

Dimensional band engineering in asymmetrical van der Waals heterostructures

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SUMMARY

Van der Waals materials enable the construction of atomically sharp interfaces between compounds with distinct crystal and electronic properties. This is dramatically exploited in moiré systems, where a lattice mismatch or twist between monolayers generates an emergent in-plane periodicity, giving rise to electronic properties absent in the constituent materials. In contrast, vertical superlattices, formed by stacking dissimilar materials in the out-of-plane direction on the nanometer scale, have received far less attention despite their potential to realize analogous emergent phenomena in three dimensions. Through angle-resolved photoemission spectroscopy and density functional theory, we investigate six-to-eight-layer transition metal dichalcogenide (TMD) heterostructures constructed from pairs of stacked few-layer materials. Counterintuitively, we find that even these single superlattice units can host fully-delocalised bands, evidencing a robust coherent interlayer coupling across lattice-mismatched interfaces over extended spatial scales. We show how uncompensated semimetallic phases and energetically-mismatched topological surface states are readily and exclusively stabilized within such asym-

metrical architectures. These findings establish two-component heterostructures in the intermediate layer-regime as platforms to invoke and control unprecedented combinations and instances of the diverse quantum phases native to many-layer TMDs.

KEYWORDS

2D Materials, angle-resolved photoemission, ARPES, transition metal dichalcogenides, density functional theory, artificial heterostructures

INTRODUCTION

Transition metal dichalcogenides (TMDs) are popular components for functional devices due to the ease in which their vast array of intrinsic properties can be augmented^{1–6}. This is facilitated through anisotropic bonding, enabling both the isolation of TMD flakes of arbitrary thicknesses and their subsequent recombination into stacks with atomically sharp interfaces without the need for epitaxial registry^{7–11}. These procedures can both alter the electronic properties inherent to the component compounds, and induce otherwise-inaccessible correlated phenomena through the fine tuning of the laboratory-defined relative orientations, or ‘twist angle’^{12,13}. Despite van der Waals bonding, however, the interlayer hopping along the *c*-axis in TMDs is significant, driving orbital-dependent bandwidths of up to several electron volts in bulk systems^{14–17}. This is yet to be exploited in artificial heterostructures¹⁸, with current research largely rooted to homo- and heterobilayer systems, and thus to TMD properties in the 2D limit. This precludes, for example, the fine-tuning of band gaps through band quantisation^{19–21}, the induction of k_z -mediated topological phases²², or the modification of charge density wave and magnetic transitions dependent on interlayer coupling^{23–25}.

Here, through nano-focused angle-resolved photoemission (nano-ARPES) and first principles calculations, we show how vertical 6-8 layer heterostructures, constructed simply by interfacing pairs of few-layer TMD flakes, possess emergent bands sensitive to the entire spatial extent of the hybrid system. Despite the absence of well-defined periodicity along the asymmetric *c*-axis, the fully delocalised bands mimic discretized three-dimensional states of ordered systems, but coexist alongside layer-locked states to produce an overall-spatially dependent electronic structure capable of supporting electronic phenomena usually reserved for bulk compounds.

We give special focus to k_z -mediated topological phase transitions, triggered by the interfacing of the few-layer TMD flakes, which produce pairs of distinct topologically non-trivial surfaces that are each defined largely by a single component material, unlike any naturally existing topological system. Similar phenomena should be expected for asymmetric heterostructures constructed from any pair of TMDs, and thus our findings unveil an enormous parameter space within which customizable electronic frameworks, mixing 2- and 3D properties from across the TMD family, can be produced and fine-tuned.

RESULTS

Theoretical Framework

Figure 1 overviews the mechanism underpinning our findings. Fig.1(A) illustrates the lattice structure of a 6-layer MoSe₂-WSe₂ heterostructure, composed of three WSe₂ layers stacked atop three MoSe₂ layers along the crystalline *c*-axis. Each monolayer possesses D_{3h} symmetry, with

an in-plane polarisation $\mathbf{P}$ arising from M–Se dipoles (where $M = \text{Mo or W}$). The 2H stacking sequence results in a π rotation of adjacent layers, aligning their polar axes anti-parallel. In this heterostructure, the polarisation $\mathbf{P}$ of MoSe_2 layers slightly exceeds that of WSe_2 layers, reflecting the greater electronegativity difference between Mo and Se compared to W and Se. However, the stronger atomic spin-orbit interaction (SOI) of W dominates the spin physics of the system. Coupled with $\mathbf{P}$, this SOI generates an out-of-plane spin-orbit field, $B_{\text{SO}} \propto (\mathbf{P} \times \mathbf{k})_z$, which induces a Zeeman-like spin splitting of energy bands. The effect is most pronounced at the K points of the Brillouin zone, as shown in Fig. 1(B) and (C), where the spin splitting in WSe_2 ($\Delta E_{\text{SO}}^{\text{W}}$) is more than twice that in MoSe_2 ($\Delta E_{\text{SO}}^{\text{Mo}}$).

At the interface, the mismatch in spin-orbit coupling strengths gives rise to a hierarchical valley-spin polarisation. The MoSe_2 valence bands are entirely contained within the $\Delta E_{\text{SO}}^{\text{W}}$ gap of WSe_2 , as shown in Fig. 1(D). This behaviour reflects the in-plane orbital nature of the K-point states, which are dominated by $d_{\parallel} = d_{xy}, d_{x^2-y^2}$ orbitals. These orbitals exhibit negligible out-of-plane coupling, suppressing interlayer hybridisation and preserving the monolayer-like electronic structure at K. By contrast, states at the Γ point are dominated by d_{z^2} orbitals, which extend into the van der Waals gap and exhibit substantial interlayer overlap. This leads to strong hybridisation at Γ , forming a broad bonding–anti-bonding energy window across the heterostructure, as depicted in Fig.1(E). While time-reversal symmetry suppresses spin splitting at Γ , the resulting band structure at this point is highly sensitive to interlayer coupling, in contrast to the robust monolayer-like dispersion retained at K. This dichotomy is evident in the full low-energy band structure of the 6-layer system (Fig.1(F)), where the K valleys retain their original characteristics while the Γ valley forms a cascade of hybridised bands.

This disparity highlights the importance of Γ -derived orbitals in band engineering, where artificial heterostructures can exploit interlayer hybridisation to tune the out-of-plane ($\parallel k_z$) dispersion by controlling layer composition, ordering, and alignment. Indeed, in the above simple case of a 6-layer MoSe_2 - WSe_2 heterostructure, though discretized, the bonding-antibonding formation of states at and around the Γ point closely approximate a k_z -integrated bulk band structure of a bulk 2H-TMD system. This implies that, with only a few layers, the bulk band dispersion can be significantly restored and even controllably altered to exhibit a mixed characteristic between two or more materials. To emphasize the significance of this, in Fig. 1(G-H), we compare the calculated electronic structure of the interfaced system to experimental band structures of individual free-standing 3ML WSe_2 and MoSe_2 flakes. In each case, the number of d_{z^2} -derived bands at Γ , which differ only by their discrete k_z quantum number, is tripled relative to the respective monolayers as the three dimensional, k_z dispersive, band continuum of the bulk limit begins to take form. The theoretical prediction in Fig. 1(F) demonstrates that, by simply combining these 3ML components, the evolution towards a 3D band continuum is entirely unhindered despite the interface between dissimilar compounds, and electrons at Γ become fully delocalised through all six layers despite the enhanced spatial scales.

More obvious approaches to bulk-like band engineering would rely on the assembly of numerous monolayers with fixed relative orientations, stacked sequentially and periodically to replicate bulk periodicity in momentum space through the curation of a well-defined unit cell, similar to that of the naturally occurring 4Hb polymorph of TaSe_2 with alternating 1T/1H layers²⁶. By bypassing this labor-intensive approach to instead employ much simpler, two-component heterostructures in the intermediate layer regime, the same essential three-dimensional electronic behavior can be accessed within an architecture that lends itself more naturally to fine tuning with e.g. layer thickness or twist angles. More generally, access to an extra dimension within which electronic properties can be tailored and controlled is of great relevance for nano-quantum device applications, where miniaturisation plays a major role.

Delocalised band formation in two-component stacks

To demonstrate how this concept of achieving bulk-like band characteristics with mixed material properties can be realised in real systems, in Figure 2 we show the electronic structure of a $(\text{WSe}_2)_3/(\text{MoSe}_2)_5$ (Fig. 2(A)) and a $(\text{MoSe}_2)_3/(\text{WSe}_2)_3$ (Fig. 2(E)) heterostructure constructed by interfacing two few-layer TMD flakes on graphite/n-type silicon substrates (see Methods). This pair of heterostructures thus closely approximate opposite surfaces of a single MoSe_2 - WSe_2 system, and the modest total layer numbers enable unambiguous comparisons of stacked regions relative to the two component flakes. Photoemission spectra acquired from the stacked heterostructure regions are displayed in Fig. 2(B, F).

As exemplified in Fig. 1(G-H), there is a one-to-one correspondence between the number of discrete sub-bands within the d_{z^2} -manifold at the Γ point of 2H-structured TMDs and the number of monolayers within the system^{27,28}. These bands collectively describe a single three-dimensional d_{z^2} -derived band which is quantised in k_z due to the finite size of the system along the c -axis^{28–30}. Therefore, as basic band theory stipulates that periodicity in momentum space cannot be achieved without periodicity in real space, the number of discrete k_z sub-bands visible within the overlapped regions would not be expected to reflect the full extent of the heterostructures which lack a well-defined unit cell. Yet, the photoemission spectra in Fig. 2(B,F) demonstrate that the number of k_z sub-bands is not only increased relative to equivalent datasets acquired from the constituent flakes (shown in full in Fig. S1 in the supplemental information), but also matches the total layer number in real space (i.e. eight for (B) and six for (F)) of the entire heterostructure. The electron mean free path of less than 0.7 nm perpendicular to the surface, applicable to our photoemission experiments, precludes that the experimental result originates from a superposition of spectra from weakly-interacting top and bottom TMD flakes which each have thicknesses of ~ 0.7 nm per monolayer³¹. This alternate scenario is further discarded through constant-energy k_x - k_y contour mapping in Figure S2 in the supplemental information. Instead, the six or eight distinct d_{z^2} sub-bands at Γ are delocalised throughout the structure, and are therefore accessible to a surface sensitive probe.

