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Epitaxial Synthesis of Monolayer PtSe₂ Single Crystal on MoSe₂ with Strong Interlayer Coupling

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Supporting Information

ABSTRACT: PtSe₂, a layered two-dimensional transition-metal dichalcogenide (TMD), has drawn intensive attention owing to its layer-dependent band structure, high air stability, and spin-layer locking effect which can be used in various applications for next-generation optoelectronic and electronic devices or catalysis applications. However, synthesis of PtSe₂ is highly challenging due to the low chemical reactivity of Pt sources. Here, we report the chemical vapor deposition of monolayer PtSe₂ single crystals on MoSe₂. The periodic Moiré patterns from the vertically stacked heterostructure (PtSe₂/MoSe₂) are clearly identified *via* annular dark-field scanning transmission electron microscopy. First-principles calculations show a type II band alignment and reveal interface states originating from the strong–weak interlayer coupling (SWIC) between PtSe₂ and MoSe₂ monolayers, which is supported by the electrostatic force microscopy imaging. Ultrafast hole transfer between PtSe₂ and MoSe₂ monolayers is observed in the PtSe₂/MoSe₂ heterostructure, matching well with the theoretical results. Our study will shed light on the synthesis of Pt-based TMD heterostructures and boost the realization of SWIC-based optoelectronic devices.

KEYWORDS: PtSe₂, PtSe₂/MoSe₂ heterostructure, two-dimensional material, chemical vapor deposition, interlayer coupling

Platinum diselenide (PtSe₂) is an intriguing layered material due to its helical spin texture induced by local Rashba effect¹ and strong interlayer coupling.^{2,3} Recent work also revealed that the strong interlayer coupling can

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Figure 1. Reaction system and spectroscopy characterizations of PtSe₂/MoSe₂ vertical heterostructures. (a) Reaction system used to synthesize PtSe₂ and PtSe₂/MoSe₂ vertical heterostructure and the atomic crystal structure of PtSe₂/MoSe₂. (b) Growth mechanism of PtSe₂/MoSe₂ heterostructure. (c and d) Optical images of as-synthesized PtSe₂/MoSe₂ heterostructure with different styles. From the optical images, the size of the overlapped vertical heterostructure is about 40 μm , and the area of the vertical heterostructure is larger than 1000 μm^2 . (e) The Raman spectra in the positions 1 and 2 of the heterostructure (inset shows the optical image of the vertical heterostructure). The A_{1g} mode located at 240 cm^{-1} confirms that the crystal is MoSe₂. The Raman peaks located at 175 and 205 cm^{-1} originate from the E_g mode of PtSe₂. The Raman peaks located at 240 cm^{-1} can be contributed to the A_{1g} vibration mode of MoSe₂. These indicate that the as-synthesized PtSe₂ and MoSe₂ form the vertical heterostructure. Notably, the A_{1g} mode of MoSe₂ from the PtSe₂/MoSe₂ heterostructure shows a little shift due to the coupling between PtSe₂ and MoSe₂.

induce a PtSe₂ transition from a semimetal (bulk) to a semiconductor (monolayer) with a band gap increasing from 0 to 1.2 eV.^{4,5} The narrow bandgap of few layer PtSe₂ renders it an excellent candidate for broadband mid-infrared detectors.^{3,6,7} Furthermore, field-effect transistors (FETs) based on few-layer PtSe₂ display high mobility and good stability in air.⁵ All these fascinating results indicate that PtSe₂ can be an attractive candidate for various applications in electronic and optoelectronic devices.⁸ Therefore, controlled synthesis of high-quality and atomically thin PtSe₂ layers is urgently required. So far, the mechanical exfoliation has been widely adopted to produce PtSe₂ monolayers. However, this method is low yield and time-consuming and usually leads to small size PtSe₂ flakes. Although few-layered PtSe₂ can be synthesized by selenization of Pt films or molecular beam epitaxy (MBE),^{9–12} synthesis of large size monolayer PtSe₂ single crystals is yet to be achieved, due to the low chemical reactivity of Pt.^{1,2,12,13} Here, we demonstrate the synthesis of monolayer PtSe₂ using the chemical vapor deposition (CVD) method. Various substrates including SiO₂/Si, Al₂O₃, and MoSe₂ have been

used for the growth of PtSe₂. It is found that PtSe₂ monolayers can only be epitaxially grown on MoSe₂ substrate, forming a PtSe₂/MoSe₂ vertical heterostructure. Such structure is confirmed by the Moiré fringe from annular dark-field scanning transmission electron microscopy (ADF-STEM). First-principles calculations show that the formed heterostructure has a direct band gap and forms a type II band alignment. A more striking result lies in the emergence of interface states located within the original bandgap. These states are hybridized by the wave functions of Se-p_z and Pt/Mo-d_z² orbitals from the PtSe₂ monolayer and MoSe₂ monolayer whose intrinsic interlayer couplings are strong and weak, respectively, in their own multilayers. The edge states of PtSe₂ on MoSe₂ observed with electrostatic force microscopy (EFM) compellingly support the existence of the theoretically predicted interface states. The charge transfer from PtSe₂ to MoSe₂ probed by ultrafast electron dynamics further demonstrates the interlayer coupling and band alignment in the PtSe₂/MoSe₂ heterostructure. Our work is helpful toward the synthesis of a PtSe₂ monolayer and

