ARTICLE

Van der Waals epitaxial growth and optoelectronics of large-scale WSe$_2$/SnS$_2$ vertical bilayer p–n junctions

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High-quality two-dimensional atomic layered p–n heterostructures are essential for high-performance integrated optoelectronics. The studies to date have been largely limited to exfoliated and restacked flakes, and the controlled growth of such heterostructures remains a significant challenge. Here we report the direct van der Waals epitaxial growth of large-scale WSe$_2$/SnS$_2$ vertical bilayer p–n junctions on SiO$_2$/Si substrates, with the lateral sizes reaching up to millimeter scale. Multi-electrode field-effect transistors have been integrated on a single heterostructure bilayer. Electrical transport measurements indicate that the field-effect transistors of the junction show an ultra-low off-state leakage current of 10^{-14} A and a highest on–off ratio of up to 10^7. Optoelectronic characterizations show prominent photo-response, with a fast response time of 500 μs, faster than all the directly grown vertical 2D heterostructures. The direct growth of high-quality van der Waals junctions marks an important step toward high-performance integrated optoelectronic devices and systems.

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The emerging two-dimensional (2D)-layered semiconductors have shown considerable potential for designing next-generation integrated electronic and optoelectronic systems, due to their many unique physical and structural properties[1–14]. In particularly, diverse 2D-layered semiconductors can be flexibly combined to form diverse vertical van der Waals (vdWs) heterostructures[15–23] with atomically sharp interfaces and tunable band alignment, opening up vast opportunities for fundamental investigation of novel electronic and optical properties at the limit of single atom thickness and potential applications in novel device concepts[9, 17, 19, 21, 24–30]. The current studies of 2D van der Waals heterostructures have been largely limited to the mechanically exfoliated and restacked flakes[17, 20, 26, 31–34], which is arduous and clearly un-scalable for practical technologies. Some recent progresses have also shown that 2D vertical heterostructures can be produced by direct vapor phase growth[35–42]. Compared to the mechanical stacking approach, the direct growth strategy could offer unique advantages of easy size control, clean interface, and potential for practical industrial applications. However, direct vapor growth of large-scale high-quality 2D atomic layered vertical heterostructures, especially p–n junctions, remains a great challenge.

As an important p-type 2D semiconductor with excellent physical properties, layered tungsten diselenide (WSe$_2$) has attracted great attention as a promising material for future scaled device applications[43]. Tin disulfide (SnS$_2$), as a member of IV–VI A group, and being an important n-type layered semiconductor, has drawn considerable attention due to the advantages of low-cost, earth-abundant, nontoxic, and enviromentally friendly[34, 44, 45]. Recently, 2D heterostructures combining the p-type WSe$_2$ and n-type SnS$_2$ have aroused great interest. Wang et al.[34] have reported the preparation of few-layer/few-layer stacked WSe$_2$/SnS$_2$ device through a mechanically exfoliated and restacked method, and investigated their anti-ambipolar behavior. Zhang et al.[35] demonstrated the growth of few layers of WSe$_2$ on the pre-prepared randomly oriented micaoplates of SnS$_2$. Herein, we report a two-step vapor phase route to controlled growth of large-scale WSe$_2$/SnS$_2$ vertical bilayer p–n junctions on SiO$_2$/Si. The as-

grown junctions are highly crystallized, with their lateral sizes reaching up to millimeter scale, representing the largest size of atomic layered vertical heterostructures ever been achieved. Backgate field-effect transistors were fabricated with high on–off ratio, ultra-low leakage current, and show fast photoresponse speed comparing favorably to mechanically staked 2D vertical junctions. The direct growth of high-quality van der Waals junctions marks an important step toward high-performance integrated optoelectronic device and systems.

Results

Characteristics of WSe$_2$/SnS$_2$ heterostructure. Figure 1a shows a top view of atomic structure illustration of the WSe$_2$/SnS$_2$ bilayer heterostructure, in which the bottom WSe$_2$ monolayer and the top SnS$_2$ monolayer are stacked by weak vdWs force. Figure 1b shows the relative band alignment of the bilayer WSe$_2$/SnS$_2$ heterostructure calculated by Vienna ab initio simulation package (VASP). The calculation details could be found in the Supplementary Figs 1 and 2. The valence band maximum of WSe$_2$ is higher than that of the conduction band minimum of SnS$_2$, forming a type-III broken-gap heterojunction[17, 20]. Both of the conduction band offset (ΔE_c, 1.69 eV) and the valence band offset (ΔE_v, 1.64 eV) of WSe$_2$/SnS$_2$ are larger than those of any other reported directly grown 2D heterostructures[36, 37, 40, 41, 46, 47]. The large band offset may cause efficient interlayer charge transfer between the bottom and the top layers, providing an ideal structural base for high-performance optical and electrical applications[40, 48].

The WSe$_2$/SnS$_2$ vertical bilayer heterostructures were grown via a two-step chemical vapor deposition (CVD) strategy. Large-scale WSe$_2$ monolayers were first grown on the SiO$_2$/Si substrate, through a controlled vapor deposition process. The pre-prepared large-scale WSe$_2$ monolayers were then used as templates for subsequent van der Waals epitaxial growth of SnS$_2$ monolayers in vapor phase to achieve the vertical bilayer heterostructures. The two-step vapor growth process is shown schematically in Fig. 1c, and the detailed descriptions about the growth are included in Method section.
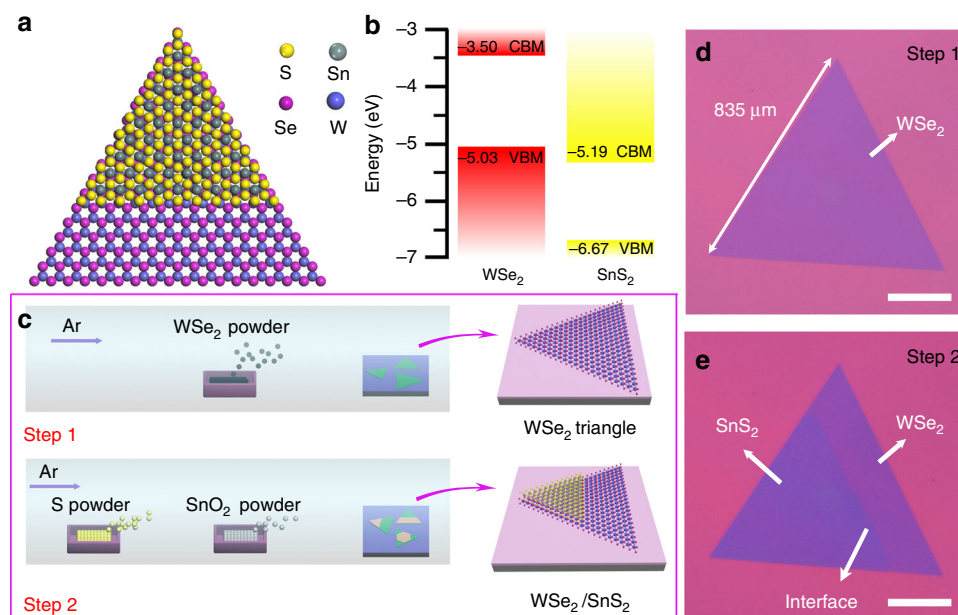

