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Ultrafast dynamics in van der Waals heterostructures

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Abstract

Van der Waals heterostructures are synthetic quantum materials composed of stacks of atomically thin two-dimensional (2D) layers. Because the electrons in the atomically thin 2D layers are exposed to layer-layer coupling, the properties of van der Waals heterostructures are defined not only by the constituent monolayers, but also by the interactions between the layers. Many fascinating electrical, optical, and magnetic properties have recently been reported in different types of van der Waals heterostructures. In this review we focus on unique excited-state dynamics in transition metal dichalcogenide (TMDC) heterostructures. TMDC monolayers are the most widely studied 2D semiconductors, featuring prominent exciton states and accessibility to the valley degree of freedom. Many TMDC heterostructures are characterized by a staggered band alignment. This band alignment has profound effects on the evolution of the excited states in heterostructures, including ultrafast charge transfer between the layers, the formation of interlayer excitons, and the existence of long-lived spin and valley polarization in resident carriers. Here we review recent experimental and theoretical efforts to elucidate electron dynamics in TMDC heterostructures, extending from time scales of femtoseconds to microseconds, and comment on the relevance of these effects for potential applications in optoelectronic and valleytronic/spintronic devices.

Main text

Advances in the isolation and manipulation of atomically-thin sheets of two-dimensional (2D) crystals, starting with the investigations of graphene a decade ago, have ushered in a new era of basic scientific research and technological innovation. 2D layers with diverse properties can now be prepared separately and then stacked together to form new types of quantum materials, known as van der Waals (vdW) heterostructures. The ability to combine materials with monolayer precision enables the design and creation of functional 2D materials that do not exist in nature. Today we have at our disposal a wide variety of atomically thin 2D layers, ranging from semiconducting MoS₂ and insulating hexagonal boron-nitride (h-BN) to magnetic CrI₃ and superconducting NbSe₂, that can be stacked one upon the other. Since the electrons in atomically thin layers are exposed, different quantum states found in the individual layers can interact and couple to one another in ways that are not possible in other systems.

VdW heterostructures constitute a vast family of new quantum materials, since they are defined not only by the combination of constituent monolayer materials, but also by the stacking sequence and relative crystallographic alignment of the layers. Further control of physical properties in 2D vdW heterostructures can be achieved through the application of electrostatic gating and fields, as well as substrate and strain engineering. Many fascinating physical phenomena have been reported in different vdW heterostructures, as exemplified by transport measurements revealing Hofstadter butterfly states, fractional Chern insulators, gate-tunable Mott insulators, unconventional superconductivity, etc¹⁻⁷. In addition to electrical transport, there has also been great progress in the study of the optical properties and excited-state dynamics in vdW heterostructures. Here we review the new dynamical phenomena that emerge in semiconducting vdW heterostructures composed of stacked transition metal dichalcogenide (TMDC) layers. We focus our discussion on TMDC heterostructures, since the individual TMDC layers, with their many distinctive and intriguing properties, have already been well characterized and provide a strong basis for understanding the emergent new properties of heterostructures.

TMDC semiconductors (MX₂ layers with 2H symmetry and M = Mo, W; X = S, Se, Te) exhibit direct gaps at monolayer thickness. They feature strong light-matter interactions and dramatically enhanced electron-electron interactions, with the optical properties largely defined by exciton states. The exciton binding energies in monolayer TMDCs are hundreds of meV— as much as two orders of magnitude larger than in typical bulk semiconductors like silicon or GaAs^{8,9}. In addition, TMDC monolayers provide a platform to investigate and control the valley degree of freedom — often designated as valley pseudospin — associated with the energetically degenerate K and K' valleys and accessible optically through the presence of valley circular dichroism. The valley pseudospin in TMDC is, moreover, coupled to the electron/hole spin due to strong spin-orbit interactions^{10,11}.

Understanding the dynamic interplay and evolution of the charge, spin, and valley excitations in vdW heterostructures is of fundamental scientific interest. It is also of central importance for many potential applications of TMDC materials in optoelectronics, spintronics, and valleytronics. The dissociation of optically excited excitons into free carriers is, for example, critical for photovoltaic devices, while the ability to control and stabilize valley polarization is essential for valleytronic applications. The formation of vdW heterostructures in TMDC layers can profoundly affect their excited-state dynamics, ranging from the dissociation of intralayer excitons and the formation of interlayer excitons to the relaxation of spin and valley polarization. The use of vdW heterostructures provides a powerful platform to control and optimize the dynamic response of the constituent materials. In this review, we

survey recent progress in probing electron dynamics, extending from femtoseconds to microseconds, in TMDC heterostructures. On short time scales ($\lesssim 1$ ps), the dynamics is dominated by the charge transfer and energy relaxation processes in the heterostructure. On longer time scales ($\gtrsim 1$ ps), the recombination of interlayer excitons and relaxation of the spin and valley degrees of freedom become relevant. The rate of these processes can vary by orders of magnitude depending on the configuration, temperature, and doping of the heterostructure. We will also touch upon the dynamics of lateral transport of spin and valley polarization in TMDC heterostructures. We describe the physical mechanisms that underlie the different types of dynamic response in TMDC heterostructures and distinguish the behavior from that of the constituent layers, as well as mention briefly the implications for potential new technologies.