While counterintuitive, these findings are entirely consistent with the discussion surrounding Figure 1: The array of hybridized bands at Γ belonging to the collective band structure of the finite six or eight layer crystal structure closely mimics the discretized k_z -projected band manifold of ordered systems. For bands derived from orbitals with significant interlayer hopping potential, the k_z dispersion is therefore effectively constructed without the need for a periodic repeating unit. To further test this description, the experimental band dispersions of both WSe_2 - MoSe_2 heterostructures are compared to layer-projected, density functional theory (DFT)-based slab calculations in Fig. 2(C,G), (see Methods). Not only is the electronic structure around the Γ point extremely well reproduced in each case, but the energetics of the d_{z^2} band manifold are identical between layer-integrated and top layer-projected calculations, implying full c -axis delocalisation. Together, this verifies the present interpretation while also demonstrating a negligible role of collective electron phases and large twist angles (the latter chosen experimentally in order to decouple Moiré effects, see Figure S3 in the supplemental information), which are both neglected by these calculations.

To further scrutinize the observed three-dimensional behavior, in Figure 2(D,H) we track the evolution of the delocalised states at Γ with changing photon energy, thus mapping their behavior with changing k_z ³². These spectra can be compared to equivalent datasets for a three-layer MoSe_2 and WSe_2 flake (Figure S1 (F,I) in the supplemental information). For both the individual TMD flakes and the artificial heterostructures, each d_{z^2} -subband is two-dimensional (i.e. non-dispersive along k_z) in-line with their assignment as dimensionally confined states, though each exhibits a photon energy-dependent spectral weight. In the eight- or six-layer hybrid systems (Fig. 2(D,H)), it is apparent that these spectral weight variations are periodic in k_z , with each

sub-band illuminated sequentially. This is consistent with their collective assignment as a singular d_{z^2} -orbital derived band, which remains quantized in k_z due to the finite length scales of the total hybrid systems along the asymmetric c -axis. Though discrete, this periodic behavior is exactly as would be expected for three-dimensional bands in a bulk 2H-structured TMD system. Indeed, the overlaid solid lines, which well capture the observed periodicity, are a tight-binding model for an idealized bulk structure with alternating WSe₂ and MoSe₂ layers along the c -axis. We note that, due to significant k_z broadening in photoemission generally³², the majority of these sub bands can be captured simultaneously when probed with a single photon energy, as evidenced by the in-plane band dispersions shown in Fig. 2(B,F). We stress that, while the observed three-dimensional band dispersions in Fig. 2 exhibit finite-size effects, the key properties of bulk TMDs are, in general, present and fully-developed in their six (or fewer)-monolayer variants despite k_z quantisation^{27,28,33–37}. Asymmetric heterostructures constructed analogously to the above proof-of-principle examples are thus generically suited to host the electronic properties of many-layer TMDs. Nevertheless, we expect the underpinning mechanism driving these emergent delocalised bands to hold for pairings with larger total thicknesses, thus producing artificial 3D band properties closer to the true bulk limit.

To finalize this Section, in Figure S4 of the supplemental information, we show how equivalent phenomena is observed for mismatched combinations of two or three WSe₂ and MoSe₂ bilayers. The number of k_z sub-bands within the d_{z^2} -manifold again reflects the full c -axis extent of the system despite ill-defined unit cells, demonstrating how the periodic k_z -dispersions expected for ordered solids are emulated when interfacing two-or-more TMD flakes in the intermediate layer regime. The apparent resilience of the observed band delocalization to interface(s) with significant lattice mismatching can be understood as a natural consequence of the orbital character of TMD band structures more generally: The transition metal and chalcogen orbitals which extend into the van der Waals gap contribute bands only to the $\bar{\Gamma}$ point, and therefore interlayer band hybridisation channels are always available.

Orbital-dependent band localisation

While the presence of delocalised electron behavior within the d_{z^2} orbital manifolds of the finite heterostructures is clear, the same is not true for regions of the electronic structure derived from in-plane orbitals. This stark contrast in orbital-dependent coupling is a hallmark of 2H-type transition metal dichalcogenides generally. The details of the $d_{||}$ K-point valence bands are largely equivalent in monolayer and bulk 2H-TMD systems due to their minimal out-of-plane hopping potential^{20,38,39}, whereas d_{z^2} -derived Γ -point states exhibit substantial out-of-plane coupling to drive significant k_z dispersion in bulk materials^{16,27,28,40–42}, thus underpinning the indirect-to-direct bandgap transition observed in few-layer systems^{20,21,43}. This natural orbital disparity interplays with the inherent asymmetry of heterostructures constructed by interfacing two dissimilar TMD flakes, ensuring a spatial dependence to the broader electronic structure along the c -axis between limits defined by the distinct component materials. The scale of this dependence is therefore dependent on orbital type.

In Figure 3 and Figures S5 and S6 of the supplemental information, this real space evolution is explored in full. In Fig. 3(A), the orbitally-resolved WSe₂ and MoSe₂ terminations of the experimentally realized (MoSe₂)₃/(WSe₂)₃ heterostructure are compared. The valence band maxima at K and Γ , derived exclusively from $d_{||}$ and d_{z^2} -orbitals respectively, represent the two extremes of c -axis delocalisation: The details of the spin-orbit splitting at K is determined only by the local crystal structure, while the band structure at Γ is equivalent between terminations and indeed between the top and bottom layers (shown explicitly in Figure S5 of the supplemental information). The rest of the band structure behaves similarly, with the real-space electronic structure dependence directly determined by the $d_{||}/d_{z^2}$ orbital ratio, further influenced by hy-

bridization between bands of differing orbital origins. In artificial, asymmetric heterostructures, this therefore produces an overall layer-dependent electronic structure despite the presence of fully delocalised band features. This is in stark contrast to naturally occurring TMDs, wherein the overall symmetry of the system precludes real space band structure variations despite a similar orbital-dependent localisation.

The asymmetry of our artificial heterostructures can also be expected to modify the spin structure relative to natural TMD systems. As discussed earlier, in a natural 2H-TMD, each constituent TMD layer, owing to its D_{3h} symmetry, can only exhibit an out-of-plane spin-orbit field, whose direction is opposite to that of the neighbouring layers. Consequently, this implies that in-plane spin textures, including chiral spin-momentum locking types arising from the Rashba effect⁴⁴, are effectively suppressed. Furthermore, the hidden out-of-plane spin textures of each layer can only become accessible at the surface, where translational symmetry breaking disrupts the natural cancellation of B_{SO} along the stacking axis.

In contrast, our artificial structures can naturally accommodate both in-plane Rashba-type and out-of-plane Zeeman-like spin textures due to their unique heterostructural properties. Specifically, the chiral Rashba spin polarisation can emerge naturally from the potential gradient formed at the $\text{MoSe}_2/\text{WSe}_2$ interface and propagate throughout the entire structure via d_{z^2} and other out-of-plane orbitals. To elucidate the implications of this, in Fig. 3(B-F), the $(\text{MoSe}_2)_3/(\text{WSe}_2)_3$ heterostructure is compared to an idealised six-layer $(\text{MoSe}_2/\text{WSe}_2)_3$ system, where the calculated layer-projected spin polarisation for the chiral (x) and out-of-plane (z) components is shown for both the asymmetric and idealised cases. As can be observed, in both configurations, strikingly similar patterns of in-plane and out-of-plane spin polarisation emerge, which remain valley-specific. Particularly, in both cases, the chiral (x) component is significantly enhanced around the Γ point, where the d_{z^2} contribution is dominant. As with the discussions surrounding the k_z dispersions on show in Fig. 2, this again demonstrates how the key physics of ideally-stacked TMD heterostructures are very closely approximated by our simpler but asymmetric structures.

Creation of layer-dependent semimetallic phases

The asymmetric WSe_2 - MoSe_2 heterostructures discussed thus far exhibit dissimilar top and bottom surfaces due to orbital-dependent band localisation. While the global symmetries of the asymmetric unit are fundamentally altered relative to naturally occurring TMDs or to an idealized stack, its layer-dependent electronic structure is derivative of the bulk forms of the component materials. For the specific cases considered so far, the similarities in the WSe_2 and MoSe_2 lattice constants⁴⁵ and in the energetics of the relevant W 5d and Mo 4d orbital manifolds precludes significant deviations of the formed hybrid electronic structure from those of the parent compounds. We stress however, that such a similarity in material components is not a necessary criterion to stabilize dimensionally-mixed frameworks: The mechanism underpinning our findings should apply generally to pairs of 2D materials with non-negligible out-of-plane hopping, even when the two components differ substantially. Such a mismatching could be used to engineer entirely unique quantum phases.

To exemplify the power of this eventuality, in Fig. 4, we showcase a $(\text{WSe}_2)_4/(\text{NbSe}_2)_2$ heterostructure. NbSe_2 is metallic, whereas WSe_2 is semiconducting. Consequently, the energy bands in WSe_2 are effectively lower than those in NbSe_2 by the energy gained from filling the valence bands with an additional electron, transferred from the W^{+4} ion compared to the Nb^{+3} ion. Despite this, not only do the number of k_z subbands at Γ continue to reflect the total layer number of the heterostructure thereby demonstrating the presence of fully delocalised bands, but the system becomes semimetallic, with the shallowest binding energy sub-band at the Γ point forming a Fermi surface, shown inset in Fig. 4(B) and in Figure S7 of the supplemental

information. This Fermi pocket at Γ is the only Fermi band crossing on the top layers of the artificial heterostructure, unlike the electronic structure of any naturally occurring bulk or few-layer TMD.

The significant charge transfer between WSe_2 and NbSe_2 more generally was previously found to enable p -type ohmic contacts^{46,47}. For the purposes of this work, the charge transfer (calculated explicitly in Figure S8 of the supplemental information) energetically aligns the $\text{W-}d_{z^2}$ manifold of WSe_2 to a predominantly $\text{Se } p_z$ -derived band manifold of NbSe_2 . Despite the mixed-orbital origin, the delocalised states at Γ form unhindered, again facilitated by interlayer interactions between out-of-plane orbitals.

In Fig. 4(C), the experimental picture is compared to DFT calculations. While, as with the previous heterostructures, there is strong quantitative agreement for the states at Γ , these calculations reveal a fine structure that was absent in the previous examples. In particular, there is a pronounced subband-dependent splitting around Γ of the states near the Fermi level. We attribute this to be a natural consequence of the mixed-orbital origin of this hybrid band manifold, shown explicitly through orbital-resolved DFT calculations in Figure S9 of the supplemental information.

Nevertheless, as verified by the layer-resolved calculations in Figure S10 of the supplemental information, all sub-bands at Γ are again present and at the same energy in each layer of the heterostructure, evidencing the presence of fully delocalised electrons along the c -axis and hence the formation of a discretized three-dimensional band manifold. Indeed, the k_z periodicity in the spectral weight of the experimentally observed sub-bands, shown in Fig. 4(D), is again well matched to the periodicity of bulk TMD calculations.