Fig. 1 Synthesis of large-scale type-III WSe$_2$/SnS$_2$ heterostructure. **a** Schematic of vertically stacked WSe$_2$/SnS$_2$ vdW heterostructure. **b** Band alignment of type-III WSe$_2$/SnS$_2$ junction. **c** Schematic illustrating the two-step vapor expitaxy growth of WSe$_2$/SnS$_2$ heterostructure. **d** Typical optical image of as-grown large-scale monolayer WSe$_2$ triangular flake achieved after step 1. **e** Optical image of as-grown vertically stacked WSe$_2$/SnS$_2$ heterostructure after step 2 by using the same flake in Fig. 1d. All the scale bars: 200 μm
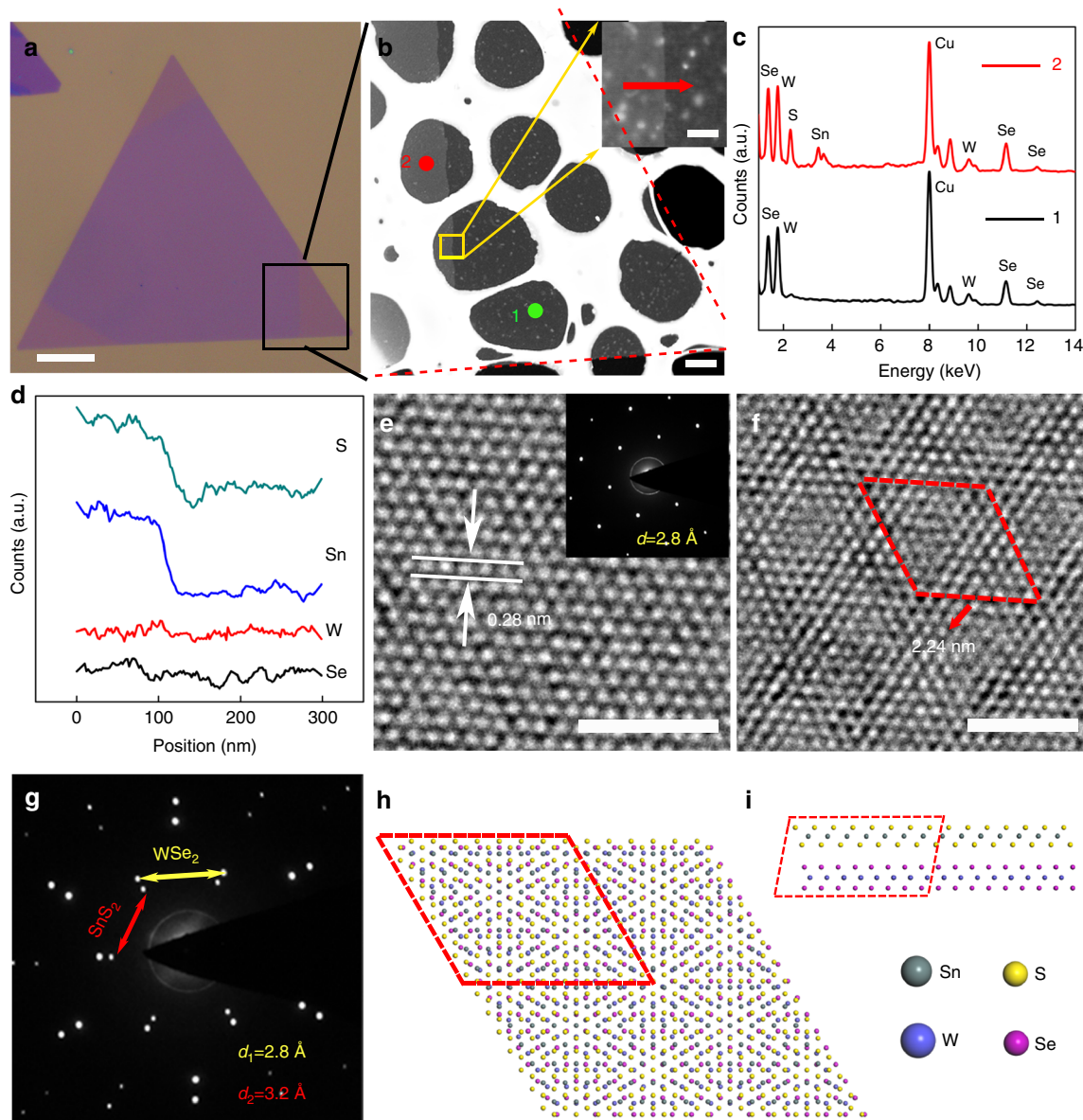
Fig. 2 Atomic structure of the vertically stacked WSe_2/SnS_2 heterostructure. **a** A typical optical image of the heterostructure with three interfaces at the corners of the triangle flake. Scale bar, 30 μm. **b** Low-resolution TEM image of the interface from the black rectangle region in **a**. Scale bar, 5 μm. Inset is the enlarged interface image highlighted in the yellow rectangle. Scale bar, 100 nm. **c** EDS results of point 1 and point 2 in **b**, marked by green and red colors, respectively. **d** Line scans of S, Sn, W, Se elements distribution across the red arrow in the inset of **b**. **e** HRTEM image taken on the green point 1 region in **b**. Scale bar, 2 nm. Inset is the SAED pattern of the bare WSe_2. **f** HRTEM image taken on the red point 2 region in **b**, indicating the vertical stacked WSe_2/SnS_2 vdW heterostructure with Moiré pattern. Scale bar, 2 nm. **g** The SAED pattern collected from point 2 region shows two sets of electron diffraction patterns, corresponding to WSe_2 and SnS_2, respectively. **h**, **i** Top view and side view of the atomic model of the WSe_2/SnS_2 vdW heterostructure, respectively. The supercell is highlighted by red dashed lines

For further understanding the two-step growth process, we have closely characterized the same WSe_2 monolayer domain before and after the second step growth of SnS_2 monolayer. Figure 1d gives the optical image of a typical as-grown large-scale WSe_2 triangle flake, with the size measured to be 835 μm, and Fig. 1e is the corresponding WSe_2/SnS_2 vertical heterostructure obtained after the second step growth. The pre-grown WSe_2 triangular domain is partially covered by the SnS_2 domain, which can be distinguished from the optical contrast in the image. The size of the vertical junction can be well controlled by the growth time of both the bottom WSe_2 and the top SnS_2 layers, with the maximum lateral size reaching up to millimeter scale, which is about one order of magnitude larger than both the staked or synthetic vertical bilayer heterostructures reported previously[36, 37, 40–42, 49]. More detailed morphology information can be found in Supplementary Fig. 3.