Band alignment in TMDC heterostructures

In describing the single-particle electronic states in a vertical TMDC heterostructure, most authors in the literature consider the states to be largely localized within the individual layers. This approximation holds well for electronic states close to the band gap due to unusually weak interlayer coupling in TMDCs at the relevant K and K' points in the Brillouin zone (Fig. 1a)¹². Therefore one can directly examine the relative energy difference, or band alignment, of material-specific electronic band extrema, just as is commonly done for heterostructures and quantum wells based on bulk materials^{13,14}. An important distinction for atomically thin layers is that the concept of band bending near an interface does not apply¹⁵.

Semiconductor heterostructures can have different types of band alignment depending on the energy difference of the conduction and valence band extrema in the constituent layers (Fig. 1b)^{13,14}. The lowest-lying states for electrons and holes reside in the same layer for a type-I heterostructure¹⁶, but are separated in different layers for a type-II heterostructure^{13,17}. Further offsets in energy could, in principle, lower the conduction band minimum (CBM) of one layer to a position below the valence band maximum (VBM) of the other layer, yielding a type-III heterostructure¹⁸.

The type of band alignment has profound effects on the excited-state dynamics in a vdW heterostructure. In a type-I heterostructure carriers can only flow from the layer with the larger band gap to the layer with the smaller band gap (assuming that they do not have excess energy greater than the band offsets). The same applies to energy transfer through the exchange of virtual photons. In a type-II heterostructure, on the other hand, electrons accumulate in the layer with the lower CBM, while holes accumulate in the other layer^{17,19,20}. Energy transfer can, however, still occur from the larger-gap to the smaller-gap material²¹.

There have been numerous theoretical studies of the band alignment in TMDC heterostructures^{13,14,18,22-24}. The result of one recent calculation is shown in Fig. 1c. Many of the theoretical studies make use of DFT or related methods and cannot accurately account for the effects of doping (Fermi level difference), dielectric screening, and excitonic interactions²⁵. They provide nonetheless guidelines for realizing specific types of heterostructures and combination of band gaps. Although theoretical studies are advancing rapidly, at present a definitive determination of heterostructure band alignment must rely on experiment^{26,27}.

127 In the following, we describe experimental findings concerning the dynamics of charge and energy
 128 transfer for representative TMDC heterostructures, followed by a summary of the relevant theoretical
 129 studies.
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131
 132 **Fig. 1 Band alignment in vertical vdW heterostructures of TMDCs.** (a)
 133 Calculated electronic states in a MoS₂/WS₂ vertical heterostructure,
 134 showing layer-localized states near the band edges at the K point¹². (b)
 135 Schematic of allowed charge transfer in heterostructures with type-I (top)
 136 and type-II (bottom) band alignment¹⁶. (c) Calculated band-edge energies
 137 for various TMDCs²² based on different theoretical treatments: DFT-PBE
 138 (blue) and G₀W₀ (pink).

139 Charge transfer and energy transfer in TMDC heterostructures - Experiment

140 Following the predictions of type-II band alignment in TMDC heterostructures, several experimental
 141 studies were reported that aimed (among other goals) to validate these theoretical results by probing
 142 the associated charge transfer (CT) or energy transfer (ET) processes. Vertical heterostructures have
 143 been examined for various material combinations prepared with different fabrication methods,
 144 including stacking of layers exfoliated from bulk crystals and from layers grown by chemical vapor
 145 deposition (CVD), as well as heterostructures grown directly by CVD.

146
 147 Ultrafast optical measurements using pump-probe spectroscopy provide the possibility of accessing
 148 charge and energy transfer processes with femtosecond (fs) time resolution. In initial experiments,
 149 Hong *et al.* examined the dynamics of the MoS₂/WS₂ heterostructure. Following excitation by an
 150 ultrafast laser pulse resonant with the lower-energy MoS₂ A exciton, they observed a transient change
 151 in reflectivity near the *higher-energy* WS₂ exciton (Fig. 2a)¹⁹. Based on theoretical predictions of type-
 152 II band alignment of the two materials, this transient response was identified as arising from CT of a
 153 hole from the MoS₂ monolayer to the WS₂ monolayer. By deconvolving the instrument response from
 154 the rise-time of the signal, the authors were able to provide an upper limit of 50 fs for the charge
 155 transfer time. Ceballos *et al.* observed similar dynamics in a heterostructure of MoS₂/MoSe₂, without
 156 spectrally resolving the reflection of the probe²⁸. They concluded, based on the theoretically predicted
 157 band alignment, that electrons were transferred from MoSe₂ to MoS₂. In addition, when exciting both
 158 layers (using excitation resonant with the higher-energy exciton feature in MoS₂) and comparing the

transient reflectivity signal of the monolayers to that of the heterostructure, the authors identified the presence of hole transfer in the opposite direction, *i.e.*, from MoS₂ to MoSe₂ (Fig. 2b).