The observed c -axis delocalisation, persisting even for this energetically-mismatched scenario, is facilitated by the lowering of the total energy of the system by partially lifting the constraints of 2D quantization. Along the c -axis, electrons form standing waves due to the finite thickness of the artificial crystals. In Figure S8 of the supplemental information, we quantify this picture through the computation of the hopping probabilities for the 4ML- WSe_2 /2ML- NbSe_2 heterostructure. The hopping paths across the interface between nearest-neighbour chalcogen p_z and out-of-plane transition metal d -orbitals are comparable to the equivalent interlayer interactions in natural TMD systems, but longer-range interactions are essentially absent. While tunneling is limited to the two layers forming the interface, the formation of delocalised bands over the entire c -axis extent is enabled additionally through electronic standing wave formation either side of the interface. Together, this produces a longer-range electronic coupling that acts to unify the heterostructure into a single lattice unit.

This standing wave picture can be expected to break down as one or both flakes approach the infinite-layer limit and electrons at the interface gain access to a bulk reservoir, ultimately preserving the quantized electronic structure of the remaining few-layer component. This is tested and shown explicitly in Figure S11 of the supplemental information through the characterization of a second overlap region within the sample in Fig. 4(A); between a 4ML- WSe_2 flake and a many-layer NbSe_2 crystal. While charge transfer from the semiconducting top-layer still occurs in addition to some normalization of band features relative to the isolated 4ML- WSe_2 top-layer, there are no additional well-defined d_{z^2} -subbands.

k_z -mediated topological phases

Though orbital-dependent, the presence of delocalised electronic behavior in asymmetric artificial heterostructures prompts the question of whether additional surface-localised states are produced by the truncation of global crystalline symmetries. While surface states, both topologically trivial and non-trivial, are commonplace in naturally occurring bulk TMDs, the disparate surfaces unique to asymmetric heterostructures would result in pairs of surface states with mis-

matched, surface-specific, properties.

To explore this potential, in Fig. 5 we search for surface states enforced by topological phase transitions driven by out-of-plane delocalised electron behavior.^{14,22,48} The families of three-fold symmetric 1T and 2H-structured TMDs possess a series of band inversions along their k_z axes ($\parallel \Gamma$ -A)^{14,15,22,48–58}. These inversions, entirely contained to the chalcogen p -orbital manifold, generate up to five Dirac crossings (both bulk Dirac points and topological surface states (TSSs)) energetically stacked at the surface Brillouin centre. While the underpinning mechanism is equivalent for the dozen TMDs explicitly shown to host these states to date, the ladder of topological band crossings produced is delicately dependent on material-specific parameters, and thus are fingerprints of each individual system. The minimal criteria to generate topological ladders in TMDs are only that there exists a discrepancy in the k_z -bandwidths of in- and out-of-plane chalcogen p -orbital-derived states, and that C_3 symmetry is intact to maintain bulk Dirac crossings (though not crucial for the properties of surface Dirac states). The presence of bands well approximating a (discretized) k_z dispersion along with orbital hopping asymmetries (discussed thus far for d -orbitals) imply that the above conditions are met in the experimental heterostructures considered here. Previous ARPES studies have shown that 4-5 monolayers is sufficient to stabilize the topologically non-trivial properties of bulk TMD systems in full^{34,35}. Such physics is therefore relevant to the intermediate-layer regime considered here.

Figure 5 overviews the realisation of non-trivial band topology in our proof-of-principle MoSe₂-WSe₂ heterostructures. In bulk 2H-TMDs like WSe₂, there is one experimentally resolvable TSS centred ~ 1.9 eV below the VBM formed from the anticrossings of a k_z -dispersive Se p_z -derived band with mixed character Se- $p_{x,y}$ and W- $d_{xz,yz}$ bands along k_z ²². This TSS is visible in a spectrum acquired from the bulk region of the flake used for device construction shown in Fig. 5(A), which is compared to band dispersions from the pair of WSe₂-MoSe₂ heterostructures and their respective 3ML top layers. Experimental zoom-ins of the region wherein the bulk band inversion occurs and top-layer projected DFT calculations are provided in Fig. 5(B) and (C), respectively. While quasi-linear band dispersions are present in all cases, both 3ML TMD flakes undergo significant band renormalization when stacked atop a dissimilar flake. In 3ML-WSe₂, both experiment and theory demonstrate a small local SOC-mediated gap between a pair of bands at the binding energy where the Dirac crossing occurs in the bulk limit. When interfaced to form a 3ML-WSe₂/5ML-MoSe₂ heterostructure, however, the lower of these two bands shifts to higher binding energy to give way to a gapless TSS with well-defined upper and lower branches which merge into the surrounding bands at higher $k_{\parallel}$, as for the case of bulk WSe₂. Similarly contrasting behavior is evident for the second, thinner, heterostructure: While the smaller atomic SOC strength of Mo precludes resolving the finite band gaps for the isolated 3ML flake, a distinct crossing point emerges when stacked, differing from the states of 3L or 5ML-MoSe₂ (Figure S1 of the supplemental information). In Figure S9 of the supplemental information, orbital-resolved calculations for this second heterostructure reveal how the TSS sits within a band manifold of predominantly $p_{x,y}$ character, flanked by a p_z -derived band on each side. Moreover, with reference to Figures. S5 and S6 of the supplemental information, one can verify that the spectral weight of the Dirac points is in each case localised to the top- and bottom-most monolayers, and decays exponentially with decreasing proximity to the WSe₂-MoSe₂ interface. These observations demonstrate that the surface states are a property of the collective lattice unit rather than its individual components, and are entirely in line with the k_z -mediated band inversions from which these topological states derive²².

In contrast to k_z -mediated TSS found in naturally occurring TMDs, the appearances, energetic positions and characteristic chiral momentum-locked spin textures of these Dirac crossings (Fig. 5(D)), can differ between the two oppositely-orientated surfaces, with a ~ 55 meV discrepancy extracted for the specific (MoSe₂)₃/(WSe₂)₅ configuration from the layer-resolved calculations in Figure. S6 of the supplemental information, consistent with the experimental

datasets from oppositely-orientated WSe_2 - MoSe_2 structures in Fig. 5. This physics should apply to any pair of TMDs which are susceptible to k_z -mediated topological phase transitions, each with a unique set of Dirac crossings with surface-dependent behavior. This could be utilized to drastically augment the five available Dirac cones in the 1T-structured TMD (semi)metals $(\text{Pd}, \text{Pt}, \text{Ni})(\text{Se}, \text{Te})_2$ which have high sensitivity to relative hopping parameters in the unit cell^{22,48,59,60}. For example, compared to PtSe_2 , PdTe_2 hosts an additional k_z -band crossing to produce a TSS at Fermi level¹⁴. It follows that an asymmetric heterostructure formed from these two compounds would host a hybrid k_z -dispersion with a band inversion close to the quantum critical point, potentially enabling *in situ* switching of TSS contributions to transport.

DISCUSSION

In conclusion, this work elucidates a new and straightforward method to engineer designer electronic structures in artificial bulk-like systems of transition metal dichalcogenides. By interfacing two few-layer TMD flakes, emergent bands with characteristics derived from both parent compounds are created that are delocalised throughout the heterostructure. This physics can persist when orbital manifolds are energetically misaligned across the interface, and even in the presence of large twist angles.

This produces a scenario wherein the bulk-like band dispersions of 3D systems and the layer-locked electron behavior of 2D systems coexist within the same asymmetric structure. One particularly striking consequence of these contrasting behaviors is the production of k_z -mediated topological phases that stabilize surface layer-localised topological states with properties set by local crystal parameters, unlike any topologically non-trivial system existing in nature. When combined with controlled lattice-mismatching, this approach could offer opportunities to engineer a coexistence of strong electronic correlations and non-trivial band topology that, while extremely rare naturally, are pathways towards exotic phases such as topological superconductivity, quantum spin liquids and topological Mott insulators⁶¹. Alternatively the non-equivalence of oppositely localized surface states, enforced by inherent *c*-axis structural asymmetry, could be exploited for 2D transistor-like components where the asymmetric surface electron transport can be controlled with band filling or layer-thickness. While demonstrated using flakes with sizes of only tens of microns, new methodologies for creating wafer-scale 2D material flakes⁶² could be exploited for this purpose.

We envision that combinations of any of the > 30 stable TMD systems² could produce hybrid three-dimensional band properties analogous to those shown here with further applicability to other layered materials with out-of-plane orbital-derived band manifolds at Γ , including two-dimensional magnets. Together, the simplicity of this approach and the enormity of the phase space available together provide a new and accessible route towards a function-led construction of mixed-dimensional artificial systems.

METHODS

Heterostructure Fabrication

To construct the heterostructures characterised in this study, few-layer flakes of graphite, MoSe₂, WSe₂ and NbSe₂ were exfoliated onto PDMS film and transferred onto n-type Si substrates. After each stacking stage, the samples were rinsed with diisopropylamine, isopropanol and ethanol to remove polymer residues, and annealed in a constant-flow Ar furnace at 200-250 degrees. These procedures were performed in an Ar environment for samples containing NbSe₂, with a hot plate used in place of a furnace. The component flakes comprising the heterostructures have thicknesses determined through comparisons of photoluminescence spectra and optical images to those of known references. An additional, *in situ* metric is provided by photoemission spectra obtained by probing the non-overlapping regions of each flake where available, wherein the number of distinct quantized k_z -sub-bands within the d_{z^2} -manifold at Γ matches the number of monolayers along the c-axis^{27,28}. All samples were transported in standard sample boxes (sealed in an Ar environment for NbSe₂-containing samples), and exposed to air briefly prior to photoemission measurements without consequence to the overlap regions.

Angle-resolved Photoemission

All heterostructures were pre-characterised with NanoESCA III at FMMA (ROR: 04z91ja70)⁶³ following a 3 hour UHV anneal at 270°C, where an extraction voltage of 12kV and a HeI plasma discharge lamp was used for electronic structure measurements at room temperature. The data in Figure S3 of the supplemental information were measured in this way. All other displayed ARPES data were collected using either *p*-polarised or unpolarised synchrotron light of energies between 60 and 144 eV at the MAESTRO beamline of the Advanced Light Source. Samples were cooled to cryogenic temperatures following a further 3+ hour UHV anneal at 270°C. The base pressure of the setup was better than $\sim 1 \times 10^{-10}$ mbar. Regions of interest (ROI) were identified through *in situ* spatially resolved valence band mapping, examples of which are shown in Figure S12 of the supplemental information. The focused beam spot size is better than 2 μm in diameter. Beam exposure times to the regions of interest were minimized to reduce the risk of radiation damage, though we note that no such damage was identified for any of the heterostructures characterized within this study.

