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Photoinduced charge transfer in transition metal dichalcogenide heterojunctions – towards next generation energy technologies

Dana B. Sulas-Kern, * Elisa M. Miller * and Jeffrey L. Blackburn *

Increasing interest in using two-dimensional transition metal dichalcogenides (2D TMDCs) in optical energy conversion technologies creates a demand for improving the yields and lifetimes of photogenerated charge carriers. Despite inherently fast photocarrier decay in neat 2D TMDCs, the unique photophysics in these quantum-confined systems motivates continued effort to control the evolution of photoexcited states and create functional devices. An intriguing strategy to accomplish this goal is to employ TMDCs in heterojunctions with appropriate semiconductors, where energy level offsets drive photoinduced charge transfer (PCT) across material interfaces. PCT in TMDC-based systems can be optimized for many different applications, such as driving free carriers to photocatalytic sites for redox reactions like water splitting, extracting charge to perform work in photovoltaics or photodetectors, and manipulating the spin and momentum valley electronic degrees of freedom for quantum computing systems. Here, we review recent strides in optimizing PCT for such applications through greater fundamental understanding of the photophysics that occurs at TMDC/semiconductor interfaces. After giving an overview of isolated TMDC properties, synthetic methods, and the basics of PCT, we discuss TMDCs in heterojunctions with several classes of materials, including other TMDCs, small molecule semiconductors, polymers, single-walled carbon nanotubes, quantum dots, perovskites, and electrolytes. In addition to highlighting the unique benefits of each materials category, we also identify parallels across common themes, such as the roles of charge-transfer states, spin, electronic coupling, delocalization, interfacial atomic morphology, and the precise design of energy landscapes to direct charge and energy motion. We hope to capture a broad range of the valuable work in this fast-paced field to inspire new research directions for employing PCT in targeted TMDC-based systems.

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Broader context

Photoinduced charge transfer across material interfaces is a critical step in the fundamental operation of energy-related (and other) technologies, especially when employing excitonic materials where additional driving force provided by interfacial energy level offsets is needed to separate Coulombically-bound electron-hole pairs. Monolayer transition metal dichalcogenides (TMDCs) are excitonic two-dimensional semiconductors with unique properties that are controllable by quantum confinement, promising many benefits for energy conversion and storage, including photovoltaic solar energy harvesting, solar fuels generation, and energy-efficient next-generation computing strategies. Heterostructures between TMDC monolayers and other inorganic or organic semiconductors have emerged as a powerful strategy for transforming the energy of photons into the long-lived separated charges that drive these energy applications. Here, we review recent progress on the current understanding of both fundamental and applied aspects of interfacial photoinduced charge transfer within TMDC-based heterostructures and the associated implications for energy technologies.

1. Introduction

Nanomaterials offer unique advantages for a wide variety of energy-related technologies. The confinement of charge carriers to nanoscale dimensions can lead to distinctive optical and

electronic properties, especially near or below the Bohr radius, which specifies the typical Coulomb-mediated electron-hole distance in a bulk material. Such quantum effects arise in materials confined in three dimensions (e.g. semiconductor nanocrystals and fullerenes), two dimensions (e.g. single-walled carbon nanotubes and semiconductor nanowires), and one dimension (e.g. graphene, borophene, and a host of two-dimensional semiconductors). A multitude of quantum

National Renewable Energy Laboratory, Golden, CO 80401, USA.
E-mail: Jeffrey.Blackburn@nrel.gov

confinement effects exist, but some of the most important for photoresponsive energy conversion materials are: size-tunable electronic and optical band gaps;^{1,2} possible ultra-high charge carrier mobilities, in some cases approaching the ballistic limit;^{3,4} markedly altered kinetics for excited-state processes relative to bulk;^{5,6} and symmetry-dependent optical selection rules.^{7–9}

In this review, we focus on a particular class of quantum-confined two-dimensional semiconductors comprised of transition metal dichalcogenides (TMDCs). TMDCs are layered materials with the structure MX_2 , where M is a transition metal (*e.g.* Mo, W, Zr, Pt, *etc.*) and X is a group VI chalcogen (*e.g.* S, Se, or Te). The two-dimensional, covalently-bonded MX_2 sheets are held together into larger crystal structures with relatively weak van der Waals forces between layers. Several different crystal structures can exist, which causes the TMDCs to range from semiconducting (commonly a stable H phase) to quasi-metallic or metallic (most often unstable 1T' and 1T phases, see Section 6). TMDCs have a number of unique properties that make them promising candidates for energy conversion, energy storage, and information processing. Some compelling traits of TMDCs that we will discuss in detail are strong direct band gap absorption in the visible region of the solar spectrum,¹ high charge carrier mobilities and diffusion lengths,^{10,11} appropriate energetics and promising kinetics for photoinduced catalysis,^{12–14} and a strong correlation between spin and photon degrees of freedom based on unique momentum-valley physics.^{15,16} Importantly, many of these desirable properties of TMDCs can be accentuated, improved, or synergistic in heterojunctions with complementary materials (Fig. 1), offering new avenues for optimizing functional TMDC-based devices.

Here, we review recent progress in the development of TMDC-based heterostructures, focusing specifically on the current understanding of both fundamental and applied aspects of interfacial photoinduced charge transfer and its implications for energy technologies (Fig. 1). Photoinduced charge transfer (PCT) across material interfaces is a critical step in the fundamental operation of energy-related (and other) technologies, especially when employing excitonic materials where additional driving force provided by interfacial energy level offsets is needed to separate Coulombically-bound electron–hole pairs. For example, PCT is central to optimizing thin-film photovoltaic device performance by driving spatial separation of charge carriers and hindering recombination. In this capacity, PCT underlies the function of TMDCs in solar cells and photodetectors as components in active absorber layers or as extraction layers. More recently, the decreasing cost of photovoltaics along with the intermittent nature of solar electricity has driven interest in strategies to convert photon energy into value-added fuels or chemical precursors. In this capacity, PCT underlies the function of TMDCs in solar fuel generation, where the energy of photogenerated excited states can be stored in chemical bonds by converting protons, carbon dioxide, nitrogen, and other chemical inputs into molecules that can be used on demand as fuel in off-peak hours. Computing has also emerged as a dominant and growing component of our total energy consumption, motivating new strategies for information processing (computation, communication, encryption, *etc.*) that differ from the digital methods that have dominated over the last 50 years. In this capacity, PCT in TMDCs provides a compelling route for encoding quantum information *via* manipulation of spin-valley locked states, motivating strong interest in

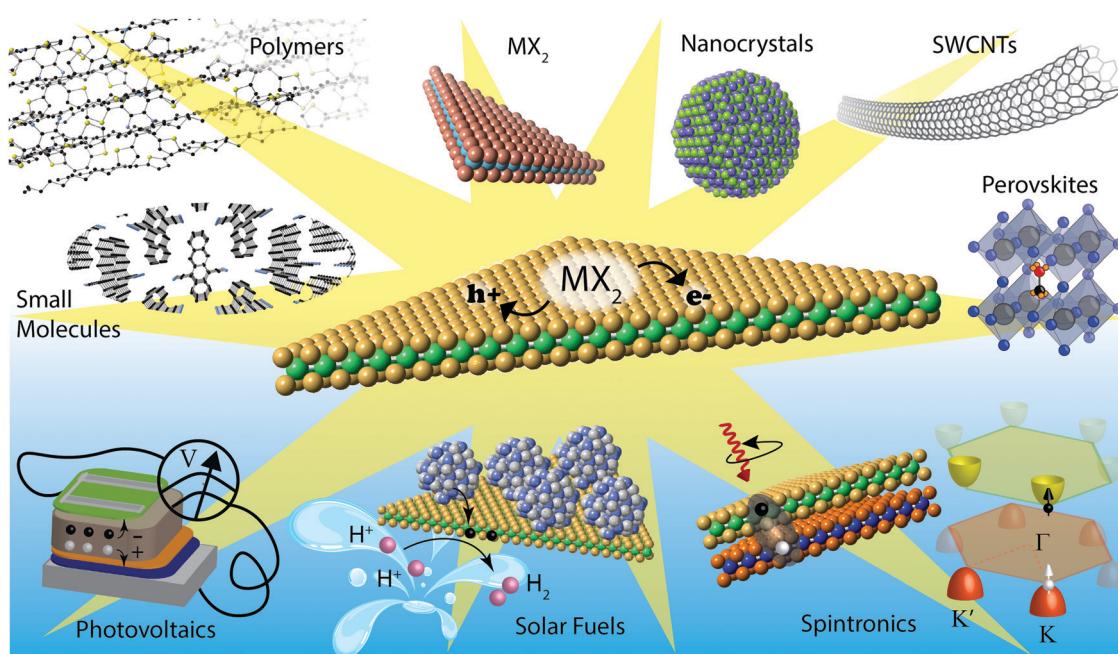


Fig. 1 We discuss photoinduced charge transfer across TMDC-based heterostructures with various organic and inorganic semiconductors (top). Such heterostructures enable a number of emerging energy technologies (bottom).

TMDCs for spintronics and photon-based quantum information technologies.

In this review, we discuss the role of PCT in TMDC-based heterostructures for enabling many of these exciting technologies. Importantly, we also note that there is a wealth of pioneering literature on bulk TMDC photochemistry and photophysics that goes back multiple decades,^{17–19} and recent reviews summarize several important aspects of TMDCs.^{9,20,21} The explosion of studies into monolayer 2D semiconductors is heavily indebted to these pioneers of the TMDC field, and we recommend that readers explore the reviews on other aspects of TMDCs that we will point out when relevant for understanding PCT. Here, we focus on more recent work specifically covering the role of PCT in mono- and few-layer TMDC-based heterostructures, a topic which has not been covered in great detail in other reviews. With this focus, we hope to highlight recent successes and future directions for harnessing the promise of layered semiconductors for renewable and sustainable energy conversion and storage devices.