Transmission electron microscope (TEM) measurements were conducted to further investigate the crystal quality and structure of the as-grown WSe_2/SnS_2 heterostructures. Figure 2a shows the optical image of a typical WSe_2/SnS_2 heterostructure for TEM characterization and Fig. 2b shows its corresponding TEM image at the marked interface region of the sample after transferred onto a copper grid (see method), with the inset showing the local high-magnification image of the interface. Fig. 2c shows the elemental energy dispersive X-ray spectroscopy (EDS) collected from both the monolayer (green, point 1 in Fig. 2b) and bilayer
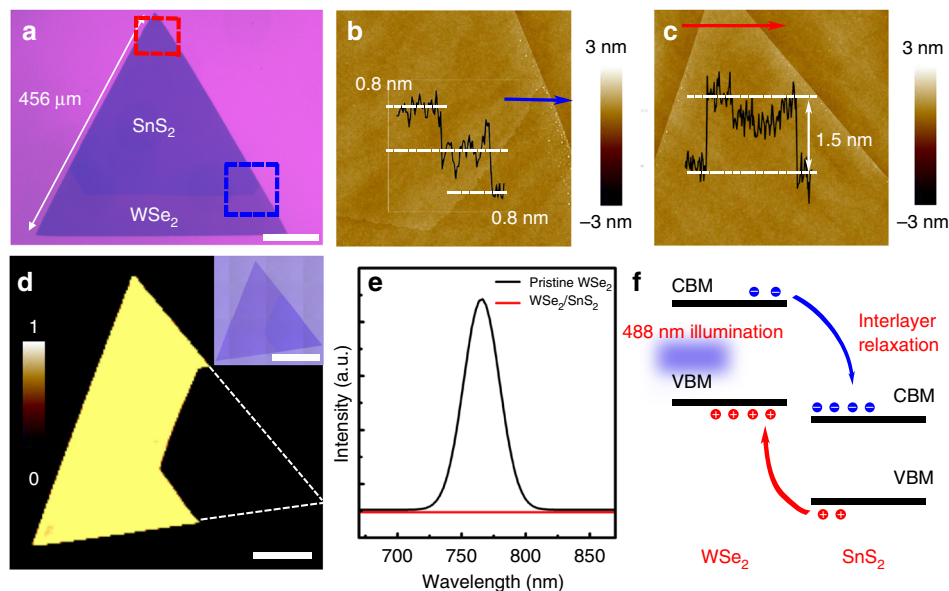
Fig. 3 AFM and PL characterization of the vertically stacked WSe_2/SnS_2 heterostructure. **a** Optical micrograph of a large-scale 1 L SnS_2/1 L WSe_2 stacked triangular flake grown on SiO_2/Si. Scale bar, 100 μm. **b** AFM image of the blue rectangle region in **a**. Inset is height profile along blue arrow, indicating the thickness of bottom layer and top layer is 0.8 and 0.8 nm, respectively. Corresponding to 1 L SnS_2 on 1 L WSe_2. **c** AFM image of the red rectangle region in **a**. Inset is the height profile across the red arrow, indicating the thickness of the heterostructure is 1.5 nm (1 L WSe_2 + 1 L SnS_2). **d** PL intensity mapping (720–780 nm). Scale bar, 60 μm. Inset image is the optical image of the sample used for PL characterization. Scale bar, 100 μm. **e** PL spectra observed from bare WSe_2 region (black curve) and WSe_2/SnS_2 vdW heterostructure region (red curve). **f** Schematic diagram of WSe_2/SnS_2 heterostructure band structure and photoexcitation, interlayer relaxation process in WSe_2/SnS_2 heterojunction

(red, point 2 in Fig. 2b) regions, respectively. Except the Cu signal from the grid, only elements W and Se were collected from the monolayer region, while apart from W and Se, elements Sn and S were also detected at the bilayer region, indicating the formation of WSe_2/SnS_2 heterostructure, which can also be well demonstrated by the element line scans across the interface region (Fig. 2d). The high resolution transmission electron microscope (HRTEM) image and the selected electron diffraction pattern (SAED) (Fig. 2e) show the bottom region is well crystallized with the measured lattice spacing of 0.28 nm, well consistent with the value of (100) plane spacing of WSe_2. The bilayer heterostructure region shows obvious Moiré patterns (Fig. 2f), caused by the overlapping lattices between SnS_2 and WSe_2. The smallest periodic repeated cell is demarcated by the red dashed rhombus, with a lattice constant of 2.24 nm. The corresponding SAED shows two different sets of hexagonally arranged diffraction patterns (Fig. 2g), with the calculated lattice spacings consistent with the SnS_2 (0.32 nm) and WSe_2 (0.28 nm), respectively[44]. The large lattice misfit (14.3%) indicates that the SnS_2 domain is stacked on the WSe_2 through vdW epitaxy[36, 37, 40–42]. Figure 2h and i gives the top and side views of the theoretical atomic structure model of the WSe_2/SnS_2 heterostructure with Moiré patterns, consistent with the experimental observation shown in Fig. 2f, with the periodic repeated cell marked by the red dashed rhombus, corresponding to 7 × 7 SnS_2 stacked on 8 × 8 WSe_2[41].

The thickness of the as-grown heterostructures was further confirmed by atomic force microscope (AFM) measurements. Figure 3b and c is the AFM images detected at the selected stack region (red dashed rectangle) and the interface region across from SnS_2 to WSe_2 (blue dashed rectangle), respectively, as marked in Fig. 3a. The insets of the AFM images show the corresponding line scan height profile, indicating that the thickness of both the bottom and the top layer are 0.8 nm, with a total thickness at the stack region of 1.5 nm, well demonstrating the achieved bilayer heterostructures (1 L WSe_2 + 1 L SnS_2).

Room temperature photoluminescence (PL) mapping (720 nm - 780 nm) and their corresponding local spectra obtained from a typical heterostructure domain with most of its surface being bilayer stacked (Fig. 3d, e). The results indicate that the bottom uncovered WSe_2 monolayer exhibits strong PL emission with a dominant emission peak locating at 766 nm, corresponding to the recombination of excitons[50, 51], whereas the bilayer WSe_2/SnS_2 region shows apparent PL quenching, with essentially no detectable PL (Fig. 3e). The PL quenching in the stack region indicates the interaction induced energy (charged carrier) transfer between the WSe_2 and the SnS_2[48]. According to the band alignment of WSe_2/SnS_2 as shown in Fig. 1b, the conduction band minimum of SnS_2 is about 1.78 eV lower than that of WSe_2, whereas the valence band maximum of SnS_2 is about 1.67 eV lower than that of WSe_2. Thus, the photo-excited electrons and holes in WSe_2 prefer to transfer to low-energy states in SnS_2, rather than forming excitons in WSe_2, However, being a typical indirect semiconductor, SnS_2 is normally inradiative[44, 52]. The charge transfer from WSe_2 to SnS_2 will consequently lead to the significant PL quenching of the heterostructures (Fig. 3e), as schematically exhibited in Fig. 3f[37, 40, 41, 46, 48, 53, 54].