Figure 2. Atomic structure of the vertically stacked PtSe₂/MoSe₂ heterostructure and lateral boundary. (a) Experimental atomic-resolution ADF-STEM image of PtSe₂/MoSe₂, showing the periodic Moiré pattern where the monolayer PtSe₂ stacks on top of monolayer MoSe₂. Inset shows the FFT pattern obtained from (a), where the lattice constants of 0.376 and 0.332 nm correspond to the lattice of PtSe₂ and MoSe₂, as highlighted by the yellow and green circles, respectively. (b and c) Inverse FFT image of (a) by selectively filtering out the PtSe₂ (b) and MoSe₂ (c) lattice information in the FFT pattern, respectively. The 1T phase of PtSe₂ and 1H phase of MoSe₂ are confirmed by their discrete contrast which are consistent with the overlaid atomic models. (d) Low-magnification STEM image of the lateral boundary in a bilayer region. The left part is the PtSe₂/MoSe₂ heterostructure, while the right part is bilayer MoSe₂. (e and f) Atomic-resolution images of the highlighted regions in (d), showing the initial stage (e) and the overlapping region (f) of the lateral boundary. The initial stage shows a sharp change from PtSe₂ to MoSe₂ lattice with some tiny regions of bright contrast along the edge, indicating both PtSe₂ and MoSe₂ lattices have a sharp edge termination without any chemical bonding. The PtSe₂ and MoSe₂ gradually overlapped with each other along the boundary. (g and h) The top (g) and side (h) views of the schematic atomic models of the overlapping lateral boundary.

84 demonstrates its potential in electronic and optoelectronic
85 devices.

86 RESULTS AND DISCUSSION

87 Herein, the epitaxial growth of PtSe₂ on MoSe₂ was achieved
88 by using PtCl₂ and MoO₃/NaCl mixed powders as sources.¹⁴
89 More information about the growth is provided in the
90 Methods section. Figure 1a illustrates the reaction system for
91 the growth of PtSe₂ crystals. Figure 1b shows the proposed
92 growing mechanism. Monolayer PtSe₂ single crystals were
93 obtained on a MoSe₂ substrate with a one-step CVD method,
94 as shown in Figure 1c,d. Generally, most of the as-grown
95 samples were vertically stacked PtSe₂/MoSe₂. We believe that
96 the large lattice mismatch between PtSe₂ and MoSe₂ (1T for
97 PtSe₂ and 1H for MoSe₂) hinders the epitaxial growth of PtSe₂
98 and MoSe₂ in-plane heterostructure. Figure 1c shows the
99 hexagonal PtSe₂ monolayers atop the MoSe₂ monolayer with a
100 lateral size of ~30 μm. Such size is much larger than the
101 previously reported value.¹³ Atomic force microscopy (AFM)
102 was conducted to determine the height of the as-prepared
103 PtSe₂/MoSe₂ heterostructure. The thickness of PtSe₂ is ~0.8
104 nm, confirming its monolayer nature (Figure S1). More optical
105 images along with the size distribution of PtSe₂ flakes are
106 provided in Figure S2. The second layer MoSe₂ which coexists

with monolayer PtSe₂ can also be found in some synthesized
samples. The area of the PtSe₂/MoSe₂ heterostructure (Figure
1c) can be up to ~1000 μm². The size comparison is shown in
Figure S3.^{15–22} Meanwhile, we also observed that PtSe₂
monolayers can grow not only epitaxially on top of MoSe₂
but also partially overlap with MoSe₂ due to the different
growing rates of PtSe₂ and MoSe₂, as shown in Figure 1d. This
should be attributed to the nucleation formation of PtSe₂ on
the edge of MoSe₂, which then grows outward (down the
step). The Raman spectrum and thickness of PtSe₂ with a
similar morphology is shown in Figure S4.