Theoretical Calculations

Electronic structure calculations were performed within Density Functional Theory using the Perdew-Burke-Ernzerhof exchange-correlation functional⁶⁴, as implemented in the VASP programme package^{65,66}. Due to the close similarity between the lattice parameters of 2H-WSe₂ and 2H-MoSe₂, the experimentally reported bulk structure of 2H-WSe₂⁶⁷ used for both compounds in constructing (WSe₂)_{*n*}/(MoSe₂)_{*m*} heterostructures. A supercell containing $n = 3$ and $m = 3$ or 5 layers was employed, with a vacuum spacing of 15 Å to prevent spurious interactions between periodic images. The plane-wave cut-off energy was set to 400 eV. The Brillouin zone was sampled using a k-point mesh of $10 \times 10 \times 1$. Spin and orbital projections were obtained using Wannier functions^{68,69}, downfolded from the DFT Hamiltonian, with the valence *d* orbitals of the transition metal atoms and the Se 4*p* orbitals chosen as projection centres.

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Oliver J. Clark (oliver.clark@diamond.ac.uk).

Materials availability

This study did not generate new materials.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- No original code was used during this study.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

ACKNOWLEDGMENTS

O. J. C. thanks Phil D. C. King for useful discussions. O. J. C., M. S. F. and M. T. E. acknowledge funding support from ARC Discovery Project DP200101345. M. T. E. acknowledges funding support from ARC Future Fellowship FT2201000290. O. J. C., D. M. and M.T.E. acknowledge travel funding provided by the International Synchrotron Access Program (ISAP) managed by the Australian Synchrotron, part of ANSTO, and funded by the Australian Government. D. M. was supported by the FLEET Centre of Excellence (ARC grant CE170100039). A.A., R.V.B. and M.S.B. gratefully acknowledge the Research Infrastructures at the Center for Computational Materials Science at the Institute for Materials Research for allocations on the MASAMUNE-IMR supercomputer system (Project No. 202112-SCKXX-0510) and MAHAMERU BRIN HPC facility under the National Research and Innovation Agency of Indonesia. M.S.B. acknowledges support from Leverhulme Trust (Grant No. RPG-2023-253). A.A. had support from the Indonesia Endowment Fund for Education (LPDP), NIB/202209223311735. R.V.B. and M.S.B. are grateful to E-IMR center at the Institute for Materials Research, Tohoku University, for continuous support. B. C. and S. L. H. acknowledge the facilities, and the scientific and technical assistance of Microscopy Australia (ROR: 042mm0k03) enabled by NCRIS and the Government of South Australia at Flinders Microscopy and Microanalysis (ROR: 04z91ja70), Flinders University (ROR: 01kpzv902). The work at the University of Warwick was supported by EPSRC, UK through Grant EP/T005963/1. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF)

AUTHOR CONTRIBUTIONS

OJC, DM, T-H-YV, MTHB, FM and MTE performed the nano-ARPES measurements. OJC and BC performed the nano-ESCA measurements. OJC constructed the heterostructures shown

throughout the manuscript, with the exception of the bilayer system shown in Fig. S4 of the supplemental information which was constructed by T-H-YV. T-H-YV also performed atomic force microscopy on the WSe_2 - NbSe_2 heterostructure. AA, RVB and MSB performed the theoretical calculations. CJ, AB and ER provided user support at BL 7 MAESTRO of the Advanced Light Source. BC and SLH provided access for the nano-ESCA instrument at Flinders University, South Australia. SHL and ZM supplied semiconductors used in device construction. GB supplied the NbSe_2 crystals used for device construction. OJC conceived the project and wrote the manuscript with significant contributions from MSB and MTE and further input from all other authors. OJC was responsible for the overall project planning and direction.

DECLARATION OF INTERESTS

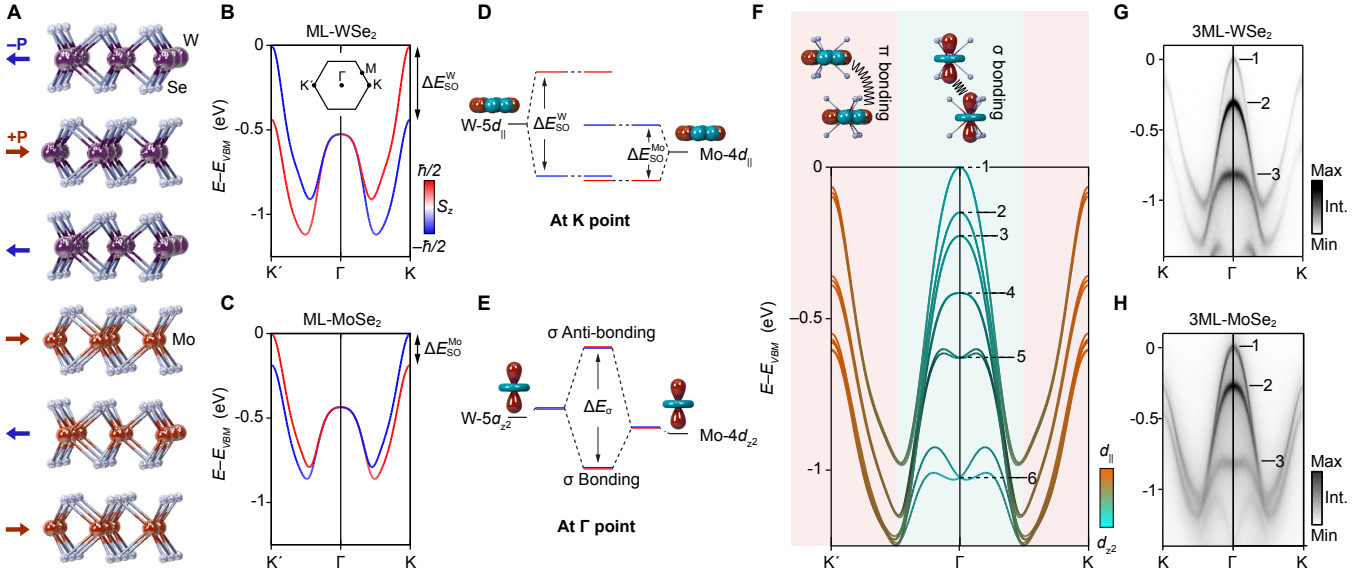
The authors declare no competing interests.

SUPPLEMENTAL INFORMATION INDEX

Document S1. Notes S1-S11 and Figures S1-S12.

MAIN FIGURE TITLES AND LEGENDS

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Figure 1. Chemical nature of an anisotropic transition metal heterostructure

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A Schematic representation of a $(\text{WSe}_2)_3/(\text{MoSe}_2)_3$ heterostructure. Due to the D_{3h} symmetry of each monolayer, a net dipole moment $\pm P$ is induced, oriented perpendicular to the stacking axis, and oppositely aligned with respect to the adjacent layer. **B** and **C** Out-of-plane spin-projected electronic band structures for monolayers of WSe_2 and MoSe_2 , respectively. The parameter $\Delta E_{\text{SO}}^{\text{W/Mo}}$ denotes the valley-dependent spin-orbit splitting at the K-point of the Brillouin zone. **D-E** Schematic energy diagrams illustrating the bonding and anti-bonding interactions at the K and Γ points, respectively, with their orbital character predominantly influenced by the in-plane $d_{||} = \{d_{xy}, d_{x^2-y^2}\}$ and out-of-plane d_{z^2} orbitals of W/Mo. **F** Orbital-projected electronic structure of the $(\text{WSe}_2)_3/(\text{MoSe}_2)_3$ heterostructure, highlighting the distinct contributions from the constituent layers. The bands at Γ are numbered from low energy to high. **G-H** Photoemission spectra collected from isolated 3ML thick flakes of WSe_2 and MoSe_2 (using 108 and 64 eV photons, respectively, and symmetrized about Γ). The bands at Γ are numbered from low energy to high.