2. Basics of interfacial photoinduced charge transfer

PCT across donor/acceptor interfaces can be viewed as a subset of kinetic processes that are available to a given excited state that is generated by photon absorption. As such, the kinetics and yield of PCT are linked to the thermodynamics of charge transfer and all other competing excited-state decay processes. Fig. 2 summarizes decay pathways for a representative photoexcited semiconducting TMDC that is either isolated or in contact with another semiconductor or metal at a heterojunction. Since we focus this review on monolayer (or few-layer) TMDCs, we restrict this overview to a prototypical direct-gap excitonic semiconductor with optical band gap E_{opt} , electronic

band gap E_{elec} , and exciton binding energy E_{XBE} . The electronic band gap of the semiconductor reflects the energy of uncorrelated charge carriers that are not bound by the attractive Coulomb potential and can therefore be written as

$$E_{\text{elec}} = E_{\text{opt}} + E_{\text{XBE}}. \quad (1)$$

The properties of photoexcited excitons in monolayer TMDCs are determined by various optical selection rules. As we further discuss in Section 5, unpolarized optical excitation produces an equivalent population of excitons in the K and K' valleys, whereas circularly polarized photons prepare excitons confined to either K or K' . Circularly polarized photons with appropriate energy can be used to excite spin up or spin down transitions. Depending on the TMDC composition, the lowest-energy transition may be spin-allowed or spin-forbidden, leading to corresponding bright and dark transitions.²²

If the absorbed photon energy exceeds E_{opt} , then the initial excited state has excess energy and is typically called “hot” or “unthermalized”. Hot excited states (both excitons and charge carriers) typically relax to the lowest-energy excited state by fast vibrational relaxation or internal conversion through the manifold of the excited multiplicity. Once in a relaxed excitonic state, the predominant pathways available to an exciton at low fluence are shown in Fig. 2a and include: radiative recombination (k_r); non-radiative recombination (k_{nr}); interaction with a trap state (k_{tr}); intervalley scattering (not shown); and charge transfer at an interface with an appropriate material (k_{CT}). At high excitation densities, additional quasiparticle interactions can occur, such as Auger processes and exciton–exciton annihilation.²³

Radiative recombination gives rise to photoluminescence (PL) with quantum yield (ϕ_{PL}) that is defined by the ratio between k_r and all other excited state decay pathways (k_x), also equivalent to k_r multiplied by the excited-state lifetime τ :

$$\phi_{\text{PL}} = \frac{k_r}{\sum k_x} = k_r \tau. \quad (2)$$

Photon emission depends on the optical selection rules discussed in Section 5. As such, circularly polarized emission can reflect the degree to which the valley polarization is retained following various photophysical processes and PCT.^{9,24,25} Radiative recombination is an unavoidable decay pathway for semiconductors, and the reciprocity relation dictates that natively high ϕ_{PL} by avoiding nonradiative recombination is essential for materials to achieve high photon-to-electron conversion efficiencies.^{26,27}

Exciton dissociation, however, decreases ϕ_{PL} and is beneficial when the carriers can be extracted. Dissociation into uncorrelated charge carriers and/or trions can occur from both hot and thermalized excitations even in isolated semiconductors with relatively large exciton binding energies.²⁸ Mid-gap states can also dissociate excitons by trapping charge carriers.^{28–31} In some applications, such defects can play a beneficial role in tuning band energetics³² or providing catalytic sites.^{33,34} Defect states are more common in TMDCs grown by chemical

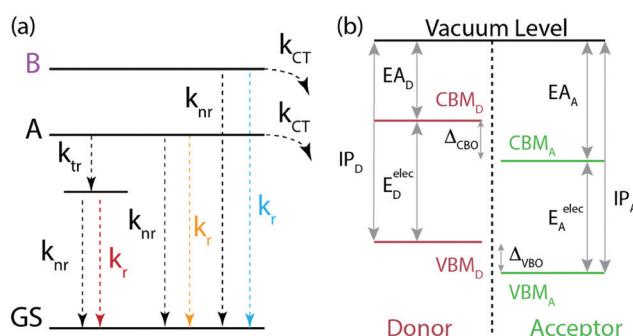


Fig. 2 (a) Schematic illustration of excited-state processes (dashed lines) in a TMDC following absorption of a photon to excite the A or B excitonic transition from the ground state (GS). Various excited state processes with rate k_x are shown, with detailed description in the main text. (b) Energy level diagram of a Type-II heterojunction between two semiconductors (before making contact) indicating properties of the donor (D) and acceptor (A) including the ionization potential (IP), electron affinity (EA), electronic band gap (E_{elec}), conduction band minimum (CBM), valence band maximum (VBM), conduction band offset (Δ_{CBO}), and valence band offset (Δ_{VBO}).

vapor deposition ($\sim 10^{12}$ – 10^{13} states cm $^{-2}$) compared to exfoliation ($\sim 10^9$ cm $^{-2}$).^{23,29}

Interfacing a TMDC semiconductor with another semiconductor or metal opens the possibility for additional excited-state deactivation pathways, the most relevant for this review being photoinduced energy transfer and PCT. In some cases, energy transfer can compete with PCT,^{35–37} although many functional TMDC-based applications require spatial separation of electrons and holes across a heterointerface (*i.e.* charge transfer) rather than funneling both carriers into one of the materials (*i.e.* energy transfer). Energy transfer can occur *via* Förster resonance energy transfer (FRET) or collisional Dexter energy transfer (DET) when the excited state's energy equals or exceeds the optical or electronic band gap of the other species in the heterojunction. FRET proceeds through resonance between transition dipole moments of transmitter and receiver species, and thus depends on the spectral overlap between the transmitter emission and receiver absorption along with the spatial alignment of their dipole orientations.³⁸ While FRET can be a long-range process, DET is short-range and requires orbital overlap between donor/acceptor. Nevertheless, both processes can be involved in excited-state diffusion toward or away from a heterojunction interface as well as exciton transfer across the interface.

The kinetics of interfacial PCT (k_{CT}) depend in large part on the thermodynamics at the interface, and the efficiency of charge transfer (ϕ_{CT}) depends on the ratio between k_{CT} and the rates of all other competing processes (k_x):

$$\phi_{\text{CT}} = \frac{k_{\text{CT}}}{\sum k_x} = k_{\text{CT}}\tau. \quad (3)$$

One of the most important characteristics for an interface that is designed to facilitate PCT is the thermodynamic driving force for charge transfer. All chemical and electrochemical reactions can be described by the change in free energy (ΔG) between reactants (with free energy G_{react}) and products (with free energy G_{prod}), where ΔG depends on the temperature (T) and the changes in enthalpy (ΔH) and entropy (ΔS) for the reaction:

$$\Delta G = G_{\text{prod}} - G_{\text{react}} = \Delta H - T\Delta S. \quad (4)$$

Reactions with $-\Delta G$ proceed spontaneously at a given temperature, and are called exergonic reactions, while $+\Delta G$ denotes endergonic reactions that are not spontaneous at a given temperature.

A typical way to establish a PCT driving force is to create a Type-II heterojunction, which is characterized by a 'staggered' band alignment, (see Fig. 2b) where the electron affinity and ionization potential of the donor are both closer to vacuum than the corresponding energies for the acceptor. This energetic alignment facilitates electron transfer from the photo-excited donor to the acceptor and hole transfer from the excited acceptor to the donor if an appropriate thermodynamic driving force exists for each charge-transfer event. Eqn (4) can be recast to describe the PCT driving force (ΔG_{CT}) using the free energy of charges as G_{prod} and the exciton free energy as G_{react} . The free energy of charges produced by PCT is the difference between the ionization potential of the donor (IP_D) and the electron

affinity of the acceptor (EA_A), and the energy of the initial excited state is the exciton energy (E_{opt}). The driving force is therefore

$$\Delta G_{\text{CT}} = (\text{IP}_D - \text{EA}_A) - E_{\text{opt}}. \quad (5)$$

Error may be introduced into eqn (5) if the donor/acceptor vacuum levels are not aligned. When this is a concern, the donor/acceptor conduction band or valence band offsets ($\Delta_{\text{CBO/VBO}}$) can be used, where ΔG_{CT} is favorable when $|\Delta_{\text{CBO/VBO}}| > E_{\text{XBE}}$. In either formulation, we assume that PCT occurs from thermalized excitons occupying the lowest-energy exciton level, even for absorption of photon energies exceeding the optical gap. In reality, 'hot' charge transfer could also occur, in which case E_{opt} would be replaced by the incident photon energy or the energy of the higher-lying exciton level from which charge transfer occurs (if this is known).

The Marcus formulation of electron transfer connects ΔG_{CT} to the rate of PCT, k_{CT} . Despite the fact that Marcus's seminal work in the 1980's predicted k_{CT} trends in solvated molecular donor-bridge-acceptor compounds, several recent studies further suggest the veracity of Marcus theory in solid-state systems, including semiconducting polymers,^{39–41} small molecules,⁴² semiconducting nanocrystals,^{43,44} single-walled carbon nanotubes,^{45,46} and TMDCs.^{44,47} In the simplest conception of Marcus theory, k_{CT} is related to the electronic coupling between donor and acceptor (V_{DA}), the charge transfer reorganization energy (λ), and ΔG_{CT} as

$$k_{\text{CT}} = \frac{2\pi V_{\text{DA}}^2}{\hbar\sqrt{4\pi\lambda k_B T}} \exp\left[\frac{-(\lambda + \Delta G_{\text{CT}})}{4\lambda k_B T}\right], \quad (6)$$

where \hbar is the reduced Planck constant, k_B is the Boltzmann constant, and T is temperature. The reorganization energy is related to the changes in molecular or lattice coordinates that accompany a charge-transfer event, taking a system from a neutral donor/acceptor pair to a charged [donor] $^+$ /[acceptor] $^-$ pair. While it is important to have a large enough ΔG_{CT} to favor charge transfer, too high of driving force can be detrimental. Large ΔG_{CT} values can reduce k_{CT} by placing the system in the Marcus inverted region (where $\Delta G_{\text{CT}} > \lambda$),⁴⁸ or it could cause energetic losses that decrease system voltage and available work.

3. Predicted and experimental band energies of monolayer TMDCs

The discussion above demonstrates the importance of the TMDC conduction and valence band energies in establishing a driving force for PCT in rationally designed TMDC heterostructures. As such, we summarize some general trends in TMDC band energies. Fig. 3 provides examples of calculations and experimental studies of TMDC band gaps.^{12,49} Two general trends can be observed for changes in the transition metal M and the chalcogen X for a given MX₂ series. For the chalcogen atoms, higher atomic mass in the periodic table (from S to Se to Te) results in smaller band gaps with conduction and valence band edges shifted progressively closer to vacuum (smaller EA and IP). For the two most common transition metals

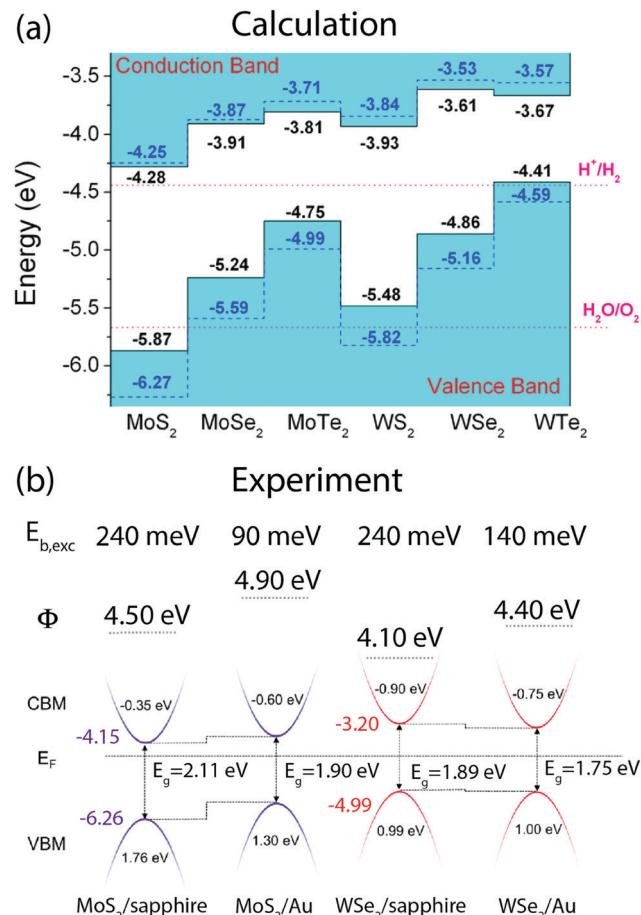


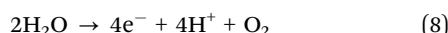
Fig. 3 (a) Calculated band energies for six TMDC monolayers.⁴⁹ Solid lines were obtained by the Perdew–Burke–Ernzerhof (PBE) method, while dashed lines were obtained by the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional. Dotted pink lines give the water reduction (H^+ / H_2) and oxidation (H_2O / O_2) potentials. Reprinted from ref. 49, with the permission of AIP Publishing. (b) Band energies for MoS_2 and WSe_2 , either on sapphire or on gold, determined experimentally using direct and inverse photoelectron spectroscopies.¹² The conduction band minimum (CBM) and valence band maximum (VBM) values given in black text are referenced to the Fermi level (E_F), whereas the workfunction (Φ) equals the E_F minus the vacuum level and is also listed. The values in colored text for MoS_2 /sapphire and WSe_2 /sapphire are absolute relative to E_{vac} for direct comparison to panel (a). The electronic band gap (E_g in this figure) is $E_g = E_{CBM} - E_{VBM}$. The exciton binding energies ($E_{b,exc}$) above each sample are calculated by subtracting the measured optical band gap (E_{opt}) from E_g . © IOP Publishing. Reproduced with permission from ref. 12. All rights reserved.