In order to demonstrate the role of MoSe₂, time-dependent
experiments were carried out. For a short growing time (3
min), only MoSe₂ can be observed. By increasing the growing
time to 10 min, the PtSe₂/MoSe₂ heterostructure can be
obtained (see Figure S5). We also used different substrates
including exfoliated MoSe₂ flakes, SiO₂/Si, and sapphire wafers
to synthesize PtSe₂ crystals. Only PtSe₂ thick flakes and
particles can be obtained on exfoliated MoSe₂ flakes (Figure
S6). For SiO₂/Si and sapphire substrates, at the growing
temperature of ~400 °C, only polycrystalline PtSe₂ films can
be obtained (Figure S7). Increasing the growing temperature
to ~810 °C will result in few-layer PtSe₂ single crystal (Figures
S8 and S9). These results are consistent with previous reports

Figure 3. Geometry information on PtSe₂(1T)/MoSe₂(1H) vertical heterostructures. (a and b) Top and side views of the geometry structure of PtSe₂(1T)/MoSe₂(1H) vertical heterostructures. The violet, green, and red rectangles denote three high-symmetry stacking local configurations which have been zoomed in in (c) Se_{inter}(PtSe₂)–Se_{inter}(MoSe₂) stacking, (d) Pt–Se_{inter}(MoSe₂) stacking, and (e) Se_{inter}(PtSe₂)–Mo stacking, respectively. And parameter *d* marked in (b) refers to the interlayer distance between PtSe₂(1T) and MoSe₂(1H).

on the growth of PtSe₂ flakes on MoSe₂.^{9,13} Based on these results, it can be concluded that the CVD-grown MoSe₂ monolayer is a good candidate for the epitaxial growth of PtSe₂ monolayer.

The successful growth of PtSe₂ monolayer on MoSe₂ can be attributed to the following two reasons: (1) The chemical reactivity between Mo precursors and Se is higher than that between Pt precursor and Se and the vapor pressure of Mo precursors is relatively higher than that of Pt precursor.¹⁴ As a result, the growing rate of MoSe₂ is faster than that of PtSe₂, which makes MoSe₂ grow first. (2) The lattice mismatch between PtSe₂ and MoSe₂ is smaller than that between PtSe₂ and SiO₂/Si (or Al₂O₃). Therefore, MoSe₂ is a favorable substrate for the epitaxial growth of PtSe₂ monolayer (comparison is provided in Table S1). We also noticed that, at a relatively high growing temperature (~810 °C), MoSe₂ flakes could be etched by H₂, which will result in MoSe₂ flakes with different geometries.

Raman spectroscopy was carried out to investigate the structure and quality of formed PtSe₂/MoSe₂ heterostructures. Figure 1e shows the Raman spectra collected from points 1 and 2 of the sample shown in Figure 1c. The sole peak located at 240 cm⁻¹ from point 1 (blue curve) corresponds to the A_{1g} mode of MoSe₂.²³ Raman peaks sitting at 175, 205, and 240 cm⁻¹ were collected from point 2 (red curve), corresponding to the E_g and A_{1g} modes of PtSe₂²⁴ and the A_{1g} mode of MoSe₂, respectively. Notably, the A_{1g} mode of MoSe₂ in the PtSe₂/MoSe₂ heterostructure shows a red shift due to the interlayer coupling between PtSe₂ and MoSe₂, which is consistent with the experimental observations reported result¹¹ and theoretical results.²⁵ Interestingly, from point 2, a Raman peak located at ~350 cm⁻¹ can be found, which could be attributed to the interlayer coupling between PtSe₂ and MoSe₂.²⁶ These results confirm the vertically stacked PtSe₂/MoSe₂ heterojunction. Next, we employed X-ray photoelectron spectroscopy (XPS) to examine the composition of the PtSe₂/MoSe₂ heterostructures. Based on XPS data (Figure S10), the atomic ratio between Se and Pt/Mo is estimated to

be ~1.97, which is very close to the stoichiometry of MoSe₂ and PtSe₂. More information about the PL spectra and PL and Raman mappings of PtSe₂/MoSe₂ heterostructures is presented in Figure S11. Note that the weak PL intensity of PtSe₂/MoSe₂ heterostructures probably results from the charge transfer between PtSe₂ and MoSe₂.

ADF-STEM was used to investigate the atomic structure of PtSe₂/MoSe₂ heterostructures. Figure 2a shows the atomic-resolution ADF-STEM image of PtSe₂/MoSe₂. The periodic Moiré patterns can be clearly observed along the basal plane of the heterostructure, which is caused by the interference from the lattice of monolayer PtSe₂ and MoSe₂. The fast Fourier transformation (FFT) of the PtSe₂/MoSe₂ is shown in the inset of Figure 2a. Two different sets of diffraction patterns close to each other were identified. The lattice constants of ~0.38 nm and ~0.33 nm correspond to PtSe₂ and MoSe₂ respective lattices, indicating the as-synthesized PtSe₂ and MoSe₂ are single crystals. This is further confirmed by the selected area electron diffraction pattern collected on a much larger region of PtSe₂/MoSe₂ (over ~5 μm in size), as shown in Figure S12, which only displays one set of diffraction pattern of PtSe₂ and MoSe₂, respectively. Moreover, the two monolayer lattices are well aligned with each other, which is a strong evidence of the vertically epitaxial growth. The FFT (inset in Figure 2a) does not show the superlattice periodicity, which is expected near the central bright spot, presumably due to its weak signal. However, the periodicity of the Moiré pattern can be directly measured in the atomically resolved image by filtering out the lattice of PtSe₂ and MoSe₂ (see Figure S13 for more details), which is estimated to be ~2.60 nm. Such a large supercell indicates the highly epitaxial feature as a result of the coupling growth between the two materials. Figure 2b,c shows the inverse FFT images of Figure 2a, which distinguishes the atomic structures of the 1T and 1H phases in PtSe₂ and MoSe₂, respectively.