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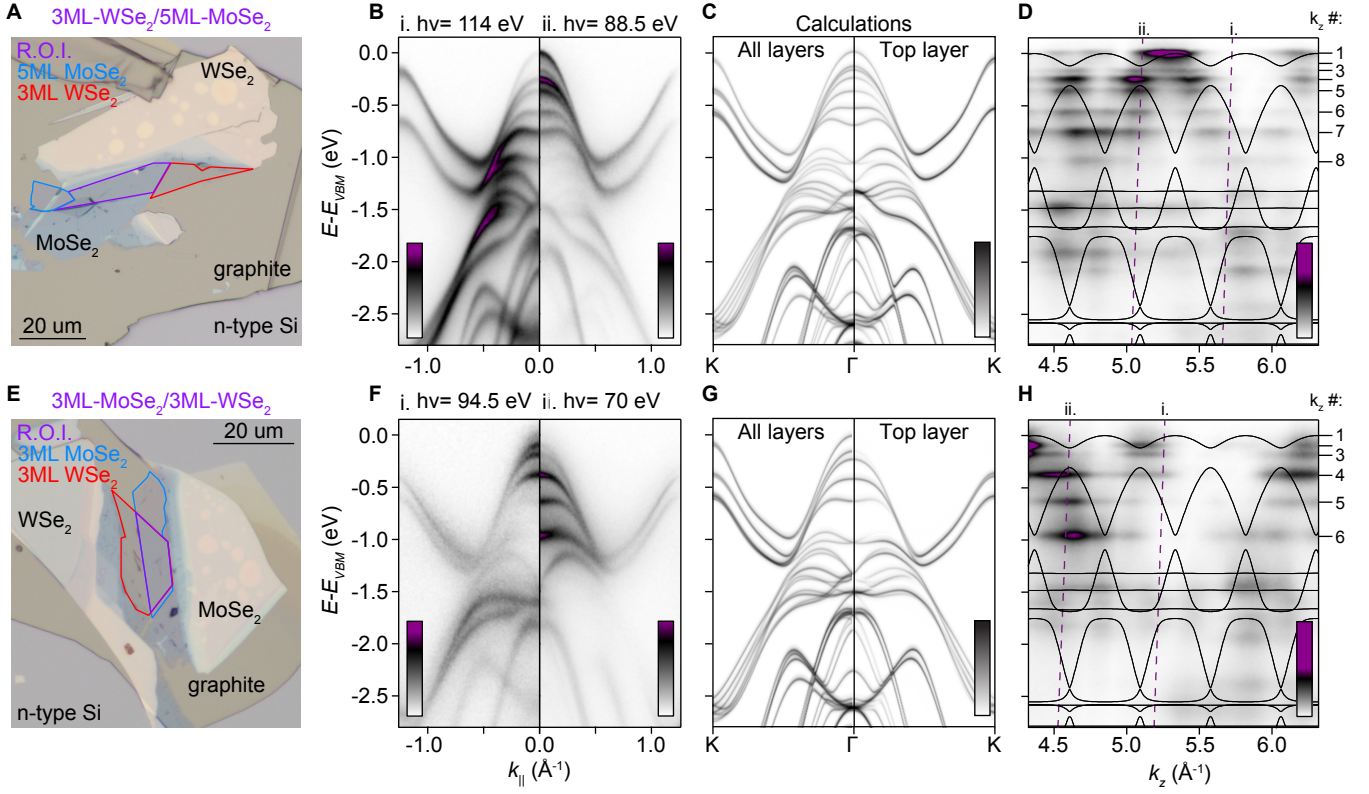
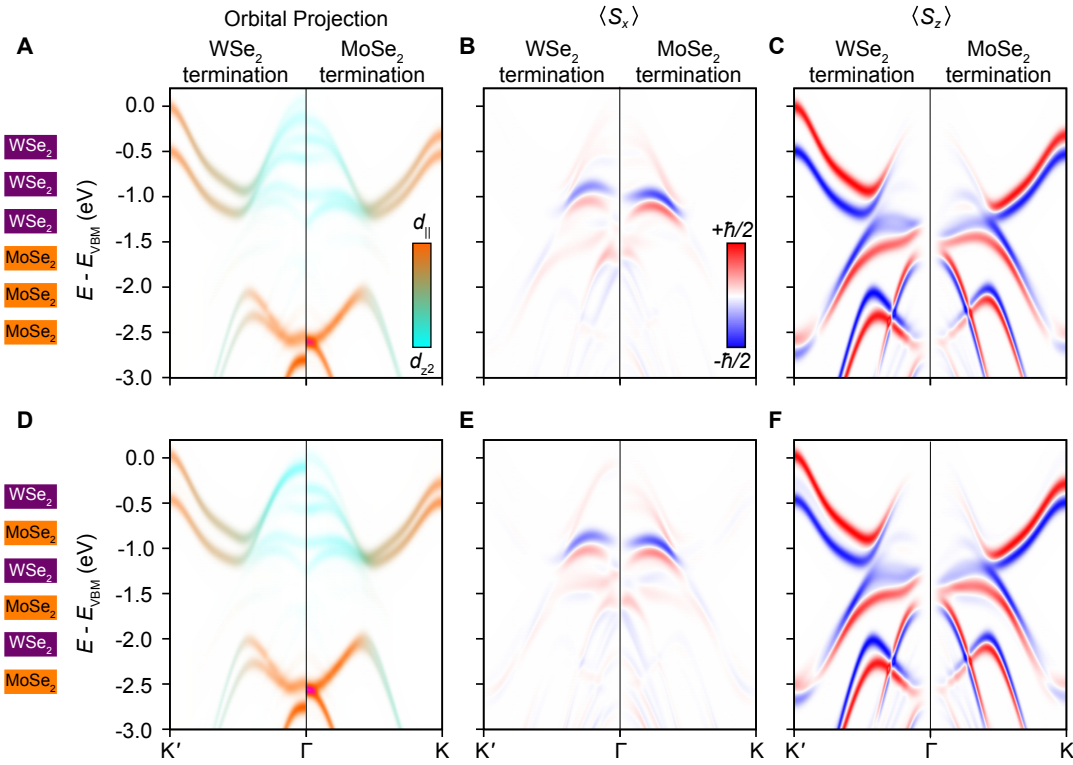


Figure 2. Multi-layer asymmetric heterostructures constructed from MoSe₂ and WSe₂ flakes

A-D Overview of a (WSe₂)₃/(MoSe₂)₅ heterostructure. **A** Optical image of the heterostructure region. The few-monolayer thick top and bottom layers are highlighted in red and blue respectively. The overlap region of interest (ROI) is highlighted in purple. **B** Band dispersions of the ROI along axes close to the K-Γ-K direction for two stated photon energies. **C** Density functional theory based slab calculations, projected through the full heterostructure (left) and to the top layer (right) along the K-Γ-K direction. **D** k_z dispersion ($h\nu = 60-144$ eV) at $k_{\parallel} = 0$. Dashed lines indicate the photon energies corresponding to the slices in (B), and solid lines are a tight-binding model (TBM) of a bulk (WSe₂/MoSe₂)_n system. An inner potential of 16 eV is chosen to best match the periodicity of the calculated band structure. k_z sub-bands of the d_{z^2} valence band maxima are numbered from low binding energy to high. **E-H** Equivalent datasets for a (MoSe₂)₃/(WSe₂)₃ heterostructure. We estimate that the Fermi level is at $E - E_{\text{VBM}} = 0.64$ and 0.67 eV for panels (B) and (F), respectively.



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Figure 3. Spin-orbital variation in the $(\text{MoSe}_2)_3/(\text{WSe}_2)_3$ heterostructure

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A Orbital-projected electronic structures calculated for both WSe_2 (LHS) and MoSe_2 (RHS) terminated configurations of the asymmetric $(\text{MoSe}_2)_3/(\text{WSe}_2)_3$ heterostructure. **B-C** Spin-projected electronic structures over an equivalent energy-momentum range to that shown in (A). The $\langle S_x \rangle$ (chiral) and $\langle S_z \rangle$ (out-of-plane) components are shown in (B) and (C), respectively. As in (A), both the WSe_2 and MoSe_2 terminations are compared. **D-F** Corresponding calculations for an idealised $((\text{MoSe}_2)/(\text{WSe}_2))_3$ heterostructure, where WSe_2 and MoSe_2 layers are alternately stacked along the c -axis. A schematic for the layer ordering in both the asymmetric and idealised heterostructures is shown on the left hand side of panel (A) and (D), respectively.

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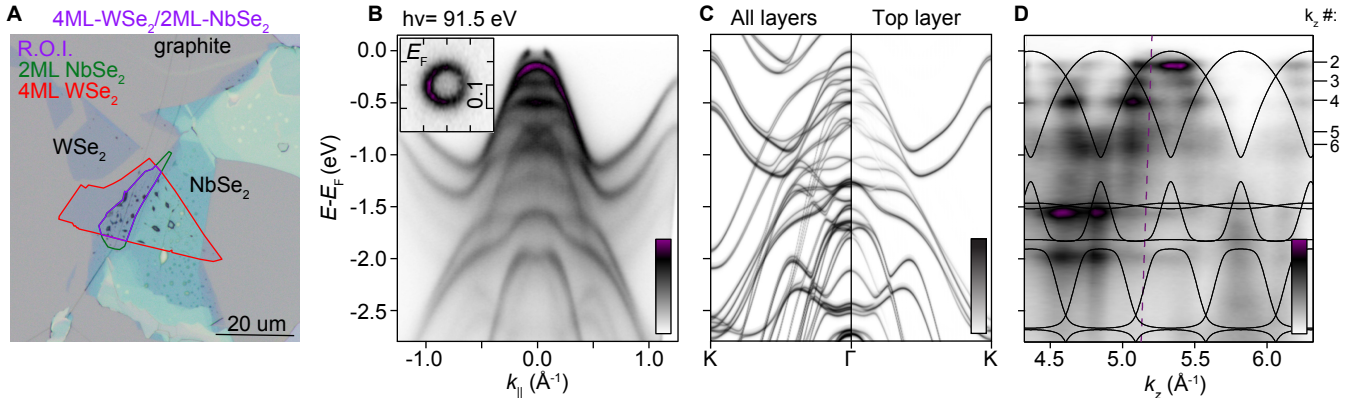
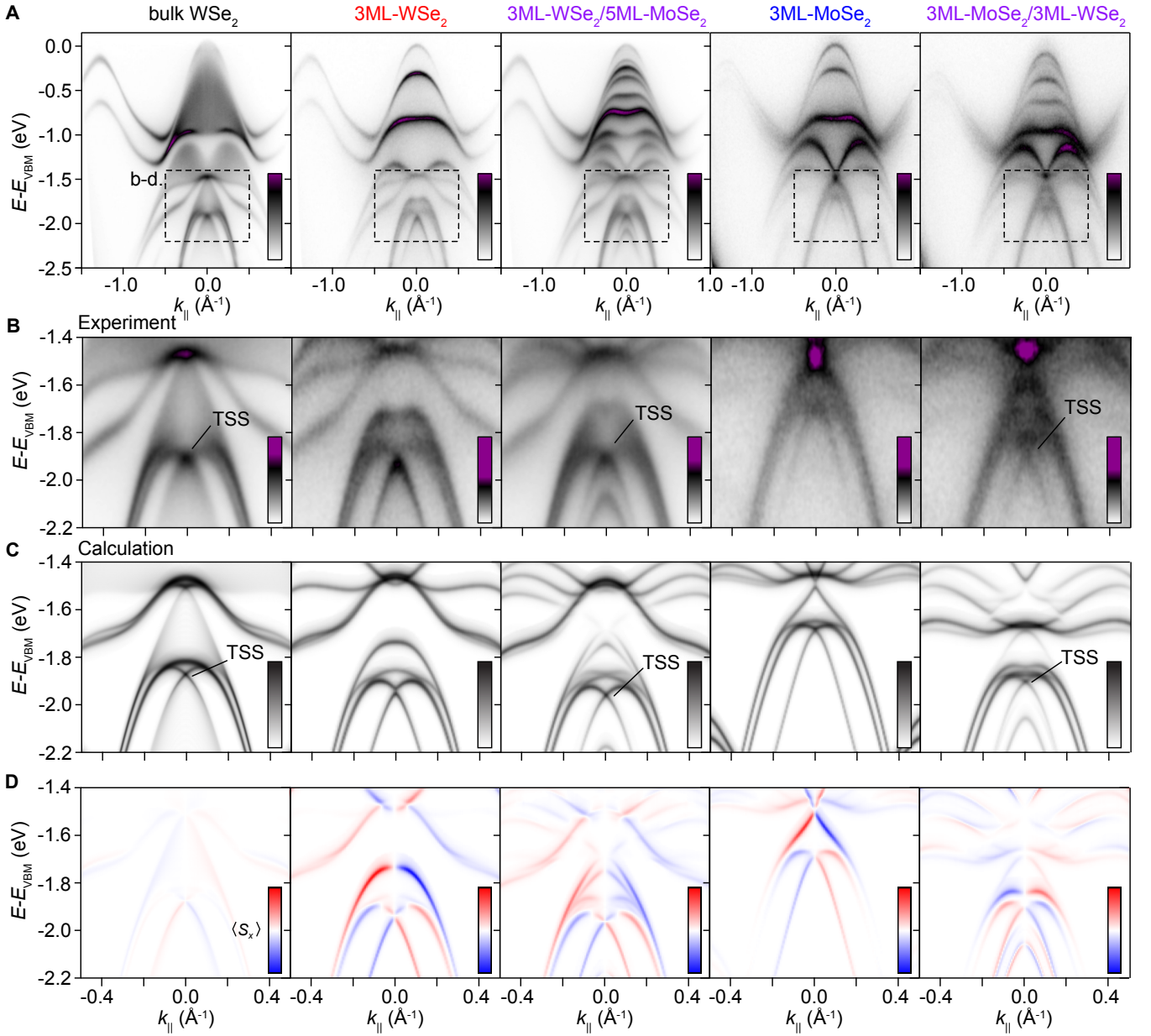