Following these first experimental investigations, several groups examined the nature of the ultrafast CT for different types of heterostructures under different conditions. Heo *et al.* compared CVD-grown and manually stacked WS₂/MoS₂ heterostructures with a focus on the dependence on the relative (twist) angle of the two constituent lattices²⁹. Measuring the transient transmission of the probe signal, they did not resolve differences in the rise time of the signal associated with CT, but did observe a pronounced difference in the decay times of the signal. Wang *et al.* examined several WSe₂/WS₂ heterostructures composed of CVD-grown layers mechanically stacked with different twist angles^{20,29}. Using pump-probe measurements, together with steady-state techniques such as reflection contrast spectroscopy, they showed the same ultrafast signature from the onset of CT, either from electrons moving from WSe₂ to WS₂ or from holes traveling in the opposite direction. They concluded that interlayer CT takes place within 450 fs, close to the duration of the pump pulses in their experiment, and does not exhibit measurable sensitivity to the twist angle. Further reinforcing this conclusion, Zhu *et al.* explored deterministically aligned heterostructures of mechanically exfoliated MoS₂ and WSe₂; they found that the CT signal appears within 40 fs regardless of twist angle (Fig. 2c)³⁰. On the other hand, the time scale of the decay was varied with the twist angle, but without any clear trend. Ji *et al.* reported a similar CT rise time for stacks of CVD-grown MoS₂ and WS₂ (Ref³¹). Such rapid interlayer CT irrespective of crystal orientation (and thus crystal momentum) is somewhat unintuitive. Chen *et al.* probed intraband transitions in a heterostructure using infrared light and suggested a potential explanation based on the rapid formation of “hot” interlayer excitons³². Additional theoretical investigations are summarized in the next section.

Fig. 2 Experimental studies of ultrafast charge transfer in vertical TMDC heterostructures. (a) Schematic and energy-resolved transient absorption spectra of a MoS₂/WS₂ heterostructure, excited by an optical pulse near the lower-energy MoS₂ A exciton feature, indicating hole transfer¹⁹. (b) Schematic and time-resolved differential reflection of a MoS₂/MoSe₂ heterostructure (blue) and of monolayer MoS₂ (purple), excited by an optical pulse above the band gaps of both materials, indicating both electron and hole transfer²⁸. (c) Charge transfer (red shading) and recombination (blue) times in heterostructures of MoS₂ and WSe₂ with different twist angles, as indicated³⁰. (d) Differential reflection at the energy of the MoS₂ A exciton following excitation at the energy of the MoSe₂ A exciton in a MoSe₂/WS₂/MoS₂ trilayer heterostructure³³. (e) PL quenching³⁴ in MoS₂/WSe₂ and (f) broadening of the features absorption features³⁵ in a MoS₂/WS₂ heterostructure compared to the response of the separated monolayers.

Further demonstrating its robustness, the signature of ~ps electron transfer was observed in a trilayer heterostructure where monolayers of MoSe₂ and MoS₂ were separated by a monolayer WS₂ (Fig. 2d, Ref.³³). The authors suggested that such rapid CT across multiple materials is coherent, rather than sequential.

CT dynamics was also revealed in investigations of the coupling between pairs of TMDC layers. CT in a MoS₂/MoTe₂ heterostructure was identified using pump-probe experiments³⁶, leading to the suggestion of MoTe₂ as a good electrical contact for other semiconducting TMDCs and metals. Later, cascaded transfer of electrons and holes across several TMDCs heterostructures was invoked to explain correlated blinking observed in the photoluminescence (PL) in those stacks³⁷.

In addition to these time-resolved pump-probe measurements, CT between two TMDC layers in a heterostructure has been inferred from quenching of the photoluminescence of the constituent monolayers^{19,20,28-33,38-40} and by broadening of the resonant features in the monolayers in optical absorption measurements^{20,35}, both phenomena arising as a consequence of the presence of additional relaxation channels in the heterostructures. A reduction in the PL intensity by factor of a few tens to a few hundreds has commonly been observed (Fig. 2e)^{19,34}. This suggests a corresponding ratio for the charge transfer time compared to the population lifetime in the isolated material. Assuming the latter to be a few hundred picoseconds for excitons in monolayer TMDCs⁴¹ at room temperature, we estimate a CT time of ~1 ps, somewhat longer than measured by pump-probe techniques. This discrepancy can be explained as the result of a small fraction of the heterostructure exhibiting poor contact between the layers, thus yielding reduced PL quenching compared to that of the ideal structure. In optical absorption measurements, linewidth broadening of heterostructures compared with that of the separate monolayers has been reported and used to estimate non-radiative decay rates comparable to those deduced from pump-probe experiments (Fig. 2f)³⁵. Extrinsic factors, such as strain introduced in fabricating the heterostructure, can potentially also play a role. The extremely rapid (few femtosecond) relaxation times inferred for high-lying states may, however, remain difficult to probe directly in the time domain, but is easily observable by lineshape analysis.