Figure 2d shows a low magnification ADF-STEM image of the lateral boundary in the PtSe₂/MoSe₂ heterostructure. The optical image of a similar structure is shown in Figure S14. The

Figure 4. Band alignment and Spatial structures of wave functions for PtSe₂(1T)/MoSe₂(1H) vertical heterostructures. (a) The band structure of PtSe₂(1T)/MoSe₂(1H) vertical heterostructure as well as projected contributions of the marked systems. (b and c) Band structures and projected contributions of the marked atoms of deformed monolayer MoSe₂ and PtSe₂ whose geometry structures are extracted from the relaxed heterostructure. (d) Band alignment of original monolayer MoSe₂ and PtSe₂ and relaxed PtSe₂(1T)/MoSe₂(1H) vertical heterostructure. All energies here take the vacuum level as a reference. (e–g) Top and side views of the spatial distribution of modular squared wave functions for the marked bands 1, 4, and 7 in (a), separately. The violet, green, and red rectangles correspond to those in Figure 3. Side views display clearly each type of atom contribution to a certain band.

underneath MoSe₂ layer is continuous, thus such structure can be considered as a grain boundary between PtSe₂ and MoSe₂ monolayers on the MoSe₂ substrate. Figure 2e,f shows atomically resolved images of two different regions along the lateral boundaries. In fact, because of the lattice mismatch between MoSe₂ and PtSe₂, the formation energy of an atomic sharp interface should be very high. Figure 2e shows the initial stage of the lateral boundary, displaying a sharp change from PtSe₂ to MoSe₂ lattice with some tiny regions of bright contrast along the edge. This indicates that both PtSe₂ and MoSe₂ lattices have a sharp edge termination without any chemical bonding. Figure 2f shows another region of the lateral boundary away from Figure 2e, where the transition region between the PtSe₂/MoSe₂ Moiré pattern and bilayer MoSe₂ shows an enhanced contrast. This is due to the overlap of the edge regions from the two monolayers, that is, the PtSe₂ layer has rolled on top of the bilayer MoSe₂ edge, forming a thicker layer which exhibits brighter contrast, as illustrated by the corresponding atomic model (Figure 2g,h). The overlapping region varies and becomes wider (Figure 2d) along the boundary, confirming the overlapping feature in the lateral boundary. This is consistent with our expectation that the PtSe₂ is more likely to climb over the MoSe₂ edge (second layer MoSe₂) during the growth to form a vertically overlapping boundary since the formation energy of an interconnected in-plane boundary is very high, due to their lattice mismatch.

It is known that the interlayer interaction offers great opportunity to study different properties in van der Waals (vdW) solids, for instance, the electronic structure from the Moiré pattern in a vdW heterostructure.^{27–29} Substantial research efforts have been devoted to weak interlayer coupled TMDs and their heterostructures, for example, MoSe₂ and WSe₂.²⁷ Strong interlayer coupled two-dimensional (2D) materials have recently been visited,^{2,5,30,31} and PtSe₂ is a representative among them. An interesting question then arises regarding the interlayer coupling of a heterostructure whose components provide strong and weak interlayer couplings, respectively. The PtSe₂/MoSe₂ heterostructure synthesized in this work offers an ideal platform for studying this special interlayer interaction. The fully relaxed atomic structure of the PtSe₂(1T)/MoSe₂(1H) vertical heterostructure is shown in Figure 3. According to the STEM measured Moiré periodicity (Figure 2), a 7 × 7 supercell of the PtSe₂ monolayer stacking over an 8 × 8 supercell the MoSe₂ monolayer is adopted for modeling the heterostructure. The optimized lattice constant of the supercell is 2.64 nm, only 1.4% larger than the experimental value of 2.60 nm. It is exceptional that MoSe₂ appears rumpling in the relaxed heterojunction, suggesting significant interlayer attraction (0.25 eV/PtSe₂) between the two layers and stronger bending strength of PtSe₂ than that of MoSe₂. The interlayer distance *d* varies from 3.15 to 3.64 Å, whose lower limit is much larger than that of PtSe₂ bilayers of 2.55 Å⁵ but slightly smaller than that of MoSe₂ bilayers of 3.20 Å,³² implying the interlayer interaction might be stronger than