Electrical transport properties of WSe_2/SnS_2 heterostructure. To further investigate the electrical charge transport properties and optoelectronic performance of the resulted WSe_2/SnS_2 vdW heterostructures, multi-electrode backgate field-effect transistors (FETs) were designed and fabricated based on a partially covered heterostructure domain grown at a (P++) Si/SiO_2 substrate, with Ti/Au thin film as the source-drain electrodes and the silicon substrate as the backgate contact electrode, as schematically in Fig. 4a. This device structure is suitable for systematically investigating the performance of different devices integrated on the same nanostructure. All the device measurements were conducted under vacuum at room temperature.
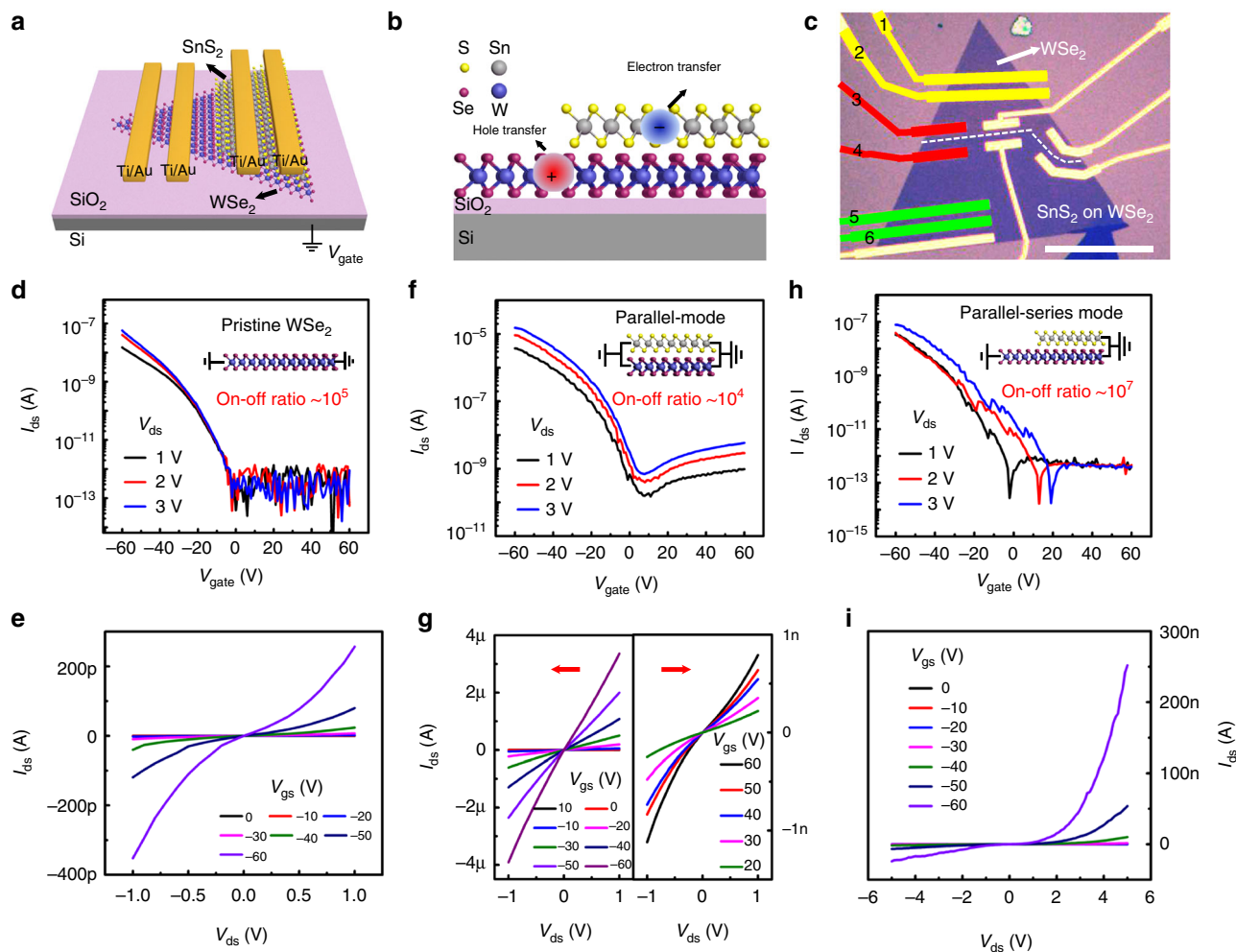
Fig. 4 Electrical characterization of the vertically stacked WSe_2/SnS_2 heterostructure. **a** Schematic diagram of the multi-electrode WSe_2/SnS_2 vdW heterostructure backgate device. **b** Front view of the WSe_2/SnS_2 vdW heterostructure. **c** An optical image of fabricated WSe_2/SnS_2 vdW heterostructure device. Scale bar, 60 μm. **d** $I_{ds} - V_{bg}$ curves of the pristine WSe_2 measured using electrodes 1 and 2, demonstrating p-type behavior. **e** $I_{ds} - V_{ds}$ output characteristics of pristine WSe_2 FET at various backgate voltages. **f** $I_{ds} - V_{bg}$ curves of the parallel-mode vdW heterostructure measured using electrodes 5 and 6, demonstrating ambipolar behavior. **g** $I_{ds} - V_{ds}$ output characteristics of the parallel-mode vdW heterostructure at various backgate voltages from −60 V to 10 V and from 20 V to 60 V. **h** $I_{ds} - V_{bg}$ curves across the p (WSe_2) − n (SnS_2) heterojunction, named parallel-series mode, demonstrating p-type behavior (measured using electrodes 3 and 4). **i** $I_{ds} - V_{ds}$ output characteristics across the p–n junction at different backgate voltages