Another dynamic process that may compete with CT is energy transfer (ET). In this latter process, an exciton created in one layer recombines, and the released energy creates an exciton in the other layer. Kozawa *et al.* reported evidence for such a process in a MoSe₂/WS₂ heterostructure (Ref ²¹) on the basis of a measured enhancement of PL from the MoSe₂ feature under excitation resonant with the WS₂ optical band gap. Recently, ET was also identified in heterostructures of MoS₂ and WS₂ separated by insulating layers of h-BN⁴². In these structures, PL quenching from the heterostructure was reduced, or even become PL enhancement, upon increasing the thickness of the h-BN spacer. This was interpreted as an ET process between B excitons in MoS₂ and A excitons in WS₂. The dependence of the enhancement on spacer thickness, with an optimum of PL enhancement for ~5 layers of h-BN and subsequent reduction of this effect with increasing layer thickness, is compatible with the predicted trend for a dipole-dipole interaction. This highlights the major difference between ET and CT processes: While the latter requires intimate coupling of the two constituent monolayers, the former, originating in dipole-dipole interactions, can act at greater distances and across insulating spacers. Although this difference between the processes is clear, there is currently little direct experimental information on the absolute rates of energy transfer for TMDC layers and in what regimes and under what conditions energy transfer competes with charge transfer.

Charge transfer and energy transfer in TMDC heterostructures – Interpretation and theory

Since most experiments have excited and probed excitonic resonances of the constituent layers, it has often been assumed that CT occurs between their direct band-edge (K/K' valley) states. Band structure calculations have shown that the K/K' states are localized around the central layer of metal atoms and have weak interlayer interactions. On the other hand, for states of different momentum,

such as in the Γ or Q valleys, the interlayer coupling may be significantly stronger. One consequence of this difference is the transition from indirect to direct band gap upon thinning TMDCs to the monolayer limit: the bulk CBM in the Q valley, more affected by interlayer coupling, lies above the K valley in monolayers^{43,44}. For the same reason, the K-valley states are not expected to show such rapid interlayer charge transfer. This contradiction with experiment is further heightened by the apparent independence of CT on twist angle and lattice mismatch, the factors that dictate the momentum difference between the initial and final states, as well as its insensitivity to temperature. Here we briefly survey some of the approaches presented in the literature to identify the mechanism responsible for the very efficient CT processes observed experimentally in vertical TMDC heterostructures.

Zhu *et al.*, following considerations relevant for CT processes in molecular systems, have pointed out the possible role of localization in bridging the momentum mismatch⁴⁵. The electrostatic attraction between the optically excited electron and hole, which leads to the formation of tightly bound excitons, gives rise to a distribution of momenta for the charge carriers across a significant range wavevectors in the Brillouin zone (BZ). This situation could explain the apparent lack of momentum conservation in the observed CT process. However, it is unclear with this effect alone could supply the large momentum required for CT in heterostructures with large twist angles³⁰. In addition, for excitation substantially above the band gap, it is unclear whether exciton formation occurs prior to charge transfer²⁸.

Several groups have also employed numerical calculations using molecular dynamics (MD) and time-dependent density-functional theory (TD-DFT) to elucidate the mechanism for interlayer charge transfer. Since accurately accounting for the effect of excitons is computationally demanding, these calculations have focused on the transfer of free charge carriers from one monolayer to its neighbor. Wang *et al.* described a process of transferring holes directly between the K valleys of the two layers mediated by the electric dipole interaction of the initial and final states, which enhances the coupling between the states to above a critical level for collective charge transfer⁴⁶. In this description, both twist angle and temperature have a significant influence on the transfer rate⁴⁶. Zhang *et al.* pointed out the significance of such dipole coupling between specific states in the vicinity of the K valley and highlighted the expected twist-angle dependence of the CT rate⁴⁷. Additionally, the authors argue that the omission of excitonic effects for above gap excitation may not be significant if the time scales for CT and exciton formation are comparable. (This argument is, however, problematic for explaining CT from excitons created directly by resonant excitation.)

A slightly different picture is presented by Long *et al.*⁴⁸ and by Li *et al.*⁴⁹ for CT processes in MoSe₂/MoS₂ and MoS₂/WS₂ systems, respectively. They propose that holes and/or electrons undergo transfer from one layer to the other due to mixing between the electronic states near the K point of both layers^{48,49}: the states into which the charge carriers are optically injected are coherently mixed (and therefore delocalized) across the two layers, so that CT need only to be driven by an intralayer relaxation process to the K-valley, mediated by phonon emission. In this model, the coupling relies on specific layer orientations to facilitate the state mixing in the heterostructure. The discrepancy between this requirement and the apparent twist-angle independence of CT in experiments is explained in terms of changes in the relative local atomic positions in the two layers across the moiré pattern of the heterostructure^{50,51}. Regardless of the twist angle of the layers, such lateral inhomogeneity provides regions where the coupling between the layers is strong³¹. In all of the above scenarios, phonons are necessary for the completion of the CT process, but not for its initiation.