that in MoSe₂. The mismatched lattices of 1L PtSe₂ (3.71 Å for theory and 3.76 Å for experiment) and 1L MoSe₂ (3.30 Å for theory and 3.32 Å for experiment) lead to continuously varied stacking orders. There are seven local stacking orders along the supercell lattice. Among them, we found three high-symmetry ones, namely Se_{inter}-PtSe₂ on top of Se_{inter}-MoSe₂ (Figure 3c, denoted by the violet rectangle), Pt on top of Se_{inter}-MoSe₂ (Figure 3d, denoted by the green rectangle), and Se_{inter}-PtSe₂ on top of Mo (Figure 3e, denoted by the red rectangle). The vertical distances of these three stacking orders are 3.64, 3.17, and 3.15 Å, respectively (Figure S15a). Correspondingly, the spatial modulations of local bandgap and valence band maximum (VBM) of this vertical heterostructure are shown in Figures S15b, S16, and S17, respectively, where the variations of bandgaps and VBMs share the same modulation pattern with that of vertical interlayer distances. The Moiré potential (VBM) for the above three high-symmetry stacking orders are -65, -5, and 0 meV, respectively.

Atom-decomposed band structures (Figure 4a) explicitly show seven emerging states (denoted bands 1–7) in addition to a type II band alignment of the heterojunctions. The valence and conduction bands are comprised of the VB of MoSe₂ (Mo-d orbital, Se-p orbital) and CB of PtSe₂ (Pt-d orbital, Se-p orbital), respectively (Figure 4b,c). Figure 4d illustrates the band alignment before and after forming the heterojunction. The junction has a direct bandgap of 0.94 eV (0.92 eV, w/SOC), reduced from a 1.51 eV (1.39 eV, w/SOC) direct bandgap of MoSe₂ and a 1.34 eV (1.19 eV, w/SOC) indirect bandgap of PtSe₂, which are in good accordance with their experimental values, that is, 1.55 eV for MoSe₂³³ and 1.13 eV for PtSe₂.⁵ These seven bands are not induced by the aforementioned substantial structural deformation of MoSe₂ or PtSe₂, as Figure 4b,c shows that the deformation does not change the shape of band structures. They are also not the case of quantum confined states²⁹ since both MoSe₂ and PtSe₂ contribute to them. Bands 1–7 are thus regarded as electronically hybridized interfacial states, which result from the frustrated strong-weak interlayer coupling between PtSe₂ and MoSe₂ layers. These hybridized interfacial states, emerging within the original bandgap of vdW heterojunctions, are of particular interest. Figure 4e–g plots the spatial distributions of the wave function norms of bands 1 (e), 4 (f) and 7 (g). They are located around the aforementioned three particular stacking positions as marked by red, green, and violet rectangles, respectively, indicating each interfacial state corresponds to one stacking configuration. The side views (Figure 4e–g) suggest that these interfacial states are comprised of p_z orbitals of the interfacial Se layer of MoSe₂ and both Se layers of PtSe₂ and d_{z²} orbital of Pt and Mo atoms, implying that the outer Se layer of MoSe₂ is not involved in forming these interfacial states. These wave functions are more localized than those of VB and CB (Figure S18) in real-space, consistent with the flat band dispersion in the *k*-space. These spatially localized bands suggest that electron–hole pairs of a given energy are excited at a certain stacking position, as marked in Figure 3a. The PtSe₂ involved in forming these bands may lead to inter- and intralayer mixed excitation mechanisms for the interlayer excitons, which should be interesting for further exploration. In the light of these, interfacial states are of particular interest in terms of exciton dynamics in the heterojunction.

As discussed above, STEM images and first-principles calculations have demonstrated the vertical stacking and emerging interfacial states in PtSe₂/MoSe₂ heterostructure due to the frustrated strong–weak interlayer coupling between PtSe₂ and MoSe₂ layers. In order to further elucidate the interfacial states and the interlayer coupling, we conducted the electrostatic force microscopy (EFM) to study the charge distribution in PtSe₂/MoSe₂ heterostructures. EFM has been proven as an effective method to evaluate the local electrical properties of 2D materials.^{34,35} The optical image and topography of PtSe₂/MoSe₂ heterostructure are shown in Figure 5a,c, respectively. The corresponding AFM image is

Figure 5. EFM measurements. (a and c) Optical image and height topography of PtSe₂/MoSe₂ heterostructure grown by one-step CVD. (b and d) Optical image and topography of transferred PtSe₂/MoSe₂ heterostructure. (e) EFM image of PtSe₂/MoSe₂, identifying the edge state at the edge of PtSe₂. (f) EFM image of transferred PtSe₂/MoSe₂ under zero bias voltage, indicating a semiconducting behavior of PtSe₂ and MoSe₂.