(Mo and W), WX_2 monolayers have smaller EA and IP values but larger band gaps than the corresponding MoX_2 monolayers.

Importantly, Fig. 3 suggests that the conduction band values of both MoX_2 and WX_2 monolayers are close enough to vacuum to reduce protons and produce hydrogen:



Some TMDC monolayers (MoS_2 and WS_2 in Fig. 3a) are predicted to have valence band energies deep enough to oxidize water to oxygen:



These attractive band energies are a primary motivator in considering TMDCs for applications in solar hydrogen generation. As with PCT across solid-state interfaces, the rates of PCT to produce H_2 and O_2 are related to the thermodynamic driving forces available for these reactions. Recent work has also begun to explore the possible utility of TMDCs in other photocatalytic transformations. In particular, the (photo)catalytic reduction of CO_2 to C-based fuels is a valuable strategy for mitigating an important climate-forcing gas and for storing cheap renewable electrons in energy-dense carbon–carbon bonds.⁵⁰ (Photo)-catalytic nitrogen fixation is also an important goal for reducing the large carbon footprint of ammonia generation for agriculture that currently constitutes ~1% of our global energy usage via the Haber–Bosch process.^{51,52} In Section 12, we further discuss the recent progress on understanding PCT in reactions containing TMDC catalysts, with particular focus on water splitting and hydrogen evolution.

4. TMDC electronic structure and relevant quasiparticles

The intrinsic band gaps in TMDC semiconductors outlined in Section 3 are a primary reason that TMDCs have gained popularity for PCT-driven technologies over other 2D systems such as graphene. While 2D systems like graphene require external perturbations to break inversion symmetry and create a finite band gap,^{53–57} semiconducting TMDCs exhibit inherent monolayer inversion asymmetry and a band gap between their partially-filled metal d orbitals. This inversion asymmetry rises from the trigonal prismatic unit cell shown in Fig. 4a, which extends into a 2D crystal layer with alternating atomic planes of M or X atoms that are offset in the x–y dimension.

Fig. 4b shows that this monolayer structure leads to a direct band gap transition at the K -point in the hexagonal Brillouin zone, but many TMDCs transition to an indirect band gap in the bulk or few-layer level. For example, bulk MoS_2 has an indirect lowest-energy transition centered near the Γ -point ($E_{ID} = 1.29$ eV) and a direct transition centered at the K -point ($E_D = 1.88$ eV).^{1,58,61} At the few-layer level, as the number of layers decreases from six (6L) to two (2L), Fig. 4c shows that the indirect gap shifts from approximately 1.35 eV to 1.58 eV. This is mostly attributable to the contribution of sulfur p_z orbitals to states near the Γ point, which causes the indirect band gap energy to be strongly dependent on interlayer coupling.⁶² Importantly, the direct transition at the K -point is not dependent on interlayer coupling due to the more localized Mo d orbitals involved in this transition.⁶² For this reason, going from 2L to 1L results in the indirect band gap becoming larger than the monolayer direct band gap at the K -point. This trend follows for all Mo and W-based TMDCs. Other TMDCs show a layer-number-dependent band gap but retain the indirect band gap as the lowest-energy transition, even for monolayers. These include HfX_2 , ZrX_2 , PtX_2 , and PdX_2 , where $X = S, Se$.^{63–65}

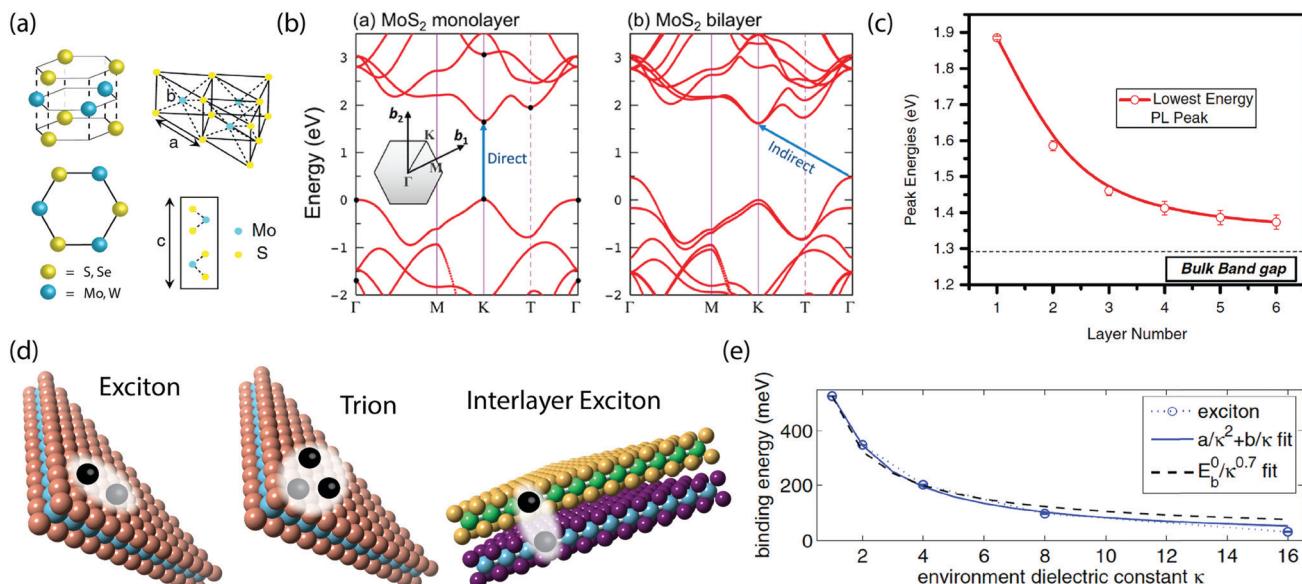


Fig. 4 (a) Left: Side and top view of atomic positions in monolayer MoS₂ lattice. Right: Crystal structure of semiconducting 2H MoS₂, showing the *a* and *b* axes, along with the *c* axis relevant for multilayer MoS₂.¹ Reprinted with permission from ref. 1. Copyright 2010 by the American Physical Society. (b) Energy-momentum diagram for monolayer and bilayer MoS₂ showing the indirect band gap near the Γ -K point for bilayer and the direct gap at the K-point for monolayer.⁵⁸ Inset shows the first Brillouin zone of the hexagonal atomic crystals. Reprinted with permission from ref. 58. Copyright 2016 American Chemical Society. (c) The lowest energy PL peak as a function of layer number for MoS₂ (red circles), along with the bulk band gap (dashed line).¹ Reprinted with permission from ref. 1. Copyright 2010 by the American Physical Society. (d) Three examples of bound quasi-particles formed between electrons (black) and holes (gray) in TMDCs. (e) Calculated exciton binding energy⁵⁹ for monolayer MoS₂ as a function of average dielectric constant, $\epsilon = \frac{1}{2}(\epsilon_{\text{top}} + \epsilon_{\text{bottom}})$, where ϵ_{top} is dielectric constant of top surface in contact with TMDC and ϵ_{bottom} is dielectric constant of bottom surface in contact with TMDC (i.e. substrate). Empirical fits are given as blue line⁵⁹ and dashed line (proposed by ref. 60). Reprinted with permission from ref. 59. Copyright 2015 by the American Physical Society.

With decreasing number of layers, dielectric screening also decreases and gives rise to strong Coulomb attractions between electrons and holes in monolayer TMDCs (Fig. 4d). As a result, the primary quasiparticles arising from photoexcitation of monolayer TMDCs are excitons. The exciton binding energy for direct bandgap monolayer TMDCs lies in the range of 0.1–0.6 eV, with a strong dependence on the dielectric environment (Fig. 4e and Table 1).^{12,59,66–72} Magnetic field dependent spectroscopic experiments⁷⁰ have also enabled estimates for the physical constants of excitons in many monolayer TMDCs, as summarized in Table 1.

Low dielectric screening in mono- and few-layer TMDCs also leads to trion formation under conditions of non-negligible dark carrier density, applied bias, high photoexcitation density, or excess carriers from PCT.^{73–75} Trions are three-particle species consisting of an exciton bound to an extra charge carrier, where excess holes give rise to positively-charged trions and excess electrons give rise to negatively-charged trions. Trion binding energies (the energy needed to separate the extra carrier from the exciton) are typically in the range of several tens of meV for most direct bandgap TMDCs and depend on the effective mass of the additional carrier bound to the exciton, the carrier density, and Fermi energy.^{76,77} Trion PL, which is observed at energies below the exciton PL peak, has been used to demonstrate the existence of excess carriers, the excess carrier type and density, and the carrier dynamics.^{73–76} At high photon fluences, multi-particle interactions can give

rise to biexcitons (four-particle), charged biexcitons (five-particle), and even higher order quasiparticles.⁷⁸

The Coulomb binding of these excitonic states can be overcome to generate separated charge carriers by employing TMDCs in heterojunctions with appropriate energy level offsets as described in Section 2. Interfacial charge-transfer states can serve as intermediates to free carrier generation (*i.e.* an electron in one material and a hole in the other material), or as sites for charge recapture if carriers are unable to escape the interface (*i.e.* the reverse process). The degree to which the interfacially-bound charges can dissociate depends on factors such as the magnitude of dielectric screening for the Coulomb potential between the two charges,⁷⁹ the presence of other low-energy states available for recombination (such as triplet excitons in organics),⁸⁰ and band bending at the interface.⁸¹ Interfacial charge-transfer states have gone by several different terminologies in the literature, such as exciplex,⁸² spatially-indirect exciton,⁸³ and interlayer exciton.^{36,84,85} Most often, the terminology is meant to imply that the bound charges reside in different materials, in contrast to intralayer excitons that are created within a single TMDC. However electron–hole separation across stacked layers within a given TMDC has also been suggested to give rise to exciplex-type character,⁸² and spatially-indirect excitons can be supported in the same material (*e.g.* MoS₂) that is separated by multiple layers of another material such as boron nitride.⁸⁶ Recent studies also suggest the existence of interlayer trions.^{87,88}