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Recent work has also explored a more direct role for phonons in the initiation of CT. Wang *et al.* considered momentum-conserving charge transfer between the layers in various regions of the BZ, including at the K, Q and Γ points for different twist angles and degrees of lattice mismatch⁵², as shown in Fig. 3a-d. The proposed mechanism involves scattering by phonons from the K valley to the Γ valley (for holes) or to the Q valley (for electrons), regions where the interlayer coupling is strong and interlayer charge transfer is rapid. After charge transfer, scattering with another phonon would bring the charge carriers back to the K-valley. For intralayer scattering within 20 fs, the entire charge transfer process would occur in less than 100 fs, as observed experimentally. A similar scheme was developed by Zheng *et al.* using a numerical MD TD-DFT calculation, although without accounting for inhomogeneities from the moiré pattern⁵³. These theories better match the observed twist-angle independence, as the coupling around the Γ and Q points is not sensitive to the layer orientation. The expected temperature dependence of this mechanism is also weak, as it only requires emission of phonons to dissipate the excess energy available from the transfer. This general mechanism has been adopted in the interpretation of recent experiments related to CT processes^{30,33,39}.

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Fig. 3 Theoretical concepts explaining the robust and ultrafast nature of CT in TMDC heterostructures⁵². (a) Schematic representation of phonon mediated electron transfer. (b) The same for hole transfer. (c) Top view of the twisted BZ of the two layers, where electron transfer between the K-points is mediated by phonon coupling to the Q-point. (d) The same for hole transfer, mediated in this case by the coupling to the Γ -point.

324 Spin and valley dynamics in TMDC heterostructures

325 The previous sections addressed carrier dynamics in TMDC heterostructures on the ultrafast time
326 scale ($\lesssim 1$ ps) relevant for interlayer charge transfer in systems with type-II band alignment. In the
327 following section, we focus on spin and valley relaxation dynamics in TMDC heterostructures, which
328 take place on considerably longer time scales.

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330 Within a TMDC monolayer, there are two distinct relaxation processes to consider. First, the
331 population decay of optically excited excitons has a characteristic time scale of few picoseconds to
332 nanoseconds, depending on choice of material, sample preparation, temperature, etc.⁵⁴⁻⁵⁸. Second,
333 the exciton spin-valley lifetime, which determines how long information can be stored in the spin-
334 valley degree of freedom, has been found to be a few picoseconds in isolated monolayer TMDCs⁵⁹⁻⁶³.
335 Both the population and the spin-valley lifetimes in type-II heterostructures, where the electrons and
336 holes reside in different layers after the rapid initial charge transfer process, can differ markedly from
337 the corresponding lifetimes in isolated monolayers.

338
339 Below we review recent experimental results on dynamics on the pico-to-micro-second time scale in
340 heterostructures and show that both the population lifetime and the spin-valley lifetime can be
341 significantly longer than for the monolayer case. We then summarize recent efforts towards
342 understanding the physical mechanisms of the corresponding intervalley scattering processes. Finally,
343 we discuss the spatio-temporal dynamics of spin and valley polarization in TMDC heterostructures.

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345 Long spin and valley lifetime in TMDC heterostructures

346 Traditional electronic devices are based on the manipulation of electron charges in the real space.
347 Using other electron degrees of freedom as the information carrier, such as spin and valley, can
348 potentially overcome fundamental limits of speed and power consumption, giving rise to intriguing new
349 concepts in spintronics and valleytronics. A long spin/valley lifetime is necessary to ensure that the
350 spin/valley information will be maintained in the idle state and can persist long enough to be
351 processed. We note that the valley lifetime discussed here should not be confused with the valley
352 depolarization time: the former can originate from different mechanisms, including the population
353 decay of the valley information carriers, while the latter only describes the intervalley scattering
354 process.

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356 TMDCs offer a promising platform for spintronic and valleytronic applications, owing to several
357 attractive properties of these materials. The valley-dependent optical selection rule allows for
358 convenient creation, manipulation, and detection of excitons in specific valleys with circularly polarized
359 light⁶⁴⁻⁶⁶. Furthermore, the spin-valley locking effect suggests that a very long spin-valley lifetime is
360 possible because intervalley scattering of electrons or holes requires both a large momentum change
361 from K to K' and a simultaneous spin flip^{10,11}. However, several groups have measured exciton spin-
362 valley dynamics using time-resolved Kerr rotation (TRKR)⁵⁹⁻⁶³, and the spin-valley lifetime was found
363 to be rather short, ranging from one to few picoseconds, even at low temperatures. This counter-
364 intuitive observation was later explained as a consequence of the exchange interaction between
365 excitons in the two valleys⁶⁷⁻⁷⁰: a bright exciton always has total momentum and spin of zero and
366 therefore does not require any change in momentum or spin to scatter to the other valley as an intact
367 exciton. This reduced spin-valley lifetime of excitons in TMDC monolayers significantly limits their use
368 in carrying spin-valley information.