presented in Figure S19. The EFM image of the heterostructure shown in Figure 5e indicates that strong charge accumulation takes place on the edge of PtSe₂, which is attributed to the charge transfer from uncovered monolayer MoSe₂ to PtSe₂/MoSe₂ heterostructure induced by the slightly lowered VB of PtSe₂ and lifted CB of MoSe₂. For comparison, EFM measurement was carried out on a transferred PtSe₂/MoSe₂ heterostructure. The optical image, topography, and EFM image are shown in Figure 5b,d,f, respectively. The absence of edge states clearly illustrates that the strong interlayer coupling is not formed in the transferred heterostructure. These results demonstrate the strong interlayer coupling between strong interlayer-coupled PtSe₂ and weak interlayer-coupled MoSe₂, which agrees well with the results of electronically hybridized interface states from first-principles calculations.

The type II band alignment offers the possibility to study the charge transfer induced by the interlayer coupling in PtSe₂/

MoSe₂ heterostructure. We further studied the charge transfer kinetics of PtSe₂/MoSe₂ heterostructure through ultrafast transient dynamics measurement. The ultrafast transient reflection dynamics of the heterostructure along with the PtSe₂ and MoSe₂ monolayers (optical images are shown as insets in Figure 6a,b) were measured using 910 nm pump

Figure 6. Ultrafast electron dynamics of MoSe₂, PtSe₂, and PtSe₂/MoSe₂ heterostructure. (a) Differential reflection kinetics of PtSe₂/MoSe₂ heterostructure (red), PtSe₂ (blue), and MoSe₂ (pink) monolayers excited at 910 nm and probed at 780 nm with the pump and probe power around 100 and 70 μ W, respectively. Inset is the optical image of PtSe₂/MoSe₂ heterostructure. The kinetics at shorter time scale is shown in (c). (b) Comparison of the normalized differential reflection kinetics of the heterostructure and monolayers. Inset is the optical image of PtSe₂. The corresponding kinetics at shorter time scale of PtSe₂ is displayed in (d).

excitation and 780 nm probe with pump and probe powers of 100 and 70 μ W, respectively. According to the reported experimental band gaps of monolayer MoSe₂ (1.55 eV)³³ and PtSe₂ (1.13 eV)⁵ as well as our band calculation results, the 910 nm pump excitation will only excite carriers in PtSe₂, since the photon energy is below the bandgap of MoSe₂. Thus, direct one-photon absorption of 910 nm wavelength will not occur in MoSe₂ layers. As shown in Figure 6, the transient response from the heterostructure is very different from that of monolayers under the same pump–probe power. First, the transient response amplitude of the heterostructure is ~ 3 times higher than that of individual monolayers (Figure 6a). Second, the initial rising time of the transient response is slightly slower in heterostructure than that in individual monolayers. Third, the subsequent decay dynamics are relatively longer for heterostructure than either PtSe₂ or MoSe₂ monolayer alone. The latter two features can be clearly visualized from the normalized transient reflection kinetics shown in Figure 6b.

Compared with monolayer PtSe₂, the relatively slow rising kinetics of the PtSe₂/MoSe₂ heterostructure proves the hole transfer between PtSe₂ and MoSe₂. More specifically, the pump (910 nm) excites electrons from the VB to the CB of PtSe₂ through one photon absorption, along with a rapid hole transfer from PtSe₂ to MoSe₂ layer due to their type II band alignment. The rising time (τ_r) of the heterostructure kinetics, which describes the hole transfer between PtSe₂ and MoSe₂, is found to be 0.5–0.9 ps. This value is longer than that of PtSe₂

monolayers and consistent with the previous reports on the charge-transfer process in heterostructures.³⁶ As a result of the hole transfer from PtSe₂ to MoSe₂, the probe reflection is modified due to the hole occupation in MoSe₂ and contributes to transient reflection signal of the 780 nm probe. The magnitude of peak transient signal is also 5 times larger than that in individual PtSe₂ or MoSe₂ monolayers.

The following decay kinetics after the maximum transient reflection of the heterostructure and monolayers can be fitted with biexponential function $I(t) = A \times \exp(-t/\tau_{d1}) + B \times \exp(-t/\tau_{d2})$, where τ_{d1} and τ_{d2} represent the fast and slow decay time constants, respectively. The fast ($\tau_{d1} = 27.5 \pm 0.3$ ps) and slow ($\tau_{d2} = 280.1 \pm 12.3$ ps) decay time constants of the heterostructure are nearly 2–3 times larger than decay time constants of individual PtSe₂ ($\tau_{d1} = 14.9 \pm 1.8$ ps, $\tau_{d2} = 88.8 \pm 9$ ps) and MoSe₂ ($\tau_{d1} = 11.7 \pm 0.9$ ps, $\tau_{d2} = 97.9 \pm 9$ ps) monolayers. The decay time of PtSe₂/MoSe₂ heterostructure is much longer than that of PtSe₂ and MoSe₂ monolayers, which suggests an efficient separation of the electron–hole in PtSe₂/MoSe₂ heterostructures.