Figure 4. Local semimetallic fermiology in an asymmetric WSe₂-NbSe₂ heterostructure

A Optical image of the heterostructure region. The few-monolayer thick top and bottom layers are highlighted in red and green respectively. The overlap region of interest (ROI) is highlighted in purple. **B** Band dispersions of the ROI along axes close to the K- Γ -K direction. The inset is a k_x - k_y contour at the Fermi level, taken with 90 eV photons. **C** Density functional theory based slab calculations, projected through the full heterostructure (left) and to the top layer (right) along the K- Γ -K direction. **D** k_z dispersion ($h\nu=60$ -144 eV) at $k_{||} = 0$. Dashed lines indicate the slices in (B), and solid lines are a tight-binding model (TBM) of bulk WSe₂ offset in energy to match the experimental scenario. An inner potential of 16 eV is chosen to optimize the match to the periodicity of the calculated band structure. k_z sub-bands of the d_{z^2} valence band maxima are numbered from low binding energy to high. We note that the spectrum in (B) is partially superimposed with that from pristine 4ML-WSe₂, most likely due to spatial integration with the 4ML-WSe₂ flake to the left of the R.O.I. We note that, due to air sensitivity of air-exposed NbSe₂, atomic force microscopy (AFM) was employed to determine the thickness of the NbSe₂ bottom layer instead of *in situ* photoemission. The step height from the WSe₂ regions (red outline in (A)) to the overlap region (purple) was found to be ~ 2.25 nm consistent with 2 ML NbSe₂.⁷⁰



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Figure 5. k_z -mediated topological phases in asymmetric heterostructures

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A Band dispersions along an axis close to K- Γ -K taken with 81 eV photons for (from left to right) bulk WSe₂, 3ML-WSe₂, a (WSe₂)₃/(MoSe₂)₅ heterostructure, 3ML MoSe₂ and a (MoSe₂)₃/(WSe₂)₃ heterostructure. Dashed rectangles show the energy-momentum region covered by the spectra in B-D. **B** Zoom ins of the spectra in A with enhanced colour contrast. **C** Top-layer projected DFT calculations for the equivalent regions **D** Equivalent plots with resolved chiral ($\langle S_x \rangle$) spin component. Fully-formed (i.e. ungapped) topological surface states (TSSs) are indicated in B and C. We estimate that the Fermi level is at $E-E_{\text{VBM}}=0.68, 0.64, 0.79$ and 0.67 eV for 3ML-WSe₂, (WSe₂)₃/(MoSe₂)₅, 3ML MoSe₂ and (MoSe₂)₃/(WSe₂)₃, respectively.

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References

1. Pham, P.V., Bodepudi, S.C., Shehzad, K., Liu, Y., Xu, Y., Yu, B., and Duan, X. (2022). 2d heterostructures for ubiquitous electronics and optoelectronics: Principles, opportunities, and challenges. *Chemical Reviews* 122, 6514–6613. URL: <https://doi.org/10.1021/acs.chemrev.1c00735>. doi: 10.1021/acs.chemrev.1c00735.
2. Chhowalla, M., Shin, H.S., Eda, G., Li, L.J., Loh, K.P., and Zhang, H. (2013). The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry* 5, 263–275. doi: 10.1038/nchem.1589.
3. Ahn, E.C. (2020). 2d materials for spintronic devices. *npj 2D Materials and Applications* 4, 17. URL: <https://doi.org/10.1038/s41699-020-0152-0>. doi: 10.1038/s41699-020-0152-0.
4. Ciarrocchi, A., Tagarelli, F., Avsar, A., and Kis, A. (2022). Excitonic devices with van der waals heterostructures: valleytronics meets twistrionics. *Nature Reviews Materials* 7, 449–464. URL: <https://doi.org/10.1038/s41578-021-00408-7>. doi: 10.1038/s41578-021-00408-7.
5. Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O.V., and Kis, A. (2017). 2d transition metal dichalcogenides. *Nature Reviews Materials* 2, 17033. URL: <https://doi.org/10.1038/natrevmats.2017.33>. doi: 10.1038/natrevmats.2017.33.
6. Regan, E.C., Wang, D., Paik, E.Y., Zeng, Y., Zhang, L., Zhu, J., MacDonald, A.H., Deng, H., and Wang, F. (2022). Emerging exciton physics in transition metal dichalcogenide heterobilayers. *Nature Reviews Materials* 7, 778–795. URL: <https://doi.org/10.1038/s41578-022-00440-1>. doi: 10.1038/s41578-022-00440-1.
7. Lisi, S., Lu, X., Benschop, T., de Jong, T.A., Stepanov, P., Duran, J.R., Margot, F., Cucchi, I., Cappelli, E., Hunter, A., Tamai, A., Kandyba, V., Giampietri, A., Barinov, A., Jobst, J., Stalman, V., Leeuwenhoek, M., Watanabe, K., Taniguchi, T., Rademaker, L., van der Molen, S.J., Allan, M.P., Efetov, D.K., and Baumberger, F. (2021). Observation of flat bands in twisted bilayer graphene. *Nature Physics* 17, 189–193. URL: <https://doi.org/10.1038/s41567-020-01041-x>. doi: 10.1038/s41567-020-01041-x.
8. Pei, D., Wang, B., Zhou, Z., He, Z., An, L., He, S., Chen, C., Li, Y., Wei, L., Liang, A., Avila, J., Dudin, P., Kandyba, V., Giampietri, A., Cattelan, M., Barinov, A., Liu, Z., Liu, J., Weng, H., Wang, N., Xue, J., and Chen, Y. (2022). Observation of Γ -valley moiré bands and emergent hexagonal lattice in twisted transition metal dichalcogenides. *Phys. Rev. X* 12, 021065. URL: <https://link.aps.org/doi/10.1103/PhysRevX.12.021065>. doi: 10.1103/PhysRevX.12.021065.
9. Nunn, J.E., McEllistim, A., Weston, A., Garcia-Ruiz, A., Watson, M.D., Mucha-Kruczynski, M., Cacho, C., Gorbachev, R.V., Fal’ko, V.I., and Wilson, N.R. (2023). Arpes signatures of few-layer twistrionic graphenes. *Nano Letters* 23, 5201–5208. URL: <https://doi.org/10.1021/acs.nanolett.3c01173>. doi: 10.1021/acs.nanolett.3c01173.
10. Stansbury, C.H., Utama, M.I.B., Fatuzzo, C.G., Regan, E.C., Wang, D., Xiang, Z., Ding, M., Watanabe, K., Taniguchi, T., Blei, M., Shen, Y., Lorcy, S., Bostwick, A., Jozwiak, C., Koch, R., Tongay, S., Avila, J., Rotenberg, E., Wang, F., and Lanzara, A. (). Visualizing electron localization of ws2/wse2 moiré superlattices in momentum space. *Science*

11. Jones, A.J.H., Muzzio, R., Pakdel, S., Biswas, D., Curcio, D., Lanatà, N., Hofmann, P., McCreary, K.M., Jonker, B.T., Watanabe, K., Taniguchi, T., Singh, S., Koch, R.J., Jozwiak, C., Rotenberg, E., Bostwick, A., Miwa, J.A., Katoch, J., and Ulstrup, S. (2022). Visualizing band structure hybridization and superlattice effects in twisted mos2/ws2 heterobilayers. *9*, 015032. URL: <https://dx.doi.org/10.1088/2053-1583/ac3feb>. doi: 10.1088/2053-1583/ac3feb.
12. Devakul, T., Crépel, V., Zhang, Y., and Fu, L. (2021). Magic in twisted transition metal dichalcogenide bilayers. *Nature Communications* *12*, 6730. URL: <https://doi.org/10.1038/s41467-021-27042-9>. doi: 10.1038/s41467-021-27042-9.
13. Guo, Y., Pack, J., Swann, J., Holtzman, L., Cothrine, M., Watanabe, K., Taniguchi, T., Mandrus, D., Barmak, K., Hone, J., Millis, A.J., Pasupathy, A.N., and Dean, C.R. (2023). Superconductivity in twisted bilayer WSe₂. arXiv:2310.11317.
14. Clark, O.J., Neat, M.J., Okawa, K., Bawden, L., Marković, I., Mazzola, F., Feng, J., Sunko, V., Riley, J.M., Meevasana, W., Fujii, J., Vobornik, I., Kim, T.K., Hoesch, M., Sasagawa, T., Wahl, P., Bahramy, M.S., and King, P.D.C. (2018). Fermiology and Superconductivity of Topological Surface States in PdTe₂. *Phys. Rev. Lett.* *120*, 156401. doi: 10.1103/PhysRevLett.120.156401.
15. Clark, O.J., Dowinton, O., Bahramy, M.S., and Sánchez-Barriga, J. (2022). Hidden spin-orbital texture at the $\bar{\Gamma}$ -located valence band maximum of a transition metal dichalcogenide semiconductor. *Nature Communications* *13*, 4147. URL: <https://doi.org/10.1038/s41467-022-31539-2>. doi: 10.1038/s41467-022-31539-2.
16. Riley, J.M., Mazzola, F., Dendzik, M., Michiardi, M., Takayama, T., Bawden, L., Granerød, C., Leandersson, M., Balasubramanian, T., Hoesch, M., Kim, T.K., Takagi, H., Meevasana, W., Hofmann, P., Bahramy, M.S., Wells, J.W., and King, P.D.C. (2014). Direct observation of spin-polarized bulk bands in an inversion-symmetric semiconductor. *Nature Physics* *10*, 835–839. doi: 10.1038/nphys3105.
17. Watson, M.D., Date, M., Louat, A., and Schröter, N.B.M. (2024). Novel electronic structures from anomalous stackings in nbs₂ and mos₂. *Phys. Rev. B* *110*, L121121. URL: <https://link.aps.org/doi/10.1103/PhysRevB.110.L121121>. doi: 10.1103/PhysRevB.110.L121121.
18. Wan, Z., Qian, Q., Huang, Y., and Duan, X. (2024). Layered hybrid superlattices as designable quantum solids. *Nature* *635*, 49–60. URL: <https://doi.org/10.1038/s41586-024-07858-3>. doi: 10.1038/s41586-024-07858-3.
19. Splendiani, A., Sun, L., Zhang, Y., Li, T., Kim, J., Chim, C.Y., Galli, G., and Wang, F. (2010). Emerging Photoluminescence in Monolayer MoS₂. *Nano Letters* *10*, 1271–1275. doi: 10.1021/nl903868w.
20. Mak, K.F., Lee, C., Hone, J., Shan, J., and Heinz, T.F. (2010). Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* *105*, 136805. doi: 10.1103/PhysRevLett.105.136805.