369

370 A general strategy for improving the spin-valley lifetime in TMDCs is to eliminate the exciton exchange
371 interaction by converting excitons into other excitations that serve as alternative carriers of valley
372 information. An additional figure of merit, the conversion efficiency, must be introduced to quantify the
373 final valley imbalance created from each optically excited exciton. To avoid loss of valley information
374 during conversion, the time scale of the conversion process (*i.e.*, the exciton population lifetime) must
375 be comparable to or shorter than the picosecond spin-valley lifetime of excitons. In monolayer TMDCs,
376 several candidates have been considered as the alternative information carriers, including trions⁷¹⁻⁷³,
377 dark excitons^{74,75}, biexcitons^{76,77}, and resident carriers⁷⁸⁻⁸¹. For example, Fig. 4a,b show the valley
378 dynamics of trions and resident electrons probed by TRKR measurement. Unlike bright excitons,
379 these excitations have non-zero total momentum and/or total spin, and therefore will not suffer from
380 rapid spin-valley relaxation through the exchange interaction. Their spin-valley lifetimes at low
381 temperatures range from tens of picoseconds to a microseconds, but the conversion efficiency from
382 the initially generated exciton has rarely been characterized. However, since the exciton population
383 lifetime is comparable to or longer than the exciton spin-valley lifetime in these cases, the valley
384 conversion efficiency is likely to be considerably less than unity.

385

386 On the other hand, the interlayer charge transfer process in type-II heterostructures provides an
387 attractive mechanism to break intralayer excitons on the femtosecond time scale. As discussed above,
388 the ultrafast charge transfer process occurs very rapidly, typically within ~50 fs, in TMDC
389 heterostructures^{19,82}. Because this time scale is much faster than exciton spin-valley relaxation, the
390 loss of spin-valley information during the conversion process is expected to be minor.

391

392 In nearly aligned heterobilayers, electrons and holes can form bright interlayer excitons after the
393 charge transfer process^{28,40,83}. Rivera *et al.* observed 40% positive circular helicity from interlayer
394 exciton emission in WSe₂/MoSe₂ bilayer and measured a spin-valley lifetime of a few nanoseconds in
395 a time-resolved photoluminescence (TR-PL) study⁸⁴, as shown in Fig. 4c. The significantly longer
396 spin-valley lifetime of interlayer excitons can be understood by noting that the electron and hole
397 wavefunctions have much smaller overlap in interlayer excitons compared to intralayer excitons; they
398 will therefore have a weaker exchange interaction and exhibit slower recombination processes (both
399 radiative and non-radiative).

400

401 Recently, there has been increasing research interest in the nature of the interlayer exciton state and
402 the origin of the circular helicity of emission in nearly aligned heterostructures. Hsu *et al.* reported
403 negative circular helicity of interlayer exciton emission⁸⁵ in WSe₂/MoSe₂ bilayer, while Ciarrocchi *et al.*
404 and Hanbicki *et al.* observed two separate interlayer exciton emission peaks with opposite signs of
405 helicity^{86,87}. Meanwhile, various configurations of interlayer excitons have been proposed as the
406 emitting state, including spin singlet zero-momentum excitons^{84,88}, spin-triplet zero-momentum
407 excitons⁸⁹, and finite-momentum excitons^{90,91}. The rich set of observations originates in part from the
408 complex conduction band structure in the WSe₂/MoSe₂ bilayer, where electron states of spin up and
409 spin down, and at K and Q valleys, are all close in energy. Furthermore, the real-space distribution of
410 interlayer excitons when a moiré pattern is present can further modify the optical selection rules^{92,93}.
411 The exact mechanisms behind these interesting observations are yet to be fully understood.

412

413 An alternative approach involves using single-particle states, such as holes in WSe₂ to carry valley
414 information in the heterostructure. Because the momentum match between electrons and holes
415 (required for efficient exciton emission) is not relevant in this approach, a large-twist-angle bilayer is

preferred to separate electrons and holes in momentum space and further reduce their exchange interaction and recombination rate. Kim *et al.* measured the spin-valley lifetime of holes in WSe₂/MoS₂ heterostructures using circularly polarized pump-probe spectroscopy⁹⁴. Figure 4d shows the measured decay dynamics of the total hole population and valley-polarized hole population in the WSe₂ layer at a temperature of 10 K. Both the population lifetime and the spin-valley lifetime of holes are around one microsecond, indicating that the decay of the spin-valley imbalance occurs primarily through population loss. On the other hand, the valley polarization remains almost a constant for a few microseconds, from which one can extract a valley depolarization time (or intervalley scattering time) exceeding 40 μ s. The other critical figure of merit, the conversion efficiency, was also determined experimentally to be close to unity for valley-polarized holes⁹⁴. The nearly ideal conversion efficiency is consistent with an interlayer charge transfer process that is far faster than intervalley scattering processes.

