
- [6] K.S. Novoselov, A. Mishchenko, A. Carvalho, A.H. Castro Neto, *Science* 353 (2016) aac9439.
- [7] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A.C. Ferrari, R.S. Ruoff, V. Pellegrini, *Science* 347 (2015) 1246501.
- [8] Q.A. Vu, J.H. Lee, V.L. Nguyen, Y.S. Shin, S.C. Lim, K. Lee, J. Heo, S. Park, K. Kim, Y.H. Lee, W.J. Yu, *Nano Lett.* 17 (2017) 453.
- [9] Q.A. Vu, Y.S. Shin, Y.R. Kim, V.L. Nguyen, W.T. Kang, H. Kim, D.H. Luong, I.M. Lee, K. Lee, D.S. Ko, J. Heo, S. Park, Y.H. Lee, W.J. Yu, *Nat. Commun.* 7 (2016) 12725.
- [10] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B.I. Yakobson, H. Terrones, M. Terrones, B.K. Tay, J. Lou, S.T. Pantelides, Z. Liu, W. Zhou, P.M. Ajayan, *Nat. Mater.* 13 (2014) 1135.
- [11] X. Ling, Y. Lin, Q. Ma, Z. Wang, Y. Song, L. Yu, S. Huang, W. Fang, X. Zhang, A.L. Hsu, Y. Bie, Y.H. Lee, Y. Zhu, L. Wu, J. Li, P. Jarillo-Herrero, M. Dresselhaus, T. Palacios, J. Kong, *Adv. Mater.* 28 (2016) 2322.
- [12] X. Duan, C. Wang, J.C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang, A. Pan, J. Jiang, R. Yu, Y. Huang, X. Duan, *Nat. Nanotechnol.* 9 (2014) 1024.
- [13] Y. Wang, W.X. Zhou, L. Huang, C. Xia, L.M. Tang, H.X. Deng, Y. Li, K.Q. Chen, J. Li, Z. Wei, *2D Mater.* 4 (2017) 025097.
- [14] Y. Deng, Z. Luo, N.J. Conrad, H. Liu, Y. Gong, S. Najmaei, P.M. Ajayan, J. Lou,

- X. Xu, P.D. Ye, ACS Nano 8 (2014) 8292–8299.
- [15] M.H. Doan, Y. Jin, S. Adhikari, S. Lee, J. Zhao, S.C. Lim, Y.H. Lee, ACS Nano 11 (2017) 3832–3840.
- [16] T. Roy, M. Tosun, X. Cao, H. Fang, D.H. Lien, P. Zhao, Y.Z. Chen, Y.L. Chueh, J. Guo, A. Javey, ACS Nano 9 (2015) 2071–2079.
- [17] H. Tan, Y. Fan, Y. Zhou, Q. Chen, W. Xu, J.H. Warner, ACS Nano 10 (2016) 7866–7873.
- [18] A. Pezeshki, S.H.H. Shokouh, T. Nazari, K. Oh, S. Im, Adv. Mater. 28 (2016) 3216–3222.
- [19] M.L. Tsai, M.Y. Li, J.R.D. Retamal, K.T. Lam, Y.C. Lin, K. Suenaga, L.J. Chen, G. Liang, L.J. Li, J.H. He, Adv. Mater. (2017) 1701168.
- [20] C.H. Lee, G.H. Lee, A.M. van der Zande, W.C. Chen, Y.L. Li, M.Y. Han, X. Cui, G. Arefe, C. Nuckolls, T.F. Heinz, J. Guo, J. Hone, P. Kim, Nat. Nanotechnol. 9 (2014) 676–681.
- [21] H.M. Hill, A.F. Rigosi, K.T. Rim, G.W. Flynn, T.F. Heinz, Nano Lett. 16 (2016) 4831.
- [22] X. Hong, J. Kim, S.F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, Nat. Nanotechnol. 9 (2014) 682.