Figure 4b gives schematically the front view of the heterostructure, with electron dominating the charge transfer process in the n-type SnS_2 layer and hole dominating transfer in the p-type WSe_2 layer, as reported in the literatures[44, 55–57]. The optical image of a typical WSe_2/SnS_2 vdW heterostructure after device fabrication is shown in Fig. 4c. Electrodes 1, 2, and 3 were deposited on top of the pristine WSe_2 region, whereas electrodes 4, 5, and 6 were deposited on the top of the stack WSe_2/SnS_2 region. As a result, three kinds of device channels were formed, (1) pristine WSe_2 channel (electrodes 1 and 2, yellow), (2) parallel-mode channel (electrodes 5 and 6, green, bilayer stacked region) and (3) parallel-series mode channel (electrodes 3 and 4, red, heterojunction region), respectively. The transport characteristic of pristine WSe_2 shows typical p-type behavior, indicating that holes dominate charge transport process, with an on–off ratio of 10^5 and a threshold voltage of −2 V (Fig. 4d). The corresponding output characteristic in Fig. 4e shows that the I_{ds} decreases with the V_g varying from −60 to 0 V, and the $I_{ds} - V_{ds}$ curves shows an inflection point at near $V_{ds} = 0$ V, indicating the existence of a Schottky barrier at the WSe_2 contacting with Ti/Au. The field-effect charge carrier mobility

is calculated to be 0.02 cm^2 V^{-1} s^{-1} ($L = 5.2$ μm, $W = 36.5$ μm, $V_{ds} = 1$ V). In addition, the transport characteristic of the parallel-mode device shows ambipolar behavior (Fig. 4f), which is attributed to the p-type WSe_2 and the n-type SnS_2[41]. The corresponding output characteristic show that the $I_{ds} - V_{ds}$ have very good linear relation at negative V_g values, and I_{ds} decreases as the back voltage varies from −60 to 10 V, following an increase as V_g varies from 10 to 60 V (Fig. 4g). The hole mobility is calculated to be 10.1 cm^2 V^{-1} s^{-1} ($L = 4.25$ μm, $W = 51$ μm, $V_{ds} = 1$ V), which is three orders higher than that of the pristine WSe_2. Moreover, the device shows an on–off ratio of 10^4 with a saturation current reaching up to 10 μA ($V_{ds} = 1$ V). The electric transport properties of the parallel-series mode device were measured using electrodes 3 and 4. The transport characteristic is p-type dominant, indicating that holes in the bottom WSe_2 dominate the charge transport across this junction. The hole mobility is calculated to be 0.149 cm^2 V^{-1} s^{-1} (Fig. 4h) ($L = 9.35$ μm, $W = 21.2$ μm, $V_{ds} = 1$ V), one order higher than that of the pristine WSe_2 device. Importantly, benefit from the existence of the barrier near the vertical junction, leading to a very low leak current (10^{-14} A), and an ultrahigh on–off ratio to 10^7, two
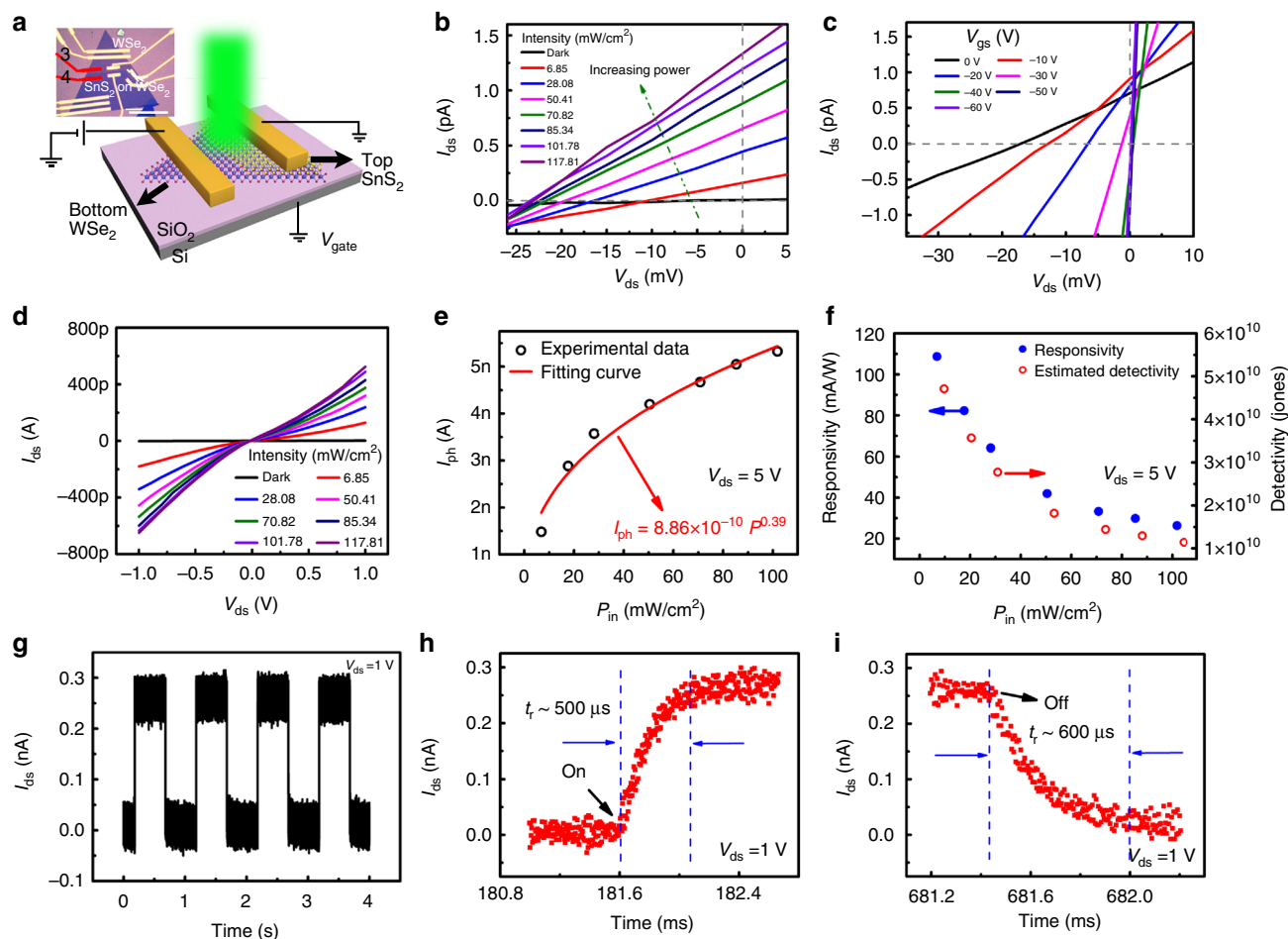
Fig. 5 Optoelectronic characterization of the parallel-series mode WSe$_2$/SnS$_2$ heterojunction. **a** A cartoon schematic of the parallel-series mode WSe$_2$/SnS$_2$ vdW heterojunction photodetector. Inset is an optical image of the heterojunction device. (measured using electrodes 3 and 4, see Fig. 4c). **b** I_{ds} − V_{ds} curves across the p–n junction under 520 nm laser illumination at different incident power. **c** I_{ds} − V_{ds} curves at various backgate voltages from −60 V to 0 V under 520 nm laser illumination at fixed 101 mW cm^{-2} power intensity. **d** I_{ds} − V_{ds} curves across the p–n junction under 520 nm laser illumination at different incident power. V_{ds} range from −1 V to 1 V. **e** Dependence of photocurrent on illumination power intensities. **f** Photoresponsivity and detectivity of the photodetector at various illumination power intensities. **g** Photocurrent response of the device, the laser light is turned on/off by a chopper worked at 1 Hz (520 nm, 101 mW cm^{-2}, V_{ds} = 1 V). **h, i** Time-resolved photoresponse of the device, namely the rise and fall times of the photocurrent measured at V_{ds} = 1 V

orders higher than that of the pristine WSe$_2$ device (10^5) and three orders higher than that of the parallel-mode device (10^4). Gate-tunable output curves show obvious current rectification behavior (Fig. 4i), indicating a p–n diode is formed across the heterojunction.