The spin-valley lifetime of resident holes in the heterostructure can be further improved by tuning the carrier concentration. Figure 4e summarizes the doping-dependent spin-valley lifetime of holes in a WSe₂/WS₂ heterostructure (red circles), as compared to the population lifetime of holes (blue triangles)⁹⁵. In charge neutral and electron-doped heterostructures, the spin-valley lifetime is similar to the population lifetime; however, for hole-doping, the spin-valley lifetime becomes orders of magnitude longer than the population lifetime. This doping dependence is a consequence of the interlayer electron-hole recombination process, as shown in Fig. 4f,g. For electron-doped or charge neutral heterostructures (Fig. 4f), all of the holes in WSe₂ are pump-generated excess holes. Therefore, when hole population decays to zero due to interlayer electron-hole recombination, no holes -- and certainly no valley-polarized holes -- remain in the WSe₂. The valley lifetime is then limited by the lifetime of the total hole excess. On the other hand, if the original hole density is much greater than the photo-generated density, excess electrons in WS₂ will recombine with holes from both valleys of WSe₂ with nearly equal probability (Fig. 4g). Consequently, a pure spin-valley imbalance (*i.e.*, equal excess and deficiency of holes in the K and K' valley) is generated, the lifetime of which can be much longer than the population lifetime and has been found to exceed 20 μ s. Furthermore, the decrease of spin-valley imbalance is negligible during the population decay, and the overall efficiency of this two-step conversion process can approach 100%⁹⁵.

Fig. 4 Dynamics of spin-valley information carriers in TMDC materials. (a-b) Spin-valley dynamics of trions (a)⁷² and resident electrons (b)⁸¹ in monolayer TMDC materials under different external magnetic fields as probed by time-resolved Kerr rotation measurements. A spin-valley lifetime of few to tens of nanoseconds is observed at low fields. (c) Time-resolved photoluminescence in a nearly aligned WSe₂/MoSe₂ heterobilayer for the same (black) and opposite (red) circularly polarized excitation, revealing a valley lifetime of few nanoseconds⁸⁴. (d) Decay dynamics of the valley-polarized hole population, the total hole population, and the valley polarization in a large-twist-angle WSe₂/MoS₂ heterostructure at charge neutrality⁹⁴. (e) Summary of the hole population (blue) and spin-valley (red) lifetimes as a function of carrier concentration in a large-twist-angle WSe₂/WS₂ heterostructure⁹⁵. (f-g) Schematic illustration of the interlayer electron-hole recombination process in electron-doped (f) and hole-doped (g) heterostructures.

Potential mechanism behind intervalley scattering

As discussed in the previous sections, the spin-valley lifetime can be limited either by the population lifetime or by the intervalley scattering process. The first limitation can be removed for valley-polarized holes in hole-doped heterostructures, making them promising candidates for spin-valley information carriers. Furthermore, directly probing hole dynamics provides relatively clean information about the decay mechanism owing to the simplicity of the valence band maximum. This configuration thus provides a valuable platform for understanding intervalley scattering processes in TMDC materials.

Figure 5a shows the decay dynamics of valley polarization at different temperature for holes in WSe₂/MoS₂ heterostructures, with the valley depolarization lifetime summarized in Fig. 5b (Ref. ⁹⁴).

479 The depolarization lifetime changes from 10 ns at 77 K to above 40 μ s at 10 K, which roughly follows
 480 a thermally activated rate: $\tau \sim \exp\left(\frac{\Delta}{k_B T}\right)$, with k_B denoting the Boltzmann constant and $\Delta \sim 20$ meV.
 481
 482

483
 484 **Fig. 5 Potential origin of intervalley scattering in WSe₂/MoS₂**
 485 heterostructures. (a) Temperature-dependent decay dynamics of valley
 486 polarization. (b) Temperature dependence of the intervalley scattering
 487 time. The process can be described as thermally activated⁹⁴. (c)
 488 Resonant Raman spectra of single-layer MoS₂ show particularly strong
 489 second-order Raman signals (peaks p1 to p4) for excitation around 2.0
 490 eV through a doubly resonant Raman (DRR) process involving K point
 491 phonons, as illustrated in (d)⁹⁶.
 492

493 The inter-valley scattering of holes in WSe₂ requires a large momentum change and a simultaneous
 494 spin flip. However, due to the strong spin-orbit coupling in WSe₂, the picture of electrons and holes
 495 with perfectly defined up and down spin states in the K and K' valleys, respectively, is not strictly valid
 496 for states away from the K and K' points. Therefore, inter-valley scattering of carriers near, but not
 497 exactly at K and K' points is allowed. This process, often designated as the Elliott-Yafet mechanism,
 498 has a characteristic temperature dependence of

$$\tau_{EY}^{-1} \sim T^2 \tau_p^{-1},$$

499 where τ_p is the momentum scattering lifetime for a spin-conserving process. The T^2 -dependence
 500 originates from the fact that at higher temperature, thermally excited carriers are further away from
 501 band minima (K or K') and will therefore scatter more efficiently. However, the predicted T^2
 502 dependence does not describe the strong observed variation with temperature, which presumably
 503 reflects from the temperature dependence of τ_p^{-1} . Indeed, a thermally activated temperature
 504 dependence is expected for phonon-assisted intervalley scattering at low temperatures, and the
 505 experimental activation energy of ~ 20 meV agrees with WSe₂ phonon energy (at the K-point) required
 506 for intervalley scattering⁹⁶. Phonon-assisted intervalley scattering, accompanied by spin flip through
 507 the Elliott-Yafet mechanism, can thus account for the observed spin-valley depolarization of holes.
 508

The important role of K-point phonons in intervalley scattering is also supported by a recent resonant Raman study⁹⁶, which reveals second-order Raman signals (peaks p1 to p4 in Fig. 5c) assigned to K-point phonons through a doubly resonant Raman (DRR) scattering process. This observation suggests a strong interaction between charge carriers and K-point phonons, which dramatically enhances their second-order Raman signals through the DRR process illustrated in Fig. 5d.