- [23] X. Liu, T. Galfsky, Z. Sun, F. Xia, E.-C. Lin, Y.-H. Lee, S. Kéna-Cohen, V.M. Menon, Nat. Photonics 9 (2014) 30.
- [24] W. Aggoune, C. Cocchi, D. Nabok, K. Rezouali, M. Akli Belkhir, C. Draxl, J. Phys. Chem. Lett. 8 (2017) 1464.
- [25] M. Buscema, D.J. Groenendijk, G.A. Steele, H.S. van der Zant, A. Castellanos-Gomez, Nat. Commun. 5 (2014) 4651.
- [26] R. Cheng, D. Li, H. Zhou, C. Wang, A. Yin, S. Jiang, Y. Liu, Y. Chen, Y. Huang, X. Duan, Nano Lett. 14 (2014) 5590.
- [27] J.S. Ross, P. Klement, A.M. Jones, N.J. Ghimire, J. Yan, D.G. Mandrus, T. Taniguchi, K. Watanabe, K. Kitamura, W. Yao, D.H. Cobden, X. Xu, Nat. Nanotechnol. 9 (2014) 268.
- [28] T. Georgiou, R. Jalil, B.D. Belle, L. Britnell, R.V. Gorbachev, S.V. Morozov, Y.J. Kim, A. Gholinia, S.J. Haigh, O. Makarovsky, L. Eaves, L.A. Ponomarenko, A.K. Geim, K.S. Novoselov, A. Mishchenko, Nat. Nanotechnol. 8 (2013) 100–103.
- [29] H. Yang, J. Heo, S. Park, H.J. Song, D.H. Seo, K.E. Byun, P. Kim, I.K. Yoo, H.J. Chung, K. Kim, Science 336 (2012) 1140–1143.
- [30] L. Britnell, R.V. Gorbachev, A.K. Geim, L.A. Ponomarenko, A. Mishchenko, M.T. Greenaway, T.M. Fromhold, K.S. Novoselov, L. Eaves, Nat. Commun. 4 (2013) 1794.
- [31] W. Jie, X. Chen, D. Li, L. Xie, Y.Y. Hui, S.P. Lau, X. Cui, J. Hao, Angew. Chem. Int. Ed. Engl. 54 (2015) 1185.
- [32] W. Kim, C. Li, F.A. Chaves, D. Jimenez, R.D. Rodriguez, J. Susoma, M.A. Fenner, H. Lipsanen, J. Riikonen, Adv. Mater. 28 (2016) 1845.
- [33] X. Li, M.W. Lin, A.A. Puzosky, J.C. Idrobo, C. Ma, M. Chi, M. Yoon, C.M. Rouleau, I.I. Kravchenko, D.B. Geohegan, K. Xiao, Sci. Rep. 4 (2014) 5497.
- [34] Y. Huang, E. Sutter, J.T. Sadowski, M. Cotlet, O.L.A. Monti, D.A. Racke, M.R. Neupane, D. Wickramaratne, R.K. Lake, B.A. Parkinson, P. Sutter, ACS Nano 8 (2014) 10743.
- [35] X. Zhou, Q. Zhang, L. Gan, H. Li, T. Zhai, Adv. Funct. Mater. 26 (2016) 4405–4413.
- [36] X. Yuan, L. Tang, S. Liu, P. Wang, Z. Chen, C. Zhang, Y. Liu, W. Wang, Y. Zhou, C. Liu, N. Gao, J. Zou, P. Zhou, W. Hu, F. Xiu, Nano Lett. 15 (2015) 3571–3577.
- [37] Y.B. Yang, J.K. Dash, A.J. Littlejohn, Y. Xiang, J. Shi, L.H. Zhang, K. Kisslinger, T.M. Lu, G.C. Wang, Cryst. Growth Des. 16 (2016) 961–973.
- [38] L.A. Burton, T.J. Whittles, D. Hesp, W.M. Linhart, J.M. Skelton, B. Hou, R.F. Webster, G. O'Dowd, C. Reece, D. Cherns, D.J. Fermin, T.D. Veal, V.R. Dhanak, A. Walsh, J. Mater. Chem. A 4 (2016) 1312.