Table 1 Summary of optical gaps, exciton binding energies, exciton size (radius), and reduced exciton mass for several common monolayer TMDCs on substrates with varying dielectric constants

TMDC	Optical bandgap (eV)	Binding energy (eV)	Electrical bandgap (eV)	Exciton radius ^a (nm)	Average ϵ^b or substrate	Reduced exciton mass used ^c	Method ^d	Ref.
MoS ₂	—	0.53	—	1.1	1	0.25m _e	DFT	59
MoS ₂	—	0.35	—	—	2	0.25m _e	DFT	59
MoS ₂	1.94	0.22	2.16	1.2	4.4 (h-BN x2)	0.28m _e	DS	66
MoS ₂	1.87	0.24	2.11	—	Sapphire	—	PES	12
MoS ₂	1.81	0.09	1.90	—	Gold	—	PES	12
WS ₂	—	0.51	—	—	1	0.18m _e	DFT	59
WS ₂	—	0.32	—	—	2	0.18m _e	DFT	59
WS ₂	2.045	0.41	2.455	1.53	1.55 (Si/SiO ₂)	0.16m _e	DS	67
WS ₂	2.06	0.18	2.24	1.8	4.4 (h-BN x2)	0.18m _e	DS	66
WS ₂	2.09	0.32	2.41	—	1.55 Si/SiO ₂	0.16m _e	RC	68
WS ₂	2.04	> 0.44	> 2.48	—	1.55 quartz	—	2PPL	69
WSe ₂	—	0.46	—	—	1	0.19m _e	DFT	59
WSe ₂	—	0.29	—	—	2	0.19m _e	DFT	59
WSe ₂	1.78	0.48	2.26	1.2	1.55 (SiO ₂)	0.18m _e	DS	70
WSe ₂	1.75	0.35	2.1	1.4	2.25 (poly/SiO ₂)	0.18m _e	DS	70
WSe ₂	1.73	0.22	1.95	1.6	3.30 (h-BN/SiO ₂)	0.18m _e	DS	70
WSe ₂	1.65	0.37	2.02	—	1.55 Si/SiO ₂	—	2PPL	71
WSe ₂	1.65	0.24	1.89	—	Sapphire	—	PES	12
WSe ₂	1.61	0.14	1.75	—	Gold	—	PES	12
MoSe ₂	—	0.48	—	—	1	0.30m _e	DFT	59
MoSe ₂	—	0.32	—	—	2	0.30m _e	DFT	59
MoSe ₂	1.64	0.23	1.87	1.1	4.4 (h-BN x2)	0.35m _e	DS	66
MoSe ₂	1.63	0.55	2.18	—	Graphene	—	STM + PL	72
MoTe ₂	—	0.38	—	—	1	0.31m _e	DFT	59
MoTe ₂	—	0.26	—	—	2	0.31m _e	DFT	59
MoTe ₂	1.18	0.18	1.36	1.3	4.4 (h-BN x2)	0.36m _e	DS	66

^a Electron–hole separation. ^b Average dielectric constant, $\kappa = \frac{1}{2}(\epsilon_{\text{top}} + \epsilon_{\text{bottom}})$, where ϵ_{top} is dielectric constant of top surface in contact with TMDC and ϵ_{bottom} is dielectric constant of top surface in contact with TMDC (*i.e.* substrate). All κ values reported as relative permittivity (ϵ/ϵ_0) where ϵ_0 is the permittivity of vacuum. ^c Reduced exciton mass, m_{exc} , defined by $m_{\text{exc}}^{-1} = m_e^{-1} + m_h^{-1}$, where m_e and m_h are electron and hole effective masses, respectively. ^d Method abbreviations: DFT = density functional theory; DS = diamagnetic shift; PES = photoelectron spectroscopy (combination of angle-resolved photoemission spectroscopy and inverse photoemission spectroscopy); RC = reflectance contrast; 2PPL = two-photon photoluminescence spectroscopy; STM + PL = scanning tunneling microscopy and photoluminescence spectroscopy.

5. Spin and valley degrees of freedom in TMDCs

Harnessing the spin and valley degrees of freedom in monolayer TMDCs has important implications for computing, where valley degeneracy combined with spin-orbit splitting of the valence band opens new avenues for information transmission.^{8,9} To this end, valleytronics and spintronics are intriguing concepts that use these nontraditional electron degrees of freedom (*i.e.* valley index or spin polarization) for information storage and processing, leading to technologies that go beyond the typical methods of manipulating only electronic charge.^{8,9}

While much of the initial progress in valleytronics is owed to the rich physics discovered in graphene,^{8,9} TMDCs promise further progress by combining similar valley physics with a natural, finite band gap. In particular, the conduction and valence band edges of both graphene and monolayer TMDCs are located at the corners of the hexagonal Brillouin zone, resulting in two degenerate but inequivalent valleys at the K and K' points, as shown in Fig. 5a–d. The large difference in momentum between the two valleys is expected to limit scattering and intervalley conversion, enabling the control of valley polarization and coherence necessary for binary information transmission.

Importantly, spin-orbit coupling (SOC) also plays an essential role in preserving robust spin and valley coherence in TMDCs. Strong SOC energetically splits the band edges at the distinct valleys, as illustrated by the projection of spin operator \hat{s}_z onto the MoS₂ band structure in Fig. 5b, where blue indicates spin-down bands and red indicates spin-up bands. The SOC gives rise to separate A and B exciton transitions (Fig. 5e) and creates locked spin and valley physics. SOC predominately splits the valence band maxima within each K valley due to the nonzero magnetic quantum number ($m_l = \pm 2$) of the constituent $d_{x^2-y^2}$ and d_{xy} orbitals, while the conduction band minimum is d_{z^2} orbital character with $m_l = 0$.^{7,90} Splitting of the valence band is on the order of hundreds of meV, with increasing magnitude for heavier metals or for larger chalcogens (see Fig. 5e, f and Table 2).^{22,90,91} Because the K and K' valleys are related by time reversal symmetry, the sign of SOC splitting is opposite between the two valleys as illustrated in Fig. 5b–d. This implies that the lowest-energy optical transition has a different spin polarization depending on which valley is excited, and intervalley relaxation is therefore suppressed as transitions would involve a spin flip in addition to the large change in momentum between valleys.^{7,90,92}

Unlike the large SOC splitting in the valence band, the conduction band was initially approximated as degenerate due to lack of first-order SOC from the $m_l = 0$ d_{z^2} orbital.⁹⁰

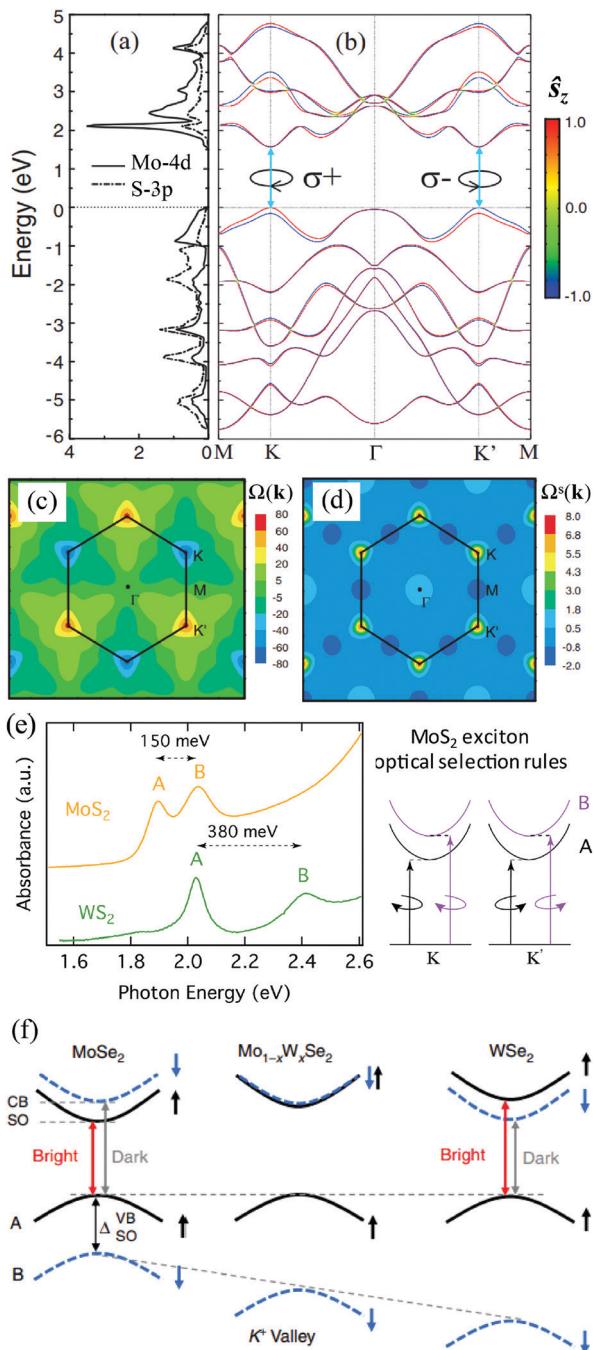


Fig. 5 (a) Calculated partial density of states for MoS_2 showing contributions from Mo-4d and S-3p orbitals along with (b) the band structure of MoS_2 with the spin operator \hat{s}_z projected as a color map, indicating spin-up (down-down) optical transitions coupled with circularly polarized light σ^+ (σ^-) at the inequivalent K (K') valleys. 2D maps in k -space show (c) Berry curvature $\Omega(k)$ and (d) spin Berry curvature $\Omega^s(k)$ highlighting differences between the K and K' high-symmetry points for MoS_2 , with units in Bohrs 2 . (e) Absorption spectra of CVD-grown MoS_2 and WS_2 showing larger splitting between A and B excitons due to larger spin-orbit coupling (SOC) with the heavier W transition metal, along with an illustration of spin-valley locking that enables creation of valley-polarized A and B excitons by exciting on-resonance with circularly polarized photons. (f) Illustration of increasing band gap and SOC with increasing W content, showing a switch from bright to dark lowest-energy transition caused by opposite conduction band SOC in WX_2 compared to MoX_2 . Panels (a-d) are reprinted with permission from ref. 7. Copyright year by the American Physical Society.⁷ Panel (f) is reprinted by permission from Springer Nature from ref. 22.²²

However, a small SOC splitting up to tens of meV is nevertheless observed due to (1) mixing with chalcogen p orbitals and (2) second-order effects of the d orbitals.^{7,96,99} Interestingly, these two SOC effects have opposite effects on the conduction band splitting, which leads to material-dependent energetic ordering between spin up and spin down states as indicated by the change in sign between MoX_2 and WX_2 values in Table 2 and Fig. 5f. That is, the heavier transition metal (*i.e.* W compared to Mo) contributes greater negative splitting, while the larger chalcogen atom (*i.e.* Se compared to S) contributes greater positive splitting (for the sign convention used here).^{22,91,99} Because only transitions between bands of like-spin are allowed in monolayer TMDCs, the positive or negative conduction band splitting determines whether the TMDC monolayers have optically bright spin-allowed ground state transitions (*i.e.* in MoX_2) or optically dark spin-forbidden ground-state transitions with much longer lifetimes (*i.e.* in WX_2).¹⁰⁶

Experimentally, spin and valley coherence can be optically probed using circularly polarized light, because the lack of inversion symmetry in combination with three-fold rotational symmetry in monolayer TMDCs allows only one of the K or K' valleys to couple to light with a given polarization.^{15,16,24,25,107–111} Although this is a valley-dependent optical selection rule, polarized light that is tuned to an appropriate energy can be used to selectively excite either the spin-up or spin-down transition. Despite the difference in momentum and spin between valleys that should suppress interconversion, neat monolayer TMDCs exhibit valley depolarization over 100's of femtoseconds to 10 picoseconds, even at low temperatures.^{15,111–115} Because these short timescales may limit the realistic use of the spin-valley polarized states, development of Type-II heterojunctions has emerged as a promising strategy to slow depolarization times to nanosecond or even microsecond scales,^{24,25,110} which we discuss further in Section 8.