Spin-valley transport in TMDC heterostructures

The efficient generation of pure spin-valley imbalance in hole-doped WSe₂/WS₂ heterostructures provides a convenient way to create pure spin-valley current (Fig. 6a), which lies in the heart of spin-valley-tronic devices. Jin *et al.* performed space-and-time-resolved pump-probe spectroscopy to track the evolution of the spin-valley imbalance and to image the flow of pure spin-valley diffusion currents (Fig. 6b). Figure 6c shows experimental results for a hole-doped WS₂/WSe₂ heterostructure at an initial electrostatic hole doping of $p_0 = 1 \times 10^{12} / \text{cm}^2$. At zero time delay, the spin-valley imbalance matches the pump beam spatial profile (half-width of $\sim 1.5 \mu\text{m}$); the signal is negligible for a pump-probe separations greater than $3 \mu\text{m}$, as expected based on the convolution with probe spatial profile. At finite delay time, the spin-valley imbalance diffuses out of the excitation region, generating a pure spin-valley current. This leads to a strong decrease and increase of signal, respectively, in regions near and far away from the pump beam. The spin-valley current propagates to distances over $8 \mu\text{m}$ within 800 ns. Such direct imaging of the experimental spin-valley current flow (Fig. 6c) allows us to determine important physical parameters by comparison with a diffusion-decay model (Fig. 6d). We infer a diffusion constant of $D = 0.2 \text{ cm}^2/\text{s}$, a spin-valley lifetime of $\tau = 20 \mu\text{s}$, and deduce a spin-valley diffusion length of $l = \sqrt{D\tau} = 20 \mu\text{m}$.

Fig. 6 Spin-valley transport in a vdW heterostructure⁹⁵. (a) Optical excitation of pure spin-valley imbalance at the left edge of a device will create a pure spin-valley diffusion current flowing to the right without any associated charge current. (b) Experimental configuration for direct imaging of the spin-valley current flow with space-and-time resolved pump-probe spectroscopy using pump and probe beams focused to lines on the sample at defined spatial separation. (c-d) Experimentally measured spatio-temporal evolution of the pure valley imbalance in the heterostructure (c) and a simulation of the results using a diffusion-decay model (d) for an initial hole doping of $10^{12}/\text{cm}^2$.

The efficient generation of spin-valley current with remarkably large current densities reflects the nearly ideal conversion of photogenerated excitons into a spin-valley imbalance. Still higher spin-

valley currents may be achievable in TMDC heterostructures by increasing the initial hole doping level to enable stronger optical pumping, as well as by improving the device quality to enhance the diffusivity. The long spin-valley lifetimes and diffusion lengths of valley-polarized holes in TMDC heterostructures hold promise for the generation, transport, and detection of spin-valley information and open exciting opportunities for the realization of future spintronic and valleytronic devices.

Concluding remarks

Despite the rapid progress in the study of excited-states in van der Waals heterostructures summarized above, many outstanding questions remain in understanding charge transfer processes and the spin and valley relaxation dynamics.

A complete picture of the underlying mechanism for the CT process in TMDC heterostructures remains elusive. First, the mechanisms developed to date do not account for the Coulombic interactions between electrons and holes, despite the existence of strongly bound excitons both in the TMDC monolayers^{8,97,98} and in the heterostructures⁴⁰. Though one can argue that the excitonic states are superpositions of the quasiparticle band states and, hence, are affected similarly, a quantitative picture in which excitonic correlations are taken into account remains a theoretical challenge. In this context, it would also be interesting to learn whether the dielectric environment of the heterostructure, which affects the excitonic interactions, also significantly influences the rate and efficiency of CT processes. In addition, the fact that changes in the dielectric screening of Coulombic interactions in TMDCs modify the quasiparticle band structure may provide a route to test the role of the Q and Γ valleys in CT processes. Second, the time-domain probes of CT to date have been limited in their by the instrumental response function and have not generally yielded precise CT times. In addition, optical measurements, with their limited spatial resolution, average over moiré patterns formed between the two layers. This may lead to a washing out of predicted trends for CT times. Overcoming these limitations by improved temporal resolution and/or spatial resolution (such as through near-field techniques) would provide important experimental information to inform and test further theoretical models.

Similarly many outstanding questions exist regarding spin and valley dynamics in TMDC heterostructures. Much more work is required to understand fully the intrinsic spin and valley dynamics in TMDC heterostructures and the dependence of the dynamics on the constituent TMDC materials, their relative crystallographic alignment, and their stacking order in multilayers. It remains, for example, unclear what factors define the ultimate limit for the spin-valley lifetime in TMDC heterostructures; also unknown is the role played by defects, edges, and grain boundaries, as well as possible effects from large-period moiré superlattices formed in TMDC heterostructures with small twist angles.

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