It is well reported that vapor grown TMDs monolayers usually have very low mobility, mainly caused from the carrier scattering by the inevitable lattice defects induced during the vapor synthesis and device fabrication processes[58, 59], which is also demonstrated in the pristine WSe$_2$ monolayer device. The mobility can be greatly improved from the heterostructured channels, i.e., the parallel-mode and the parallel-series mode devices, which can be attributed to several reasons. Firstly, the electrons and holes can be efficiently separated with less interactive scattering and faster transfer in the type-III band alignment heterostructures[40]. Secondly, the van der Waals force in the interface will also help to suppress the extrinsic interfacial impurities to increase the mobility[60, 61]. Thirdly, comparing to a single layer of WSe$_2$, the increased carrier density in the heterostructure will enhance the screening of the interfacial Coulomb potential, which will also help to improve the mobility[61].

Photovoltaic and photoresponse properties of WSe$_2$/SnS$_2$ heterostructure. The photovoltaic and photoresponse properties of the WSe$_2$/SnS$_2$ p–n heterojunction (parallel-series mode) were investigated using electrodes 3 and 4 (see Fig. 4c). All the measurements were conducted by applying a drain voltage V_{ds} on WSe$_2$ (p-type, terminal "d"), with SnS$_2$ (n-type, terminal "s") being grounded (Fig. 5a).

Furthermore, obvious photovoltaic effect was observed in the direct grown WSe$_2$/SnS$_2$ p–n heterojunction when the junction was under 520 nm laser illumination, which further demonstrate the formation of the atomic junction. As shown in Fig. 5b, with increasing the laser power, more photoinduced electro-hole pairs will separate and contribute to a higher I_{sc}. Meanwhile, more electrons and holes excited by the laser illumination aggregate in the interface region and enhance the band bending, which will further increase the absolute value of V_{oc}. In addition, as shown in Fig. 5c, when the backgate voltage varies from 0 to −60 V, the absolute value of V_{oc} shows a decrease, with I_{sc} changed slightly. The Fermi level of WSe$_2$ moved down under negative gate voltages, leading to a less band bending and decrease the built-in potential difference, result in a smaller V_{oc}. At the same time, both negative backgate voltage and the laser illumination will

trigger an excess carrier concentration, which will reduce the lifetime of carrier and simultaneously increase the recombination. As a result, the I_{sc} changes slightly[17, 41].

Photoconductive properties of the parallel-series mode device under different laser power were also examined, as shown in Fig. 5d. I_{ph} is the photocurrent which is defined as $I_{ph} = I_{light} - I_{dark}$, and the obtained data under different laser power are shown in Fig. 5e, fitted with an equation of $I_{ph} = aP^\alpha$. In our experiments, the fitted parameters of a and α are 8.86×10^{-10} and 0.39, respectively. The responsivity (R) is calculated by the equation of $R = I_{ph}/PA$, where I_{ph} is the photocurrent, P is the incident light power density, and A is the effective area of the device channel. The responsivity of the device can reach up to 108.7 mA W^{-1} (P = 13.63 nW, V_{ds} = 5 V, device area of 198.2 μm^2), which is a lot higher than the ever repoted 2D vapor epitaxy grown p–n junction[41]. Detectivity ($D^\star$) is used to characterize the sensitivity of a photodetector. Assuming that shot noise from the dark current is the major factor limiting the $D^\star$, which can be estimated by $D^\star = RA^{1/2}/(2e\,I_{dark})^{1/2}$, where R is responsivity, A is the effective area of the device channel, e is the electronic charge, and I_{dark} represents the dark current[62, 63]. The maximum estimated $D^\star$ value of 4.71×10^{10} Jones can be obtained based on this expression (Fig. 5f). To further investigate the response speed of the WSe$_2$/SnS$_2$ p–n heterojunction photodetector, time-resolved photoresponse measurements were performed by turning on and off the laser light (520 nm, 100 mW cm^{-2}) with a chopper worked at 1 Hz. A high-speed oscilloscope was used to monitor the fast-varying signal. As shown in Fig. 5g, the photodetector exhibits the excellent stability and reliability with the on/off photoswitching behavior at V_{ds} = 1 V without additional gate voltage. The rise time (τ_r) and the fall time (τ_f) is 500 μs and 600 μs, respectively, as shown in Fig. 5h, i. Importantly, as far as we known, the response speed of the WSe$_2$/SnS$_2$ heterojunction photodetector is faster than all the CVD directly grown vertical stacked 2D heterostructures[37, 40–42, 64], even two orders of magnitude faster than most mechanical exfoliated and restacked vertical 2D heterostructures[65–67], and nearly four orders of magnitude faster than the response time of the reported pristine WSe$_2$ detector[68, 69].

To further systematically understand the high-performance of the junction (parallel-series mode) detector, the photodetectors of the pristine WSe$_2$ monolayer and the parallel-mode vertical stacked structure based on the same flake were also fabricated and comparatively investigated, as shown in Supplementary Figs. 4 and 5. From the results, the performances of the heterostructured devices (parallel-mode and parallel-series mode) are overall a lot higher than those of the pristine device. For the parallel-series mode devices, the photoinduced electron-hole pairs can be efficiently separated due to the large band offset (Fig. 1b). Meanwhile, benefit from the higher mobility comparing to pristine WSe$_2$, the electrons and holes can be transported faster to the opposite terminals after separation. Both these two factors help increasing the R value and the response speed. However, having a large dark current (10^{-8} A), the photodetectivity is greatly limited for the parallel-mode device, and this disadvantages can be greatly improved in the parallel-series mode device, which possesses the advantages of both efficiently separation, fast charge transfer and also maintain low dark current (10^{-12} A at V_{ds} = 1 V). As a result, the achieved 2D large-scale WSe$_2$/SnS$_2$ heterojunction photodetectors show great potential for high-speed and weak signal detection applications in integrated optoelectronic applications.