6. Connection between crystal structure and electronic structure

Manipulating TMDC crystal phase and geometry tunes the electronic structure. Mono- and few-layer TMDCs are typically found in one of three geometries (Fig. 6): (1) trigonal prismatic (D_{6h} point group), denoted as 2H for few layer and 1H for monolayer; (2) octahedral (D_{3d} point group), referred to as 1T; or (3) distorted octahedral, denoted as 1T'. For 3 layers or more, a 3R phase can also exist. Fig. 6b highlights calculations by Ataca *et al.*¹¹⁶ that predict stable TMDC geometries and phases (*i.e.* metal, semiconducting, or half metal, where half metal refers to the majority-spin electrons yielding conducting states at the Fermi level and the minority-spin electrons yielding a semiconductor).¹¹⁷

The most common 2D TMDCs (MoS_2 , MoSe_2 , MoTe_2 , WS_2 , WSe_2 , and WTe_2) are thermodynamically stable in the H phase, which is semiconducting. However, these TMDCs can be converted to the thermodynamically unstable metallic 1T phase with excess negative charge or strain.^{118–122} Excess charge can be added *via* characterization techniques like transmission

Table 2 Range of reported values for energy splitting within the valence band (VB) or conduction band (CB) due to spin–orbit coupling (SOC) from experimental and computational studies^{49,90,91,93–105}

	MoS_2	MoSe_2	MoTe_2	WS_2	WSe_2	WTe_2
VB SOC (meV)	147 ± 17	185 ± 3	217 ± 3	434 ± 15	471 ± 17	485 ± 4
CB SOC (meV)	4 ± 3	21 ± 1	28 ± 9	-30 ± 2	-37 ± 1	-46 ± 10

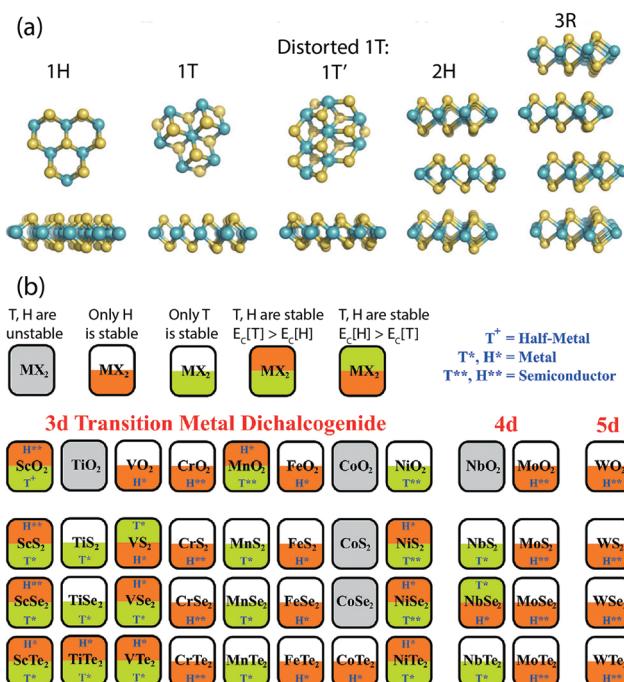


Fig. 6 (a) Common structures of TMDCs.¹²⁵ Republished with permission of Royal Society of Chemistry, from ref. 125; permission conveyed through Copyright Clearance Center, Inc. (b) Diagram of stable TMDC structures from density functional theory. For each TMDC, the stable geometry is indicated by color and lowest energy structure is identified by letter (metallic, half-metallic, or semiconductor).¹¹⁶ Reprinted with permission from ref. 116. Copyright 2012 American Chemical Society.

electron microscopy,¹²⁰ where a large flux of electrons is needed to perform the measurement. Alternatively, excess charge can be chemically imparted with dopants. Strong reductants such as *n*-butyl lithium, commonly used to exfoliate TMDCs,^{118,121,123} can convert monolayer and few layers from 1H/2H to 1T and ultimately 1T'. The 1T/1T' phase is not stable and readily converts back to the 2H or 1H phase with time and/or temperature, unless it is stabilized by approaches such as surface functionalization¹¹⁸ or coupling the TMDC to an electron donor, such as carbon nanotubes.¹²⁴

The 1T phase typically relaxes to a 1T' state with a superstructure within each layer.¹²⁵ The 1T' phase is sometimes called quasi-metallic because it possesses very similar qualities to the 1T phase along with a small band gap opening. For example, few-layer 1T' MoTe₂ has a band gap up to 60 meV due to large SOC, and other common 1T' TMDCs are predicted to have a few meV to few 100 meV band gap.^{126–129}

Strain can also manipulate TMDC electronic structure. Mechanical strain can convert a direct band gap to an indirect

band gap that decreases in energy with strain.^{119,130} Other studies have demonstrated that excess charge strains the lattice structure to an intermediate point between 2H and 1T where the band gap is reduced.^{122,131} Coupling TMDCs to a curved surface, such as Au nanoparticles, can also impart strain and charge transfer that decreases the 2H nature.¹³²

7. Synthesis of mono- and few-layer TMDCs

Many reviews have been published on growing and exfoliating TMDCs to produce mono- and few layer TMDCs.^{20,21,133–139} Growth (bottom-up approach) and exfoliation (top-down approach) produce a range of TMDC options that can be tuned for a desired application or property including thickness, lateral size, shape, purity, defects, and phase. Gas-phase TMDC growth routes, such as chemical vapor deposition (CVD) or molecular organic chemical vapor deposition, are performed in a furnace, whereas hydro/solvothermal methods grow 2D layers from solution. In all growth techniques, recipes are designed with variables such as the precursors, temperature, time, pressure, flow rate, substrates, carrier gases, and solvent. Monolayers are grown in CVD furnaces on flat substrates that can tolerate high temperatures (up to 1000 °C), such as quartz, silicon oxide, and sapphire (Fig. 7, top), and lateral sizes typically range from ~1 to 100 microns.^{133–135} Large area (~few cm), few layers, and defect-controlled flakes can also be controllably grown by varying the growth recipes.^{140–143} Solution-based hydro/solvothermal techniques can create unique interfaces with a variety of materials and shapes, such as nanoflowers and nanospheres.^{25,138,144} The hydro/solvothermal growth step typically occurs in a sealed autoclave using high temperature and pressure to create 2D TMDC nanosheets.

Exfoliation is also a viable technique because bulk TMDCs are held together by weak van der Waals forces and chemical bonds do not need to be broken to separate layers. The main TMDC exfoliation methods are micromechanical cleavage, mechanical-force-assisted liquid exfoliation, and chemical exfoliation. Micromechanical cleavage can be done with the “scotch tape method” similar to graphene mechanical exfoliation where layers are peeled off from the bulk crystal using tape.^{145,146} Compared to other approaches, mechanical exfoliation from pure bulk TMDCs typically generates 2D layers with a lower number of defects on the basal sites.¹⁴⁶ However since this method is done by hand, it is difficult to reproducibly generate similar size/thickness TMDCs in large quantities.

Solution-based exfoliation can be done *via* mechanical force or ion intercalation in solution. Mechanical-force-assisted

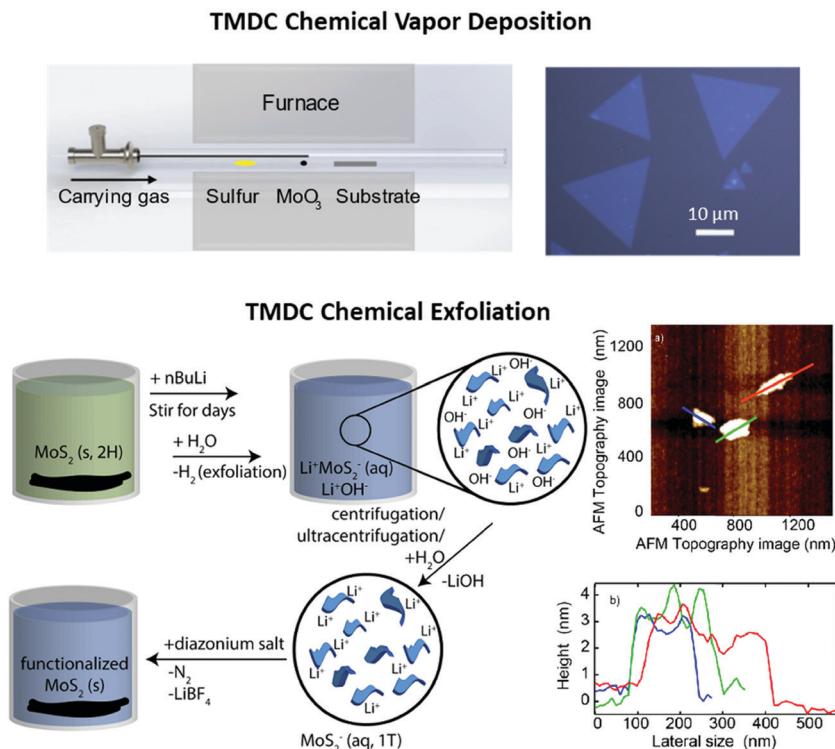


Fig. 7 Common techniques for 2D TMDC growth and exfoliation. Top: Chemical vapor deposition and optical image of 2D monolayers and few layers. Bottom: Chemical exfoliation of 2D nanosheets using *n*-butyl-lithium followed by functionalization with a diazonium salt. The atomic force microscopy image and line scan are representative of the nanosheets height and width. The AFM image is reprinted with permission from ref. 118. Copyright 2018 American Chemical Society.

liquid exfoliation is performed in a liquid with force applied by sonication or shear force. To effectively exfoliate TMDCs and prevent restacking during sonication, the solvent's surface energy should match that of the layered bulk material.^{21,147} Surfactants or polymers can enhance exfoliation by tuning the surface energy of the solution.^{148,149} This inexpensive technique results in a wide distribution of sizes and thicknesses, but centrifuging/filtering can decrease the spread. Shear-force-assisted liquid exfoliation has been proposed as a higher-throughput way to scale up the production of 2D materials.¹⁵⁰ With both of these liquid exfoliation methods, the resulting 2D layers likely have surfactant/intercalating molecules on the surface, which need to be considered or removed from the 2D layer prior to use.