21. Sun, Y., Wang, D., and Shuai, Z. (2016). Indirect-to-direct band gap crossover in few-layer transition metal dichalcogenides: A theoretical prediction. *The Journal of Physical Chemistry C* *120*, 21866–21870. URL: <https://doi.org/10.1021/acs.jpcc.6b08748>. doi: 10.1021/acs.jpcc.6b08748.
22. Bahramy, M.S., Clark, O.J., Yang, B.J., Feng, J., Bawden, L., Riley, J.M., Marković, I., Mazzola, F., Sunko, V., Biswas, D., Cooil, S.P., Jorge, M., Wells, J.W., Leandersson, M., Balasubramanian, T., Fujii, J., Vobornik, I., Rault, J.E., Kim, T.K., Hoesch, M., Okawa, K., Asakawa, M., Sasagawa, T., Eknapakul, T., Meevasana, W., and King, P.D.C. (2018). Ubiquitous formation of bulk dirac cones and topological surface states from a single orbital manifold in transition-metal dichalcogenides. *Nature Materials* *17*, 21–28. URL: <https://doi.org/10.1038/nmat5031>. doi: 10.1038/nmat5031.
23. Zhang, X., Lu, Q., Shen, Z.X., Niu, W., Liu, X., Lu, J., Lin, W., Han, L., Weng, Y., Shao, T., Yan, P., Ren, Q., Li, H., Chang, T.R., Singh, D.J., He, L., He, L., Liu, C., Bian, G., Miao, L., and Xu, Y. (2025). Substantially enhanced spin polarization in epitaxial crte2 quantum films. *Advanced Materials* *37*, 2411137. URL: <https://doi.org/10.1002/adma.202411137>. doi: <https://doi.org/10.1002/adma.202411137>.
24. Watson, M.D., Clark, O.J., Mazzola, F., Marković, I., Sunko, V., Kim, T.K., Rosnagel, K., and King, P.D.C. (2019). Orbital- and k_z -Selective Hybridization of Se $4p$ and Ti $3d$ States in the Charge Density Wave Phase of TiSe_2 . *Phys. Rev. Lett.* *122*, 076404. doi: 10.1103/PhysRevLett.122.076404.
25. Feng, J., Biswas, D., Rajan, A., Watson, M.D., Mazzola, F., Clark, O.J., Underwood, K., Marković, I., McLaren, M., Hunter, A., Burn, D.M., Duffy, L.B., Barua, S., Balakrishnan, G., Bertran, F., Le Fèvre, P., Kim, T.K., van der Laan, G., Hesjedal, T., Wahl, P., and King, P.D.C. (2018). Electronic structure and enhanced charge-density wave order of monolayer vse2. *Nano Letters* *18*, 4493–4499. URL: <https://doi.org/10.1021/acs.nanolett.8b01649>. doi: 10.1021/acs.nanolett.8b01649.
26. Ribak, A., Skiff, R.M., Mograbi, M., Rout, P.K., Fischer, M.H., Ruhman, J., Chashka, K., Dagan, Y., and Kanigel, A. (). Chiral superconductivity in the alternate stacking compound 4hbtas2. *Science Advances* *6*, eaax9480. URL: <https://doi.org/10.1126/sciadv.aax9480>. doi: 10.1126/sciadv.aax9480.
27. Chang, T.R., Lin, H., Jeng, H.T., and Bansil, A. (2014). Thickness dependence of spin polarization and electronic structure of ultra-thin films of mos2 and related transition-metal dichalcogenides. *Scientific Reports* *4*, 6270. URL: <https://doi.org/10.1038/srep06270>. doi: 10.1038/srep06270.
28. Salazar, R., Jamet, M., Vergnaud, C., Pulkkinen, A., Bertran, F., Bigi, C., Minár, J., Ouerghi, A., Jaouen, T., Rault, J., and Le Fèvre, P. (2025). Two-dimensional to bulk crossover of the WSe_2 electronic band structure. *Electronic Structure* *7*, 025008. URL: <https://doi.org/10.1088/2516-1075/addca9>. doi: 10.1088/2516-1075/addca9.
29. Chiang, T.C. (2000). Photoemission studies of quantum well states in thin films. *Surface Science Reports* *39*, 181–235. URL: <https://www.sciencedirect.com/science/article/pii/S0167572900000066>. doi: [https://doi.org/10.1016/S0167-5729\(00\)00006-6](https://doi.org/10.1016/S0167-5729(00)00006-6).
30. Milun, M., Pervan, P., and Woodruff, D.P. (2002). Quantum well structures in thin metal films: simple model physics in reality? *Reports on Progress in Physics* *65*, 99. URL: <https://dx.doi.org/10.1088/0034-4885/65/2/201>. doi: 10.1088/0034-4885/65/2/201.

31. Pan, Y., and Zahn, D.R.T. (2022). Raman fingerprint of interlayer coupling in 2d tmdcs. *12*. doi: 10.3390/nano12223949. 701
702
32. Damascelli, A. (2004). Probing the Electronic Structure of Complex Systems by ARPES. *Physica Scripta 2004*, T109 61. 703
704
33. Kim, H.g., and Choi, H.J. (2021). Thickness dependence of work function, ionization energy, and electron affinity of mo and w dichalcogenides from dft and gw calculations. *Phys. Rev. B 103*, 085404. URL: <https://link.aps.org/doi/10.1103/PhysRevB.103.085404>. doi: 10.1103/PhysRevB.103.085404. 705
706
707
708
34. Hlevyack, J.A., Feng, L.Y., Lin, M.K., Villaos, R.A.B., Liu, R.Y., Chen, P., Li, Y., Mo, S.K., Chuang, F.C., and Chiang, T.C. (2021). Dimensional crossover and band topology evolution in ultrathin semimetallic nite2 films. *npj 2D Materials and Applications 5*, 40. URL: <https://doi.org/10.1038/s41699-021-00218-z>. doi: 10.1038/s41699-021-00218-z. 709
710
711
712
35. Deng, K., Yan, M., Yu, C.P., Li, J., Zhou, X., Zhang, K., Zhao, Y., Miyamoto, K., Okuda, T., Duan, W., Wu, Y., Zhong, X., and Zhou, S. (2019). Crossover from 2d metal to 3d dirac semimetal in metallic ptte2 films with local rashba effect. *Science Bulletin 64*, 1044–1048. URL: <https://www.sciencedirect.com/science/article/pii/S2095927319303172>. doi: <https://doi.org/10.1016/j.scib.2019.05.023>. 713
714
715
716
717
36. Lan, C., Li, C., Ho, J.C., and Liu, Y. (2021). 2d ws2: From vapor phase synthesis to device applications. *Advanced Electronic Materials 7*, 2000688. URL: <https://doi.org/10.1002/aelm.202000688>. doi: <https://doi.org/10.1002/aelm.202000688>. 718
719
720
37. Fridman, N., Feld, T.D., Noah, A., Zalic, A., Markman, M., Devidas, T.R., Zur, Y., Grynspan, E., Gutfreund, A., Keren, I., Vakahi, A., Remennik, S., Watanabe, K., Taniguchi, T., Huber, M.E., Aleiner, I., Steinberg, H., Agam, O., and Anahory, Y. (2025). Anomalous thickness dependence of the vortex pearl length in few-layer nbse2. *Nature Communications 16*, 2696. URL: <https://doi.org/10.1038/s41467-025-57817-3>. doi: 10.1038/s41467-025-57817-3. 721
722
723
724
725
726
38. Riley, J.M., Meevasana, W., Bawden, L., Asakawa, M., Takayama, T., Eknapakul, T., Kim, T.K., Hoesch, M., Mo, S.K., Takagi, H., Sasagawa, T., Bahramy, M.S., and King, P.D.C. (2015). Negative electronic compressibility and tunable spin splitting in wse2. *Nature Nanotechnology 10*, 1043–1047. URL: <https://doi.org/10.1038/nnano.2015.217>. doi: 10.1038/nnano.2015.217. 727
728
729
730
731
39. Xiao, D., Liu, G.B., Feng, W., Xu, X., and Yao, W. (2012). Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett. 108*, 196802. doi: 10.1103/PhysRevLett.108.196802. 732
733
734
40. Latzke, D.W., Zhang, W., Suslu, A., Chang, T.R., Lin, H., Jeng, H.T., Tongay, S., Wu, J., Bansil, A., and Lanzara, A. (2015). Electronic structure, spin-orbit coupling, and interlayer interaction in bulk mos₂ and ws₂. *Phys. Rev. B 91*, 235202. URL: <https://link.aps.org/doi/10.1103/PhysRevB.91.235202>. doi: 10.1103/PhysRevB.91.235202. 735
736
737
738
41. Kim, B.S., Rhim, J.W., Kim, B., Kim, C., and Park, S.R. (2016). Determination of the band parameters of bulk 2h-mx₂ (m = mo, w; x = s, se) by angle-resolved photoemission spectroscopy. *Scientific Reports 6*, 36389. URL: <https://doi.org/10.1038/srep36389>. doi: 10.1038/srep36389. 739
740
741
742