Discussion
We have demonstrated direct van der Waals epitaxial growth of vertical bilayer WSe$_2$/SnS$_2$ p–n junction. The as-grown junctions are highly crystallized, with their lateral sizes reaching up to millimeter scale, representing the largest size of atomic layered vertical heterostructures ever been achieved. TEM results have shown obvious periodic Moiré patterns, indicating a large lattice mismatch (14.3%), further demonstrating the SnS$_2$ domain is stacked on the WSe$_2$ through vdW epitaxy. Strong PL quenching in the bilayer region of WSe$_2$/SnS$_2$ heterostructure was observed, coming from the efficient interlayer charge transfer between the bottom and the top layers. Multi-electrodes backgate FETs were constructed, result in three different kinds of devices integrated on one typical heterostructure flake. Their perfomance of FETs and photodetectors were systematically investigated, indicating the parallel-series mode WSe$_2$/SnS$_2$ p–n junction exhibits an ultra-low leak-off current (10^{-14} A), and a highest on–off ratio (10^7). Devices based on the parallel-series mode WSe$_2$/SnS$_2$ p–n junction exhibit an obvious positive promotion in photo-responsvity (108.7 mA W^{-1}), photodetectivity (4.71×10^{10} Jones) and photoresponse speed (500 μs), comparing to the pristine WSe$_2$, with all the values improved than all the ever reported direct grown 2D vertical p–n junctions. This study of WSe$_2$/SnS$_2$ van der Waals heterostructures marks a important step toward high-performance integrated optoelectronic devices and systems.

Methods

References

1. Novoselov, K. S. et al. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci. USA* **102**, 10451–10453 (2005).
2. Zhang, Y., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **438**, 201–204 (2005).
3. Liao, L. et al. High-speed graphene transistors with a self-aligned nanowire gate. *Nature* **467**, 305–308 (2010).
4. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS_2: a new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
5. Splendiani, A. et al. Emerging photoluminescence in monolayer MoS_2. *Nano Lett.* **10**, 1271–1275 (2010).
6. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. & Kis, A. Single-layer MoS_2 transistors. *Nat. Nanotechnol.* **6**, 147–150 (2011).
7. Zeng, H., Dai, J., Yao, W., Xiao, D. & Cui, X. Valley polarization in MoS_2 monolayers by optical pumping. *Nat. Nanotechnol.* **7**, 490–493 (2012).
8. Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A. & Kis, A. Ultrasensitive photodetectors based on monolayer MoS_2. *Nat. Nanotechnol.* **8**, 497–501 (2013).
9. Cheng, R. et al. Electroluminescence and photocurrent generation from atomically sharp WSe_2/MoS_2 heterojunction p–n diodes. *Nano Lett.* **14**, 5590–5597 (2014).
10. Duan, X. et al. Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions. *Nat. Nanotechnol.* **9**, 1024–1030 (2014).
11. Wu, S. et al. Monolayer semiconductor nanocavity lasers with ultra-low thresholds. *Nature* **520**, 69–72 (2015).
12. Duan, X. et al. Synthesis of $WS_{2x}Se_{2-2x}$ alloy nanosheets with composition-tunable electronic properties. *Nano Lett.* **16**, 264–269 (2016).
13. Fan, X. et al. Broken symmetry induced strong nonlinear optical effects in spiral WS_2 nanosheets. *ACS Nano* **11**, 4892–4898 (2017).
14. Li, H. et al. Composition-modulated two-dimensional semiconductor lateral heterostructures via layer-selected atomic substitution. *ACS Nano* **11**, 961–967 (2017).
15. Kang, J., Tongay, S., Zhou, J., Li, J. & Wu, J. Band offsets and heterostructures of two-dimensional semiconductors. *Appl. Phys. Lett.* **102**, 012111 (2013).
16. Chiu, M. H. et al. Determination of band alignment in the single-layer MoS_2/WSe_2 heterojunction. *Nat. Commun.* **6**, 7666 (2015).
17. Yan, R. et al. Esaki diodes in van der Waals heterojunctions with broken-gap energy band alignment. *Nano Lett.* **15**, 5791–5798 (2015).
18. Chiu, M. H. et al. Band alignment of 2D transition metal dichalcogenide heterojunctions. *Adv. Funct. Mater.* **27**, 1603756 (2017).
19. Nourbakhsh, A., Zubair, A., Dresselhaus, M. S. & Palacios, T. Transport properties of a MoS_2/WSe_2 heterojunction transistor and its potential for application. *Nano Lett.* **16**, 1359–1366 (2016).
20. Shim, J. et al. Phosphorene/rhenium disulfide heterojunction-based negative differential resistance device for multi-valued logic. *Nat. Commun.* **7**, 13413 (2016).
21. Zhang, K. et al. Interlayer transition and infrared photodetection in atomically thin type-II $MoTe_2/MoS_2$ van der Waals heterostructures. *ACS Nano* **10**, 3852–3858 (2016).
22. Xiao, D., Liu, G. B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS2 and other group-VI dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).
23. Lee, B. et al. Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS_2 integrated with plasmonic nanoantenna array. *Nano Lett.* **15**, 3646–3653 (2015).
24. Roy, T. et al. Dual-gated MoS_2/WSe_2 van der Waals tunnel diodes and transistors. *ACS Nano* **9**, 2071–2079 (2015).
25. Yu, W. J. et al. Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials. *Nat. Nanotechnol.* **8**, 952–958 (2013).
26. Massicotte, M. et al. Picosecond photoresponse in van der Waals heterostructures. *Nat. Nanotechnol.* **11**, 42–46 (2016).
27. Zhang, C. et al. Interlayer couplings, Moiré patterns, and 2D electronic superlattices in MoS_2/WSe_2 hetero-bilayers. *Sci. Adv.* **3**, e1601459 (2017).
28. Wang, X., Cheng, Z., Xu, K., Tsang, H. K. & Xu, J.-B. High-responsivity graphene/silicon-heterostructure waveguide photodetectors. *Nat. Photon.* **7**, 888–891 (2013).
29. Zhang, E. et al. Tunable positive to negative magnetoresistance in atomically thin WTe_2. *Nano Lett.* **17**, 878–885 (2017).
30. Wu, B. et al. Precise, self-limited epitaxy of ultrathin organic semiconductors and heterojunctions tailored by van der Waals interactions. *Nano Lett.* **16**, 3754–3759 (2016).
31. Roy, K. et al. Graphene-MoS_2 hybrid structures for multifunctional photoresponsive memory devices. *Nat. Nanotechnol.* **8**, 826–830 (2013).
32. Yu, W. J. et al. Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters. *Nat. Mater.* **12**, 246–252 (2013).
33. Ross, J. S. et al. Interlayer exciton optoelectronics in a 2D heterostructure p–n junction. *Nano Lett.* **17**, 638–643 (2017).
34. Wang, Y. et al. Light induced double 'on' state anti-ambipolar behavior and self-driven photoswitching in p-WSe_2/n-SnS_2 heterostructures. *2D Mater.* **4**, 025097 (2017).
35. Zhang, X. et al. Vertical heterostructures of layered metal chalcogenides by van der Waals epitaxy. *Nano Lett.* **14**, 3047–3054 (2014).
36. Gong, Y. et al. Vertical and in-plane heterostructures from WS_2/MoS_2 monolayers. *Nat. Mater.* **13**, 1135–1142 (2014).
37. Gong, Y. et al. Two-step growth of two-dimensional $WSe_2/MoSe_2$ heterostructures. *Nano Lett.* **15**, 6135–6141 (2015).
38. Lin, Y. C. et al. Atomically thin resonant tunnel diodes built from synthetic van der Waals heterostructures. *Nat. Commun.* **6**, 7311 (2015).
39. He, Y. et al. Strain-induced electronic structure changes in stacked van der Waals heterostructures. *Nano Lett.* **16**, 3314–3320 (2016).
40. Li, B. et al. Direct vapor phase growth and optoelectronic application of large band offset SnS_2/MoS_2 vertical bilayer heterostructures with high lattice mismatch. *Adv. Elec. Mater.* **2**, 1600298 (2016).
41. Li, X. et al. Two-dimensional $GaSe/MoSe_2$ misfit bilayer heterojunctions by van der Waals epitaxy. *Sci. Adv.* **2**, e1501882 (2016).
42. Zhou, X. et al. Vertical heterostructures based on $SnSe_2/MoS_2$ for high performance photodetectors. *2D Mater.* **4**, 025048 (2017).
43. Huang, J. et al. Large-area synthesis of highly crystalline WSe_2 monolayers and device applications. *ACS Nano* **8**, 923–930 (2014).
44. Zhou, X., Zhang, Q., Gan, L., Li, H. & Zhai, T. Large-size growth of ultrathin SnS_2 nanosheets and high performance for phototransistors. *Adv. Funct. Mater.* **26**, 4405–4413 (2016).
45. Wang, Y., Huang, L. & Wei, Z. Photoresponsive field-effect transistors based on multilayer SnS_2 nanosheets. *J. Semicond.* **38**, 034001 (2017).
46. Tongay, S. et al. Tuning interlayer coupling in large-area heterostructures with CVD-grown MoS_2 and WS_2 monolayers. *Nano Lett.* **14**, 3185–3190 (2014).
47. Shi, J. et al. Temperature-mediated selective growth of MoS_2/WS_2 and WS_2/MoS_2 vertical stacks on Au foils for direct photocatalytic applications. *Adv. Mater.* **28**, 10664–10672 (2016).
48. Yu, Y. et al. Equally efficient interlayer exciton relaxation and improved absorption in epitaxial and nonepitaxial MoS_2/WS_2 heterostructures. *Nano Lett.* **15**, 486–491 (2015).
49. Fu, L. et al. Direct growth of MoS_2/h-BN heterostructures via a sulfide-resistant alloy. *ACS Nano* **10**, 2063–2070 (2016).
50. You, Y. et al. Observation of biexcitons in monolayer WSe_2. *Nat. Phys.* **11**, 477–481 (2015).
51. Tonndorf, P. et al. Photoluminescence emission and Raman response of monolayer MoS_2, $MoSe_2$, and WSe_2. *Opt. Express.* **21**, 4908–4916 (2013).
52. Gonzalez, J. M. & Oleynik, I. I. Layer-dependent properties of SnS_2 and $SnSe_2$ two-dimensional materials. *Phys. Rev. B.* **94**, 125443 (2016).
53. Hong, X. et al. Ultrafast charge transfer in atomically thin MoS_2/WS_2 heterostructures. *Nat. Nanotechnol.* **9**, 682–686 (2014).
54. Furchi, M. M., Pospischil, A., Libisch, F., Burgdorfer, J. & Mueller, T. Photovoltaic effect in an electrically tunable van der Waals heterojunction. *Nano Lett.* **14**, 4785–4791 (2014).
55. Burton, L. A. et al. Electronic and optical properties of single crystal SnS_2: an earth-abundant disulfide photocatalyst. *J. Mater. Chem. A.* **4**, 1312–1318 (2016).
56. Liu, J., Xia, C., Li, H. & Pan, A. High on/off ratio photosensitive field effect transistors based on few layer SnS_2. *Nanotechnology* **27**, 34LT01 (2016).
57. Zhou, H. et al. Large area growth and electrical properties of p-type WSe_2 atomic layers. *Nano Lett.* **15**, 709–713 (2015).
58. Lee, Y. H. et al. Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces. *Nano Lett.* **13**, 1852–1857 (2013).
59. Zhang, Y. et al. Controlled growth of high-quality monolayer WS_2 layers on sapphire and imaging its grain boundary. *ACS Nano* **7**, 8963–8971 (2013).
60. Zhang, W., Wang, Q., Chen, Y., Wang, Z. & Wee, A. T. S. Van der Waals stacked 2D layered materials for optoelectronics. *2D Mater.* **3**, 022001 (2016).
61. Cui, X. et al. Multi-terminal transport measurements of MoS_2 using a van der Waals heterostructure device platform. *Nat. Nanotechnol.* **10**, 534–540 (2015).
62. Fang, H. et al. Visible light-assisted high-performance mid-infrared photodetectors based on single InAs nanowire. *Nano Lett.* **16**, 6416–6424 (2016).
63. Wang, P. et al. Arrayed van der Waals broadband detectors for dual-band detection. *Adv. Mater.* **29**, 1604439 (2017).
64. Xue, Y. et al. Scalable production of a few-layer MoS_2/WS_2 vertical heterojunction array and its application for photodetectors. *ACS Nano* **10**, 573–580 (2016).
65. Huo, N. et al. Tunable polarity behavior and self-driven photoswitching in p-WSe_2/n-WS_2 heterojunctions. *Small* **11**, 5430–5438 (2015).