Chemical intercalation is another route for exfoliating TMDCs (Fig. 7, bottom). The most common chemical exfoliant is *n*-butyl lithium where the Li⁺ intercalates the bulk TMDCs.^{118,123,151} This method is high yield, but the lateral size and thickness of nanosheets is not well controlled. Using *n*-butyl lithium requires great care, because H₂ is produced and could be explosive and flammable if generated in high quantities. The ion intercalation step involves charge transfer to the TMDC, which partially converts it from 2H to the 1T/1T' phase. Typically, *n*-butyl lithium exfoliation yields mixed phase nanosheets with both 1T/1T' and 2H.^{118,152} A similar idea to the chemically-induced ion intercalation is electrochemical Li⁺ intercalation where the Li⁺ ion intercalates the externally-reduced TMDCs.¹⁵³

To create heterojunctions for various applications, TMDCs need to be interfaced to other semiconductors, nanomaterials, electrodes, and substrates. Heterojunctions can be created during growth processes in the bottom-up approaches or post TMDC growth/exfoliation. Small variations in growth recipes can enable sequential deposition of different TMDC layers or other 2D materials like graphene and hexagonal boron nitride.^{154–156} Solution growth recipes can include other materials in the solution, such that the TMDCs grow directly onto these materials or substrates to create unique interfaces.^{157,158} Methods such as thin film transfers, spraying, spin-coating, physical vapor deposition, hydrothermal mixing, membrane filtration, and grinding are also used to create interfaces between TMDCs and other semiconductors (*e.g.* TMDCs, organics, quantum dots, carbon nanotubes, graphitic carbon nitride, perovskites) or substrates (*e.g.* indium-doped tin oxide, TEM grids, metallic substrates).^{25,159–163} In the following sections, we discuss several different types of TMDC heterojunctions and highlight unique aspects of controlled heterojunction fabrication (such as interfacial alignment) when relevant.

8. Photoinduced charge transfer at TMDC/TMDC heterojunctions

Heterojunctions between two (or more) different monolayer TMDCs have emerged as fascinating model systems for PCT,

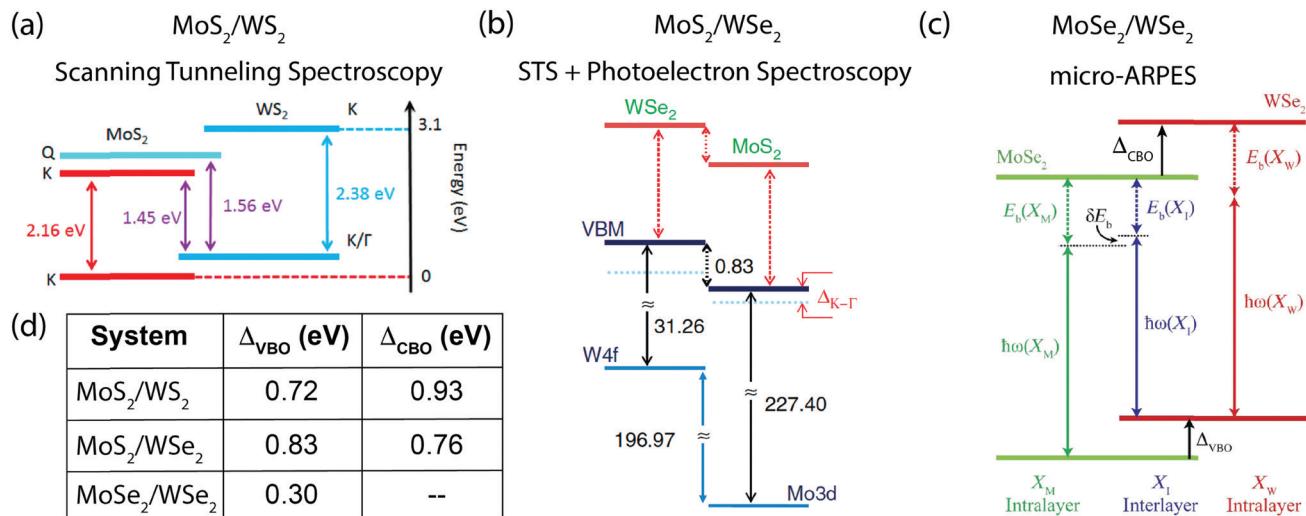


Fig. 8 Experimentally determined band alignments for select TMDC/TMDC heterojunctions. (a) MoS₂/WS₂, determined by scanning tunneling spectroscopy (STS).¹⁶⁶ Reprinted with permission from ref. 166. Copyright 2016 American Chemical Society. (b) MoS₂/WSe₂, determined by a combination of STS and photoelectron spectroscopy.¹⁶⁵ In addition to the valence band maximum (VBM) and conduction band minimum (CBM), tungsten 4f (W 4f) and molybdenum 3d (Mo 3d) core level energies are shown, as are the splitting energies between VBM at the K and Γ points ($\Delta_{K-\Gamma}$), obtained by ARPES. Reprinted by permission from Springer Nature from ref. 165. (c) MoSe₂/WSe₂, determined by micro-angle-resolved photoelectron spectroscopy (micro-ARPES).¹⁶⁷ Also highlighted are the three exciton energies [$h\nu(X_i)$] and their associated binding energies [$E_b(X_i)$] – MoSe₂ intralayer (X_M), WSe₂ intralayer (X_w), and interlayer exciton (X_I). From ref. 167. © The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (d) Table showing experimental valence band offsets (Δ_{VBO}) and conduction band offsets (Δ_{CBO}) for each of these systems.

allowing for highly controlled studies connecting charge-transfer kinetics to interfacial thermodynamics and spin/valley populations. Charge transfer in several TMDC/TMDC heterojunctions is driven by Type-II band offsets, as illustrated in Fig. 8. These band alignments are often calculated,¹⁶⁴ but a number of experimental methods are also used to determine CB and VB offsets (Δ_{CBO} and Δ_{VBO} , respectively), including scanning tunneling spectroscopy,^{165,166} photoelectron spectroscopy,¹² and angle-resolved photoelectron spectroscopy (ARPES).¹⁶⁷

Several groups have recently demonstrated a photovoltaic effect enabled by PCT in TMDC/TMDC heterojunction devices.^{136,168} For example, Lee *et al.* constructed a van der Waals stacked p-n junction between aluminum-contacted n-type MoS₂ and palladium-contacted p-type WSe₂.¹⁶⁸ The authors observed diode-like rectification at zero gate voltage, and spatial photocurrent mapping indicated that the photocurrent arose from charge separation at the MoS₂/WSe₂ vertical junction. Increasing the carrier density in the monolayers using a positive or negative gate voltage decreased the photocurrent density, as expected for either Shockley–Read–Hall (SRH) or Langevin recombination. Modeling this gate voltage dependence with either mechanism alone was insufficient to reproduce the data, suggesting that recombination is influenced by a combination of both mechanisms. Photocurrent collection improved when using graphene electrodes due to direct vertical charge transfer to graphene rather than relying on lateral diffusion through the TMDCs to the metallic contacts. Cheng *et al.* studied MoS₂/WSe₂ heterojunctions in a similar geometry,¹³⁶ where they observed good rectification, efficient electroluminescence, and external quantum efficiencies in the

range of 8% (633 nm) to 12% (514 nm) with no applied gate voltage.

These demonstrations of photocurrent generation in functional TMDC/TMDC devices are promising, but the development of design principles for further device optimization depends on a number of important fundamental considerations that we discuss in the following sections, including the time scales and yields of ultrafast charge transfer and recombination, the formation of interlayer excitons, the role of momentum in PCT and recombination, and the impact of spin-valley polarization. The bulk of our discussion centers around vertical heterojunctions fabricated by growing or stacking individual TMDC monolayers on top of each other to form bilayers or even trilayers. At the end of the section, we briefly discuss emerging but less studied lateral heterostructures, where different TMDC monolayers are covalently stitched together at coherent in-plane interfaces, typically through well-controlled vapor-phase growth methods.

8.1 Ultrafast charge transfer in TMDC/TMDC heterobilayers

Probing ultrafast charge-transfer events at Type-II TMDC/TMDC heterojunctions is often achieved using PL (Fig. 9b) and transient absorption (TA, Fig. 9c) spectroscopies.¹⁶⁹ For example, Fig. 9b shows quenching of the direct-gap PL from individual monolayers in MoS₂/WS₂ heterojunctions due to interfacial PCT.¹⁶⁹ In principle, PL quenching of the larger bandgap WS₂ layer could result from energy transfer or charge transfer when WS₂ is excited. However, energy transfer would quench only the WS₂ PL and enhance PL from the lower-gap MoS₂ layer, while charge transfer quenches both layers. In addition to mutual PL quenching, Hong *et al.* confirm

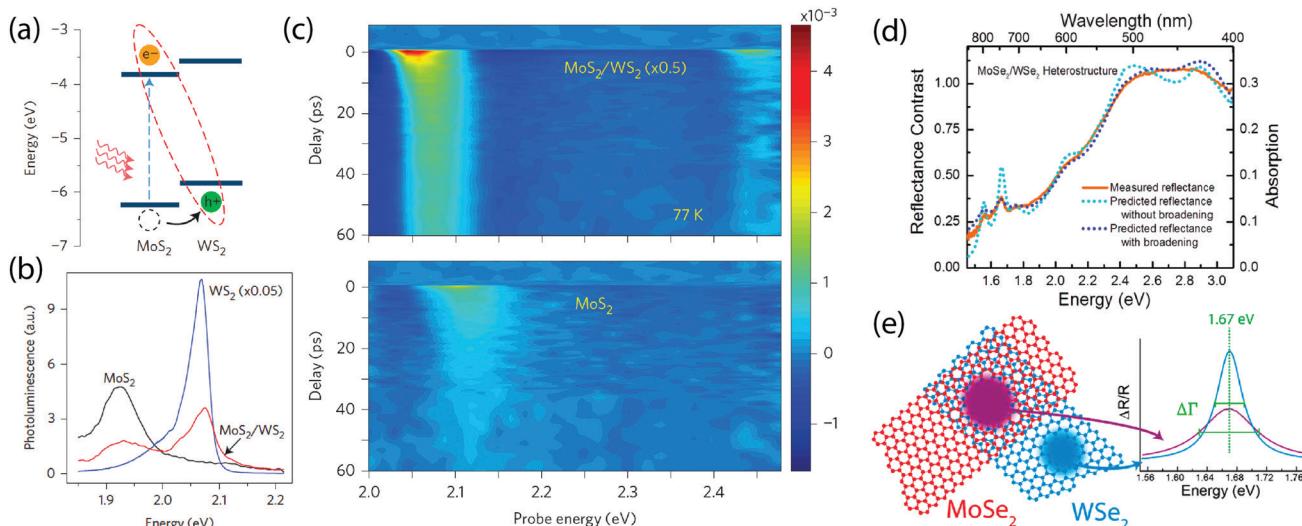


Fig. 9 (a) Schematic of band diagram of MoS₂/WS₂ bilayer that facilitates photoinduced hole transfer from MoS₂ to WS₂.¹⁶⁹ (b) PL of MoS₂ and WS₂ is quenched in this bilayer.¹⁶⁹ (c) 2D transient absorption map showing (top) WS₂ ground state bleach following pumping of lower bandgap MoS₂ and (bottom) MoS₂ only.¹⁶⁹ (d) Reflectance contrast (RC) spectra of MoSe₂/WSe₂ heterojunction, simulated from the dielectric functions of the respective monolayers with (blue dotted line) and without (cyan dotted line) additional peak broadening. Orange solid line shows the measured RC spectrum.¹⁷⁰ (e) Transient reflectance at the MoSe₂/WSe₂ interface (purple trace) and at monolayer WSe₂ only (blue trace). Panels (a–c) are reprinted by permission from Springer Nature from ref. 169. Panels (d and e) are reprinted with permission from ref. 170. Copyright 2015 American Chemical Society.