42. Alarab, F., Minar, J., Constantinou, P., Nafday, D., Schmitt, T., Wang, X., and Strocov, V.N. (2023). k-dependent proximity-induced modulation of spin-orbit interaction in MoSe₂ interfaced with amorphous Pb. arXiv:2310.11317. 743
744
745
43. Ernandes, C., Khalil, L., Almagrouk, H., Pierucci, D., Zheng, B., Avila, J., Dudin, P., Chaste, J., Oehler, F., Pala, M., Bisti, F., Brulé, T., Lhuillier, E., Pan, A., and Ouerghi, A. (2021). Indirect to direct band gap crossover in two-dimensional ws₂(1-x)se₂x alloys. npj 2D Materials and Applications 5, 7. URL: <https://doi.org/10.1038/s41699-020-00187-9>. doi: 10.1038/s41699-020-00187-9. 746
747
748
749
750
44. Bychkov, Y.A., and Rashba, E.I. (1984). Oscillatory effects and the magnetic susceptibility of carriers in inversion layers. 17, 6039. URL: <https://dx.doi.org/10.1088/0022-3719/17/33/015>. doi: 10.1088/0022-3719/17/33/015. 751
752
753
45. Kang, J., Tongay, S., Zhou, J., Li, J., and Wu, J. (2013). Band offsets and heterostructures of two-dimensional semiconductors. Applied Physics Letters 102, 012111. URL: <https://doi.org/10.1063/1.4774090>. doi: 10.1063/1.4774090. 754
755
756
arXiv:<https://pubs.aip.org/aip/apl/article-pdf/doi/10.1063/1.4774090/14263519/012111>
46. Park, H., Shin, H., Ali, N., Choi, H., Kim, B.S.Y., Kang, B., Choi, M.S., and Yoo, W.J. (2025). P-type vertical fets realized by using fermi-level pinning-free 2d metallic electrodes. Nano Letters 25, 368–375. URL: <https://doi.org/10.1021/acs.nanolett.4c05136>. doi: 10.1021/acs.nanolett.4c05136. 758
759
760
761
47. Sata, Y., Moriya, R., Masubuchi, S., Watanabe, K., Taniguchi, T., and Machida, T. (2017). N- and p-type carrier injections into wse₂ with van der waals contacts of two-dimensional materials. Japanese Journal of Applied Physics 56, 04CK09. URL: <https://dx.doi.org/10.7567/JJAP.56.04CK09>. doi: 10.7567/JJAP.56.04CK09. 762
763
764
765
48. Clark, O.J., Mazzola, F., Marković, I., Riley, J.M., Feng, J., Yang, B.J., Sumida, K., Okuda, T., Fujii, J., Vobornik, I., Kim, T.K., Okawa, K., Sasagawa, T., Bahramy, M.S., and King, P.D.C. (2019). A general route to form topologically-protected surface and bulk Dirac fermions along high-symmetry lines. Electronic Structure 1, 014002. 766
767
768
769
49. Huang, H., Zhou, S., and Duan, W. (2016). Type-ii dirac fermions in the ptse₂ class of transition metal dichalcogenides. Phys. Rev. B 94, 121117. URL: <https://link.aps.org/doi/10.1103/PhysRevB.94.121117>. doi: 10.1103/PhysRevB.94.121117. 770
771
772
50. Yan, M., Huang, H., Zhang, K., Wang, E., Yao, W., Deng, K., Wan, G., Zhang, H., Arita, M., Yang, H., Sun, Z., Yao, H., Wu, Y., Fan, S., Duan, W., and Zhou, S. (2017). Lorentz-violating type-ii dirac fermions in transition metal dichalcogenide ptte₂. Nature Communications 8, 257. URL: <https://doi.org/10.1038/s41467-017-00280-6>. doi: 10.1038/s41467-017-00280-6. 773
774
775
776
777
51. Noh, H.J., Jeong, J., Cho, E.J., Kim, K., Min, B.I., and Park, B.G. (2017). Experimental realization of type-ii dirac fermions in a pdte₂ superconductor. Phys. Rev. Lett. 119, 016401. URL: <https://link.aps.org/doi/10.1103/PhysRevLett.119.016401>. doi: 10.1103/PhysRevLett.119.016401. 778
779
780
781
52. Li, Y., Xia, Y., Ekahana, S.A., Kumar, N., Jiang, J., Yang, L., Chen, C., Liu, C., Yan, B., Felser, C., Li, G., Liu, Z., and Chen, Y. (2017). Topological origin of the type-II Dirac fermions in PtSe₂. Phys. Rev. Materials 1, 074202. doi: 10.1103/PhysRevMaterials.1.074202. 782
783
784

53. Ghosh, B., Mondal, D., Kuo, C.N., Lue, C.S., Nayak, J., Fujii, J., Vobornik, I., Politano, A., and Agarwal, A. (2019). Observation of bulk states and spin-polarized topological surface states in transition metal dichalcogenide dirac semimetal candidate Nite_2 . *Phys. Rev. B* **100**, 195134. URL: <https://link.aps.org/doi/10.1103/PhysRevB.100.195134>. doi: 10.1103/PhysRevB.100.195134.
54. Jiang, J., Lee, S., Fei, F., Song, F., Vescovo, E., Kaznatcheev, K., Walker, F.J., and Ahn, C.H. (2020). A comprehensive ARPES study on the type-II Dirac semimetal candidate $\text{Ir}_{1-x}\text{Pt}_x\text{Te}_2$. *APL Materials* **8**, 061106. URL: <https://doi.org/10.1063/5.0011549>. doi: 10.1063/5.0011549. arXiv:<https://pubs.aip.org/aip/apm/article-pdf/doi/10.1063/5.0011549/14564647/061106>.
55. Mukherjee, S., Jung, S.W., Weber, S.F., Xu, C., Qian, D., Xu, X., Biswas, P.K., Kim, T.K., Chapon, L.C., Watson, M.D., Neaton, J.B., and Cacho, C. (2020). Fermi-crossing type-II dirac fermions and topological surface states in Nite_2 . *Scientific Reports* **10**, 12957. URL: <https://doi.org/10.1038/s41598-020-69926-8>. doi: 10.1038/s41598-020-69926-8.
56. Nurmamat, M., Ereameev, S.V., Wang, X., Yoshikawa, T., Kono, T., Kakoki, M., Muro, T., Jiang, Q., Sun, Z., Ye, M., and Kimura, A. (2021). Bulk dirac cone and highly anisotropic electronic structure of Nite_2 . *Phys. Rev. B* **104**, 155133. URL: <https://link.aps.org/doi/10.1103/PhysRevB.104.155133>. doi: 10.1103/PhysRevB.104.155133.
57. Chakraborty, A., Fujii, J., Kuo, C.N., Lue, C.S., Politano, A., Vobornik, I., and Agarwal, A. (2023). Observation of highly anisotropic bulk dispersion and spin-polarized topological surface states in Cote_2 . *Phys. Rev. B* **107**, 085406. URL: <https://link.aps.org/doi/10.1103/PhysRevB.107.085406>. doi: 10.1103/PhysRevB.107.085406.
58. Kimar, Y., Kumar, S., Yenugonda, V., Oishi, R., Nayak, J., Chen, C., Singh, R.P., Onimaru, T., Shimura, Y., Ideta, S., and Shimada, K. (). Electronic states in superconducting type-II dirac semimetal: 1-t-pdse_2 . arXiv:2408.15500.
59. Ferreira, P.P., Manesco, A.L.R., Dorini, T.T., Correa, L.E., Weber, G., Machado, A.J.S., and Eleno, L.T.F. (2021). Strain engineering the topological type-II dirac semimetal Nite_2 . *Phys. Rev. B* **103**, 125134. URL: <https://link.aps.org/doi/10.1103/PhysRevB.103.125134>. doi: 10.1103/PhysRevB.103.125134.
60. Nicholson, C., Rumo, M., Pulkkinen, A., Kremer, G., Salzmann, B., Mottas, M.L., Hildebrand, B., Jaouen, T., Kim, T.K., Mukherjee, S., Ma, K., Muntwiler, M., von Rohr, F.O., Cacho, C., and Monney, C. (2021). Uniaxial strain-induced phase transition in the 2D topological semimetal IrTe_2 . *Communications Materials* **2**.
61. Tokura, Y. (2022). Quantum materials at the crossroads of strong correlation and topology. *Nature Materials* **21**, 971–973. URL: <https://doi.org/10.1038/s41563-022-01339-6>. doi: 10.1038/s41563-022-01339-6.
62. Kang, K., Lee, K.H., Han, Y., Gao, H., Xie, S., Muller, D.A., and Park, J. (2017). Layer-by-layer assembly of two-dimensional materials into wafer-scale heterostructures. *Nature* **550**, 229–233. URL: <https://doi.org/10.1038/nature23905>. doi: 10.1038/nature23905.
63. (). doi: 10.25957/flinders.nanoesca3.
64. Perdew, J.P., Burke, K., and Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868. doi: 10.1103/PhysRevLett.77.3865.

65. Kresse, G., and Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186. doi: 10.1103/PhysRevB.54.11169. 827 828 829
66. Kresse, G., and Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775. doi: 10.1103/PhysRevB.59.1758. 830 831
67. Schutte, W., De Boer, J., and Jellinek, F. (1987). Crystal structures of tungsten disulfide and diselenide. *Journal of Solid State Chemistry* **70**, 207–209. URL: <https://www.sciencedirect.com/science/article/pii/0022459687900570>. doi: [https://doi.org/10.1016/0022-4596\(87\)90057-0](https://doi.org/10.1016/0022-4596(87)90057-0). 832 833 834 835
68. Mostofi, A.A., Yates, J.R., Lee, Y.S., Souza, I., Vanderbilt, D., and Marzari, N. (2008). wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **178**, 685–699. doi: <https://doi.org/10.1016/j.cpc.2007.11.016>. 836 837 838
69. Souza, I., Marzari, N., and Vanderbilt, D. (2001). Maximally localized Wannier functions for entangled energy bands. *Phys. Rev. B* **65**, 035109. 839 840
70. Wang, H., Huang, X., Lin, J., Cui, J., Chen, Y., Zhu, C., Liu, F., Zeng, Q., Zhou, J., Yu, P., Wang, X., He, H., Tsang, S.H., Gao, W., Suenaga, K., Ma, F., Yang, C., Lu, L., Yu, T., Teo, E.H.T., Liu, G., and Liu, Z. (2017). High-quality monolayer superconductor nbse2 grown by chemical vapour deposition. *Nature Communications* **8**, 394. URL: <https://doi.org/10.1038/s41467-017-00427-5>. doi: 10.1038/s41467-017-00427-5. 841 842 843 844 845