66. Pezeshki, A., Shokouh, S. H., Nazari, T., Oh, K. & Im, S. Electric and photovoltaic behavior of a few-layer alpha-MoTe$_2$/MoS$_2$ dichalcogenide heterojunction. *Adv. Mater.* **28**, 3216–3222 (2016).

67. Yang, S. et al. Self-driven photodetector and ambipolar transistor in atomically thin GaTe-MoS$_2$ p–n vdW heterostructure. *ACS Appl. Mater. Inter.* **8**, 2533–2539 (2016).

68. Chen, J. et al. Chemical vapor deposition of large-sized hexagonal WSe$_2$ crystals on dielectric substrates. *Adv. Mater.* **27**, 6722–6727 (2015).

69. Zhang, W. et al. Role of metal contacts in high-performance phototransistors based on WSe$_2$ monolayers. *ACS Nano* **8**, 8653–8661 (2014).

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Author contributions

A.P., T.Y., and B.Z. conceived and designed the experiments. B.Z. synthesized the heterostructures. Y.F. and J.Z. performed the band structure calculation. T.Y., B.Z. carried out AFM and photoluminescence measurements. B.Z., T.Y., T.X., and L.S. carried out TEM measurements. T.Y., Z.W., and C.P. carried out the device fabrication and measurements. A.P., T.Y., and B.Z. wrote the paper with significant inputs from X.Z., Z.Q., H.L., W.H., F.M., and X.D. And A.P. supervised the research. All the authors participated in the analysis of the data and discussed the results. All the authors have read and approved the manuscript.

Additional information

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