photoinduced hole transfer in MoS₂/WS₂ heterojunctions using TA spectroscopy.¹⁶⁹ Fig. 9c shows photobleaching of the WS₂ A exciton transition (2.06 eV) following selective photoexcitation of MoS₂ (1.86 eV). Since the 1.86 eV pump photons cannot excite the WS₂ layer, the authors conclude that the WS₂ bleach arises from hole transfer from MoS₂ to WS₂. The rise time of the WS₂ bleach suggests hole transfer faster than the instrument response of ~50 fs. This strategy of pumping the lowest-energy TMDC exciton to negate the possibility of energy transfer is a ubiquitous feature of probing PCT, although appropriate experimental design and analysis can also extract PCT kinetics upon photoexcitation of higher energy excitons.

Ceballos and co-workers performed similar TA measurements on MoS₂/MoSe₂ heterojunctions formed by mechanical exfoliation and transfer stacking.¹⁷¹ The authors found electron and hole transfer times on par with or faster than the instrument response time of ~200 fs. Spatially-indirect excitons formed by charge transfer recombined on time scales of 50–300 ps, depending on excitation wavelength and fluence. The slowest decay times in the heterojunction represent approximately two-fold longer-lived states relative to excitons in separate MoS₂ or MoSe₂ monolayers.

Rigosi *et al.* suggest a simple analysis for estimating the lower bound of charge-transfer times in TMDC/TMDC heterojunctions based on steady-state optical absorption.¹⁷⁰ They produced randomly-oriented (*i.e.*, no intentional crystallographic alignment) bilayer heterojunctions of both MoS₂/WS₂ and MoSe₂/WSe₂ on quartz substrates using mechanical exfoliation and transfer techniques. The excitons' absorption transitions were broadened in the heterojunctions relative to the same transitions in individual TMDCs, with the A and B transitions broadened by about 25–30 meV and the C and D

excitons broadened by 150 ± 60 meV. The authors ruled out many possible sources for this broadening: processing conditions, doping, strain, enhanced thermal phonon scattering in heterojunctions, energy transfer between layers in the heterostructure, and intervalley scattering within individual layers of the heterostructure. Based on the staggered Type-II band alignment expected for these heterojunctions, the authors suggest that the broadening arises from ultrafast PCT. That is, the fast exciton decay causes uncertainty in its transition energy, so the uncertainty relationship $\tau = \hbar/\Delta\Gamma$ can be used to calculate the exciton population lifetime τ associated with the observed energetic broadening $\Delta\Gamma$. For the A and B transitions, the 25–30 meV broadening corresponds to an estimated lower bound for the PCT time of 25–30 fs.

PCT across TMDC/TMDC heterojunctions can also be identified by emergence of trion PL.^{73,172} For example, Bellus *et al.* identified emission from negative trions (X^-) in WS₂ following electron transfer from MoSe₂.⁷³ In this case, the electrons transferred from MoSe₂ to excitons generated *via* steady-state excitation of WS₂, producing negative trions which emit between 60 meV (low excitation power) to 80 meV (high excitation power) lower in energy than the neutral WS₂ exciton PL. The authors estimated 62 ± 2 meV for the WS₂ trion binding energy based on extrapolation of the power-dependent Stokes shift of the trion peak. Similarly, in MoSe₂/MoS₂ heterostructures, Kim *et al.* observed negative MoS₂ trions and positive MoSe₂ trions following electron transfer from MoSe₂.¹⁷²

The ultrafast charge-transfer times observed in TMDC/TMDC heterojunctions have motivated rigorous theoretical studies aimed at understanding charge-transfer mechanisms. Long *et al.* reported time-domain *ab initio* simulations of PCT and recombination across MoS₂/MoSe₂ heterojunctions.¹⁷³ Their calculations

suggest that charge separation is facilitated by excited-state delocalization between donor (MoSe_2) and acceptor (MoS_2). This interfacial quantum coherence helps to overcome the strong electron-hole Coulomb attraction, and the resulting transfer times correlate with the coherence time, nonadiabatic coupling, density of acceptor states, and coupling with high-frequency vibrational modes. For the $\text{MoS}_2/\text{MoSe}_2$ heterojunction, these considerations lead to sub-picosecond interfacial charge transfer for both electron and hole, with faster electron transfer than hole transfer. The calculations suggest that electron-hole recombination is slower in the heterojunction (680 ps) relative to neat MoS_2 (41 ps) or neat MoSe_2 (63 ps), with computed recombination times trending with experimental values (240 ps,¹⁷¹ 100 ps,^{174,175} and 125 ps,¹⁷⁶ respectively).

Wang *et al.* utilized time-dependent density functional theory and molecular dynamics to study hole transfer from MoS_2 to WS_2 (Fig. 10).¹⁷⁷ The authors found that PCT is associated with the collective motion of holes across the interface, resulting in a macroscopic dipole similar to a parallel plate capacitor. Interestingly, while this interfacial dipole field opposes the hole transfer from MoS_2 to WS_2 , it dynamically enhances the electronic coupling between the states in the two materials and ultimately enhances the hole transfer rate. The coherent charge oscillations couple strongly to Γ -point A_{1g} phonon modes that correspond to out-of-plane vibrations of sulfur atoms. This coherent ultrafast charge transfer occurs predominantly for the energetically favorable 2H stacking, but not for the 3R and AB' stacking configurations where the calculated charge-transfer rate is accordingly much slower.

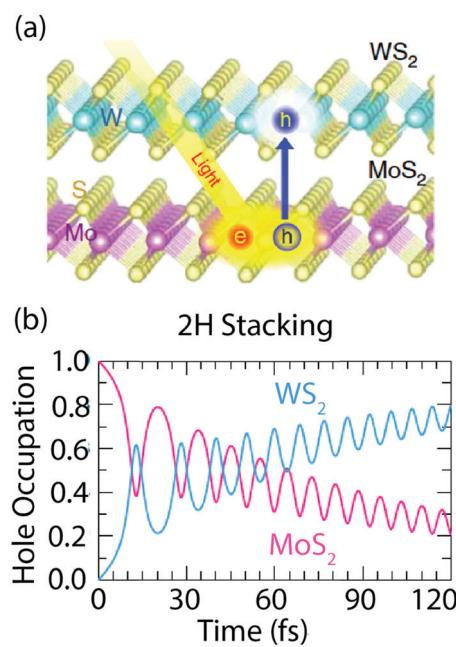


Fig. 10 Theoretical calculation of coherent charge transfer across MoS_2/WS_2 interface.¹⁷⁷ (a) Schematic of photoinduced hole transfer from MoS_2 to WS_2 . (b) Hole population dynamics modeled at 300 K resulting from photoexcitation of MoS_2 .¹⁷⁷ Reprinted by permission from Springer Nature from ref. 170.

8.2 Inter-layer excitons in TMDC/TMDC heterostructures

Following PCT, charges separated across TMDC/TMDC interfaces may still experience significant Coulomb attraction and exist as stable charge-transfer excitons. Charge-transfer states appear frequently in donor/acceptor systems, especially when dielectric screening is relatively inefficient.^{25,39,79,80,178–180} In layered 2D materials, charge-transfer states are widely referred to as inter-layer excitons (ILEs). Excellent reviews exist on ILEs²⁵ and the general behavior of charge-transfer states.¹⁸⁰ Here, we recount a few important considerations and recent discoveries.

We first note that, while ILEs could be a necessary intermediate for free carrier generation, they may simultaneously serve as a loss pathway for solar fuels or PV applications *via* charge recapture or inhibiting separation of mobile carriers that could be collected as current or driven to a catalytic center. While ILEs typically have longer lifetimes than intra-layer excitons, they still recombine significantly faster than truly free charges.^{84,85} ILE binding energies have been reported in the range of 90 to 200 meV.^{167,180,181} In other low-dielectric systems with similar charge-transfer state binding energies, it has long been debated how it is possible to reach 100% absorbed photon-to-electron internal quantum efficiency despite the existence of these low-energy interfacially-bound “traps”.^{180,182,183} To this end, Zhu *et al.* discussed the possible routes by which (i) charge generation may bypass relaxation to localized charge-transfer excitons (*e.g.* *via* charge delocalization in the donor and/or acceptor phases) or (ii) the charge transfer exciton binding energies can be countered by a potential landscape in the opposite direction (*e.g.* a free energy gradient from interfacial dipoles or structural inhomogeneity at/near the interface).¹⁸⁰

ILEs are often characterized by their sub-gap luminescence features. Fig. 11a shows that ILEs in TMDC/TMDC heterojunctions emit at energies below the emission of either isolated TMDC,^{85,184} where the $\text{MoSe}_2/\text{WSe}_2$ system exhibits ILE PL nearly 300 meV below the MoSe_2 exciton PL.⁸⁵ Interestingly, the $\text{MoSe}_2/\text{WSe}_2$ ILE can be resolved into two narrow peaks at low temperature (Fig. 11b). Some groups assign these peaks to inter-layer spin-triplet (1.39 eV) and spin-singlet (1.41 eV) transitions.^{185,186} In this suggested assignment, the energy difference of ~20 meV between these peaks represents the SOC spin-splitting in the CB. The authors suggest that breaking of the out-of-plane mirror symmetry in heterobilayers brightens the triplet transition denoted as IX_T in Fig. 11c, which is in contrast to neat monolayers where recombination between bands of opposite spin is a spin-forbidden dark transition. For rotation angle of 60° between the TMDC layers, the K valley of MoSe_2 aligns with the K' valley of WSe_2 , and the ILE spin-splitting can be resolved up to 200 K.¹⁸⁶ Both peaks show giant valley Zeeman splitting (Fig. 11d), with Lande *g*-factors of ~15 for the 1.39 eV ILE and ~11 for the 1.41 eV ILE.¹⁸⁶ Geim *et al.* provide an alternate interpretation that assigns the two peaks to an interlayer exciton (1.41 eV) and interlayer trion (1.39 eV).⁸⁸ In making this assignment, the authors suggest that the temperature dependence is inconsistent with the two peaks arising from different interlayer excitons, and they use bias-dependent