CONCLUSIONS

In summary, we have successfully synthesized PtSe₂/MoSe₂ vertically stacked heterojunctions *via* a one-step CVD method. STEM results confirm the formation of vertical and lateral heterostructures between strong interlayer-coupled PtSe₂ and weak interlayer-coupled MoSe₂. First-principle calculations confirm a direct band gap structure and type II band alignment between PtSe₂ and MoSe₂. The emerging electronically hybridized interface states within the original bandgap are the observed in CVD-grown 2D TMD heterostructures, which have been confirmed by the edge states unveiled by EFM. Ultrafast electron dynamics measurements suggest that the holes transfer from MoSe₂ to PtSe₂, confirming the theoretically predicted band alignment and strong interlayer coupling between PtSe₂ and MoSe₂. This strategy shows the way toward the synthesis of heterostructures based on group 10 TMDs, and our results show great potential of PtSe₂/MoSe₂ heterostructures for applications in electronic and optoelectronic devices.

METHODS

PtSe₂ and PtSe₂/MoSe₂ Growth. In our experiment, PtCl₂, MoO₃, and Se were used as sources (all reactants were bought from Alfa Aesar with purity more than 99%). The polycrystalline PtSe₂ film was grown in a quartz tube (1 in. diameter, 36 cm length) at 400 $^{\circ}$ C. Single PtSe₂ and PtSe₂/MoSe₂ flakes were synthesized using the same setup at 810 $^{\circ}$ C. The distance between PtCl₂ and mixed powder is ~ 5 mm. H₂/Ar was used as the carrier gas. Specifically, the alumina boat (8 cm $\times$ 1.1 cm $\times$ 1.2 cm) containing Mo and Pt precursors was put in the middle of the quartz tube. The distance between the precursors and substrate is around 1.2 cm. For PtSe₂, Ar (or Ar/H₂ mix) gas with a flow rate of 80 (80/10) sccm was used as the carrier gas, and the Al₂O₃ boat containing 10 mg PtCl₂ was put in the center of the tube. The SiO₂/Si substrate was placed on the boat with surface downside. Another Al₂O₃ boat containing 100 mg Se powder was put in the upstream zone. The temperature was ramped up to 810 $^{\circ}$ C in 16 min and kept at the reaction temperature for 15 min. Then the furnace was cooled down to room temperature naturally.

For PtSe₂/MoSe₂, the Ar/H₂ mixed gas with a flow rate of 80/10 sccm was used as the carrier gas, and the Al₂O₃ boat containing 5 mg PtCl₂ and 5 mg (4 mg MoO₃ and 1 mg NaCl) was put in the center of the tube. The distance between PtCl₂ and MoO₃/NaCl was 5 mm. SiO₂/Si or sapphire substrate was placed on the boat with surface downside. Another Al₂O₃ boat containing 10 g Se powder was put on

the upstream zone. The temperature was ramped up to 810 °C in 16 min and kept at the reaction temperature for 10 min. The furnace was then cooled down to room temperature gradually.

For PtSe₂/MoSe₂ heterostructure prepared by mechanic exfoliation and transfer, a 0.8 μm layer of poly(methyl methacrylate) (PMMA) was spin-coated on the MoSe₂ wafer and then baked at 180 °C for 4 min. Afterward, the wafer was immersed in KOH solution (1M) to etch the SiO₂ layer. After lift-off, the PMMA/PtSe₂/MoSe₂ film was transferred into DI water for several cycles to wash away the residual contaminants and then dried in air. Next, PMMA with MoSe₂ samples were transferred on PtSe₂ flakes. Last, the wafer was immersed in acetone solution to resolve the PMMA.

Raman Characterization. Raman measurements with an excitation laser of 532 nm were performed using WITEC alpha 300R Confocal Raman system. Before Raman characterization, the system was calibrated with the Raman peak of Si at 520 cm⁻¹. The laser powers were set at <1 mW to avoid overheat the samples.

AFM. AFM measurement was carried out using the Asylum Research, Cypher S system with a cantilever tip of Arrow-NCR-50-Silicon SPM-Sensor (coating on detector side: Al-coating). The force constant is 42 N/m.

XPS Characterization. XPS measurement was performed using a monochromated Al Kα source ($h\nu = 1486.6$ eV) and a 128 channel mode detection PHI original detector. XPS spectra were acquired at a pass energy of 140 eV and takeoff angle of 45°.