- [39] X. Zhou, Q. Zhang, L. Gan, H. Li, J. Xiong, T. Zhai, Adv. Sci. 3 (2016) 1600177.
- [40] X. Li, M.W. Lin, A.A. Puzosky, J.C. Idrobo, C. Ma, M. Chi, M. Yoon, C.M. Rouleau, D.B. Kravchenko II, K. Xiao Geohegan, Sci. Rep. 4 (2014) 5497.
- [41] X. Li, L. Basile, M. Yoon, C. Ma, A.A. Puzosky, J. Lee, J.C. Idrobo, M. Chi, C.M. Rouleau, D.B. Geohegan, K. Xiao, Angew. Chem. Int. Ed. Engl. 54 (2015) 2712.
- [42] X. Gong, M. Tong, Y. Xia, W. Cai, J.S. Moon, Y. Cao, G. Yu, C.L. Shieh, B. Nilsson, A.J. Hegger, Science 325 (2009) 1665.
- [43] J. Kaniewski, J. Piotrowski, Opto-electron. Rev. 12 (2004) 139.
- [44] M.M. Furchi, A. Pospischil, F. Libisch, J. Burgdorfer, T. Mueller, Nano Lett. 14 (2014) 4785–4791.
- [45] N.J. Huo, J. Kang, Z.M. Wei, S.S. Li, J.B. Li, S.H. Wei, Adv. Funct. Mater. 24 (2014) 7025–7031.
- [46] Y. Deng, Z. Luo, N.J. Conrad, H. Liu, Y. Gong, S. Najmaei, P.M. Ajayan, J. Lou, X. Xu, P.D. Ye, ACS Nano 8 (2014) 8292–8299.
- [47] M.S. Choi, D. Qu, D. Lee, X. Liu, K. Watanabe, T. Taniguchi, W.J. Yoo, ACS Nano 8 (2014) 9332–9340.
- [48] F. Wang, Z. Wang, K. Xu, F. Wang, Q. Wang, Y. Huang, L. Yin, J. He, Nano Lett. 15 (2015) 7558–7566.
- [49] R. Saran, R.J. Curry, Nat. Photonics 10 (2016) 81.
- [50] P. Perumal, R.K. Ulaganathan, R. Sankar, Y.M. Liao, T.M. Sun, M.W. Chu, F.C. Chou, Y.T. Chen, M.H. Shih, Y.F. Chen, Adv. Funct. Mater. 26 (2016) 3630.
- [51] D.B. Velusamy, R.H. Kim, S. Cha, J. Huh, R. Khazaiezhad, S.H. Kassani, G. Song, S.M. Cho, S.H. Cho, I. Hwang, J. Lee, K. Oh, H. Choi, C. Park, Nat. Commun. 6 (2015) 8063.
- [52] S.R. Tamalampudi, Y.Y. Lu, U.R. Kumar, R. Sankar, C.D. Liao, B.K. Moorthy, C.H. Cheng, F.C. Chou, Y.T. Chen, Nano Lett. 14 (2014) 2800.
- [53] H. Cai, J. Kang, H. Sahin, B. Chen, A. Suslu, K. Wu, F. Peeters, X. Meng, S. Tongay, Nanotechnology 27 (2016) 065203.
- [54] R. Lu, J. Liu, H. Luo, V. Chikan, J.Z. Wu, Sci. Rep. 6 (2016) 19161.
- [55] D.J. Late, B. Liu, J. Luo, A. Yan, H.S.S.R. Matte, M. Grayson, C.N.R. Rao, V.P. David, Adv. Mater. 24 (2012) 3549–3554.
- [56] S. Kim, A. Konar, W.S. Hwang, J.H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J.B. Yoo, J.Y. Choi, Y.W. Jin, S.Y. Lee, D. Jena, W. Choi, K. Kim, Nat. Commun. 3 (2012) 1011.