TEM and STEM Characterization. The STEM samples were prepared with a PMMA assisted method. A layer of PMMA about 0.8 μm in thickness was spin-coated on the wafer with samples deposited and then baked at 140 °C for 5 min. Afterward, the wafer was immersed in KOH solution (1 M) to etch the SiO₂ layer overnight. After lift-off, the PMMA/PtSe₂/MoSe₂ film was transferred into DI water for several cycles to wash away the residual contaminants and then fished by a TEM grid (Quantifoil Mo grid). The transferred specimen was dried naturally in ambient environment and then dropped into acetone overnight to wash away the PMMA coating layers. The STEM imaging was done in a JEOL 2100F with delta probe corrector, which corrects the aberration up to fifth order, resulting in a probe size of 1.2 Å. The imaging was conducted at an acceleration voltage of 60 kV. The convergent angle for illumination is about 35 mrad, with a collection detector angle ranging from 45 to 200 mrad. The BF-TEM and diffraction imaging was conducted in a FEI Tecnai F30 microscope operating at 80 kV. All imaging was performed at room temperature.

Ultrafast Transient Reflection Spectroscopy. An infrared optical parametric amplifier (OPA) pumped by a 60 fs, 250 kHz Ti:Sapphire regenerative amplifier (RegA) was used in the transient reflection measurements. The idler from OPA at 1840 nm used as pump is frequency doubled to 920 nm (~180 fs). The 780 nm component filtered from white light supercontinuum, which is generated from a sapphire crystal pumped with compressed remnant 800 nm beam of OPA, was used as a probe. Both pump and probe pulses were linearly polarized. A 40X reflective objective lens was used to focus the co-propagating pump probe spots onto the sample. The reflected probe was collected by the same objective lens and routed through a monochromator followed by a photodetector. The detected probe reflection was read by a lock-in amplifier referenced to a mechanically chopped pump. The probe spot size was estimated to be 2 μm. The pump photon fluency was estimated to be around 1×10^{16} photons/cm².

Calculations. Density functional theory (DFT) calculations were performed using the generalized gradient approximation for the exchange–correlation potential, the projector augmented wave method,^{37,38} and a plane-wave basis set as implemented in the Vienna *ab initio* simulation package (VASP).³⁹ For the configuration of PtSe₂(1T)/MoSe₂(1H) vertical heterostructure, a (7 × 7) supercell is adopted for PtSe₂(1T), while a (8 × 8) supercell for MoSe₂(1H) and a vacuum layer of 25 Å in thickness between periodic images was employed. The energy cutoff for the plane-wave basis was set to 500 eV for all calculations except those with spin–orbit coupling (SOC) into consideration where an energy cutoff of 300 eV is utilized. The

inclusion of SOC has little influence on the shape of the band structures but induces appreciable band energy shifts or band splitting, for example, a separation of 30–50 meV for the emerging hybridized interfacial states marked with bands 1–7 in Figure 4a. All calculations and analysis shown in Figure 4a–c were performed in the same supercell which consisted of a (7 × 7) supercell of PtSe₂(1T) and a (8 × 8) supercell of MoSe₂(1H). In optimizing the system geometry, vdW interactions were considered at the vdW-DF⁴⁰ level with the optB86b (optB86b-vdW) functional for exchange potential,⁴¹ which was recently demonstrated more accurate in describing structural properties of layered materials than other functionals.^{31,42,43} All atoms in the supercell were allowed to relax until the residual force per atom was <0.02 eV·Å⁻¹.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b09479.

Further experimental and theoretical details, including different size of vertical heterostructures, thickness and Raman spectrum of PtSe₂, optical images of PtSe₂/MoSe₂ heterostructure, growth of PtSe₂ on exfoliated MoSe₂ flakes, optical image and TEM characterization of polycrystalline PtSe₂, optical images, AFM images and Raman spectra of PtSe₂ single crystals, optical images and AFM images of PtSe₂ single crystals synthesized on sapphire substrate, XPS characterizations of PtSe₂/MoSe₂ heterostructure, PL spectra, PL and Raman mappings of PtSe₂/MoSe₂ with different shape, SEAD patterns of PtSe₂/MoSe₂ heterostructure, large-scale STEM image of vertically stacked PtSe₂/MoSe₂ heterostructure, optical image of in plane and vertical PtSe₂/MoSe₂ heterostructures, spatial distribution of interlayer distance and bandgap for PtSe₂(1T)/MoSe₂(1H) vertical heterostructure, spatial distribution of bandgap for PtSe₂(1T)/MoSe₂(1H) vertical heterostructure, spatial distribution of VBM for PtSe₂(1T)/MoSe₂(1H) vertical heterostructure, spatial structures of wave functions for PtSe₂(1T)/MoSe₂(1H) vertical heterostructures, AFM image and thickness of PtSe₂ on MoSe₂ (PDF)

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Notes

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