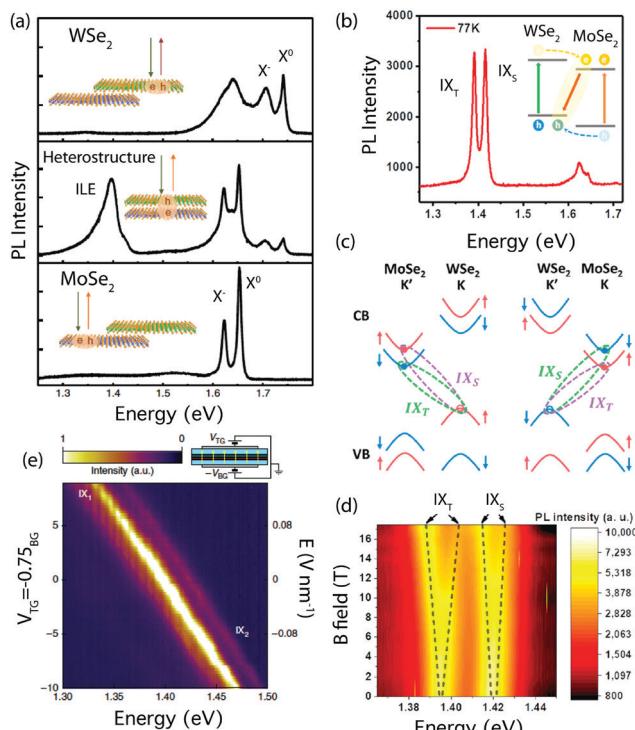


Fig. 11 Interlayer excitons in MoSe₂/WSe₂. (a) PL spectra of WSe₂ (top), MoSe₂ (bottom) and MoSe₂/WSe₂ heterostructure (middle), showing existence of neutral exciton PL (X^0), trion PL (X^-), and interlayer exciton PL (ILE).⁸⁵ Reprinted by permission from Springer Nature from ref. 85. (b) 77 K PL spectrum of MoSe₂/WSe₂ heterostructure, showing triplet (IX_T) and singlet (IX_S) ILE emission.¹⁸⁶ (c) ILE configurations at adjacent K/K' valleys of MoSe₂/WSe₂. Solid dots represent the electrons and the open circles represent the holes. Dashed lines represent formation of IX_S and IX_T , where green (purple) color represents σ^+ (σ^-) helicity PL observed experimentally.¹⁸⁶ (d) Color plot of MoSe₂/WSe₂ ILE PL ($T = 77$ K, CW excitation at 1.959 eV) as a function of applied out-of-plane magnetic field.¹⁸⁶ Panels (b–d) are reprinted with permission from ref. 186. Copyright 2019 American Chemical Society. (e) Map of ILE PL for top- and bottom-gated MoSe₂/WSe₂ bilayer device as a function of applied gate voltages V_{TG} and V_{BG} when sweeping at constant doping.¹⁸⁵ For this device, IX_1 is the triplet ILE and IX_2 is the singlet ILE. Reprinted by permission from Springer Nature from ref. 185.

doping studies to support the assignment of the lower-energy peak to an interlayer trion.

ILEs appear to retain memory of the initial valley polarization created by circularly-polarized photoexcitation of excitons in the constituent TMDC layers.^{25,186} For example, the valley polarization of the 1.41 eV ILE in MoSe₂/WSe₂ is as high as 100% at 23 K and 85% at 82 K, due to the long valley lifetime of the holes.¹⁸⁶ The systematically-varying helicity associated with peaks in the ILE manifold fine structure can be rigorously assigned and can even be used to manipulate the outgoing polarization *via* electrical control.^{185,186} The ILE emission energy can also be controlled by an out-of-plane electric field (Fig. 11e), where the field induces a strong Stark effect due to the substantial out-of-plane dipole moments caused by the opposite carriers of the ILE residing in adjacent layers.^{185,187}

ILEs in TMDC heterobilayers represent a particularly interesting model system for probing the degree to which interfacial

crystal lattice (mis)match affects orbital interactions and interfacial electronic structure. When the lattice vector of one TMDC layer is rotated with respect to the same lattice vector of the other TMDC, this rotational mismatch leads to periodic atomic registry variations in both real space and momentum space (Fig. 12a and b). Twist-angle-dependent orbital hybridization can significantly modify the transition energies of momentum-direct ILEs. Kuntsmann *et al.* recently showed for MoS₂/WSe₂ heterobilayers that the ILE PL intensity around 1.6 eV varied little with twist angle, in contrast to what would be expected for a momentum-direct ($K-K$) interlayer transition formed from the electron and hole being in the K -valley band minima in each TMDC.¹⁸⁸ DFT calculations of the twist angle dependent ILE energies suggested that the observed ILE is momentum-indirect having hybrid $\Gamma-K$ character (Fig. 12c and d). Tight-binding calculations suggested nearly double $\Gamma-K$ binding energy (0.55 eV) compared to the $K-K$ binding energy (0.29 eV) due to delocalization of the hole wave function over the two TMDC layers that enhances the electron-hole Coulomb attraction.

Karni *et al.* measured PL spectra deeper into the infrared on a similar MoS₂/WSe₂ heterobilayer with twist angle near 0° to observe the momentum-direct $K-K$ ILE near 0.97 eV (Fig. 12e).¹⁸⁷ In contrast to the $\Gamma-K$ ILE observed near 1.6 eV,¹⁸⁸ the direct $K-K$ ILE emission was extremely weak for intentionally misaligned layers. The authors also demonstrated that the energy of the $K-K$ ILE PL peak could be systematically shifted with a perpendicular applied electric field, revealing an out-of-plane dipole of roughly 0.5–0.8 e nm (24–38 D) for an electron in the MoS₂ layer and hole in the WSe₂ layer.¹⁸⁷

For heterobilayers where either the CBs or VBs are near-isoenergetic, Alexeev *et al.* recently demonstrated that interlayer hybridization can be especially strong at small twist angles (*i.e.* 0° and 60°) where Brillouin zones of the two layers are aligned (Fig. 12f).¹⁵¹ In MoSe₂/WS₂, holes in the MoSe₂ layer form ILEs with a twist-dependent superposition of electron states in the adjacent WS₂ monolayers. Hybridization is strongest near 0° and 60°, leading to a stabilization of the ILE at these angles with corresponding decrease in PL energy (Fig. 12f).

While the twist-angle-dependent optical studies discussed thus far characterize spatially-averaged ILE properties for a given twist angle, it is important to note that twist angle between the stacked 2D crystal structures leads to periodically-repeated patterns of varying atomic (and momentum) alignment as implied by Fig. 12a. This is called a Moiré superlattice, and corresponding modulation in potential energy can localize ILEs if the Moiré periodicity is on the order of 10 nm or greater.^{189,190} Large detuning of CB and VB energies in stacked heterobilayers (*e.g.* in MoSe₂/WSe₂) can lead to variations in the interlayer band gap along the heterostructure plane and deep Moiré potential wells of 100–200 meV.¹⁹⁰ Interestingly, Tran *et al.* showed that the strong connection between rotational symmetry with ILE confinement and optical selection rules results in a complex PL spectrum with multiple ILE resonances having alternating circularly polarized PL, opposing magnetic field induced PL energy shifts, and systematically varying lifetime.^{190,191}

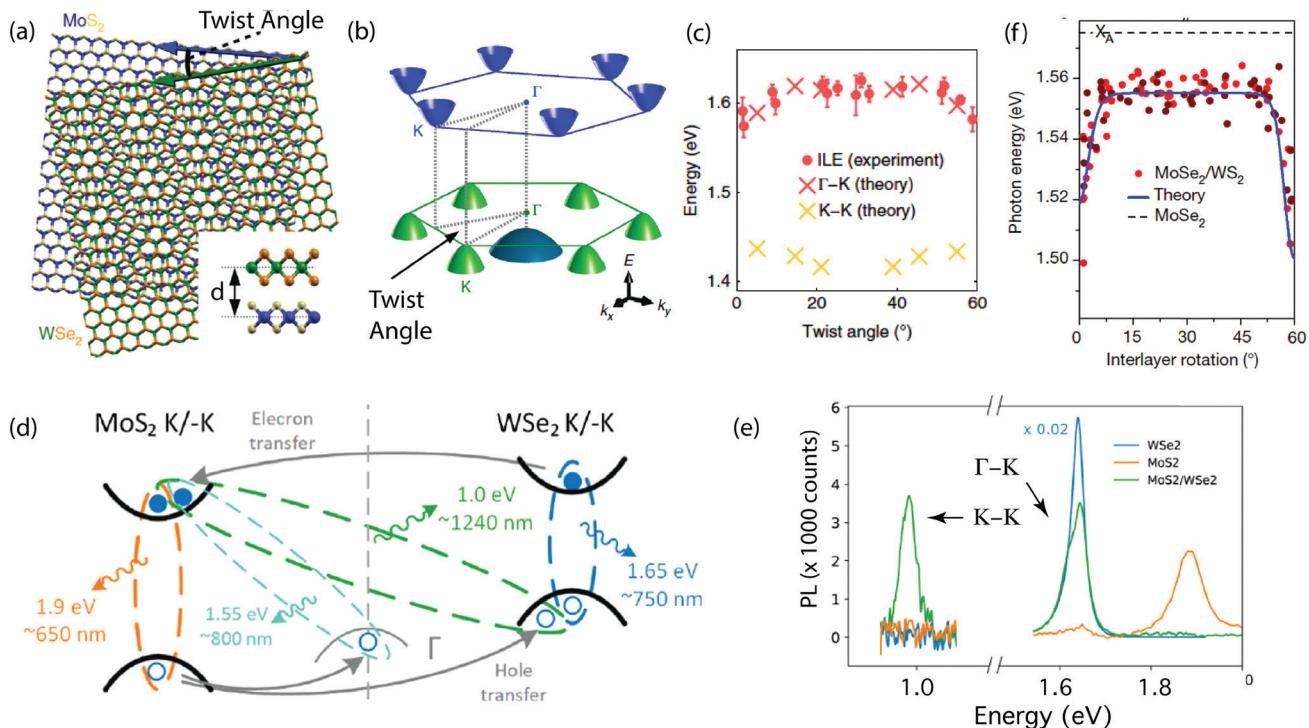


Fig. 12 Momentum-direct and momentum-indirect excitons in TMDC/TMDC hetero-bilayers. (a) Atomic structure illustration of a twisted MoS₂/WSe₂ hetero-bilayer. Inset shows side view.¹⁸⁸ (b) Two-dimensional band structure of same hetero-bilayer near the band edges. At twist angles of 0° and 60° (not shown), the K-K ILE is momentum-direct, whereas for other twist angles, both the K-K and Γ -K ILEs are momentum-indirect.¹⁸⁸ (c) Configurations and energies of the K-K and Γ -K ILEs for the MoS₂/WSe₂ hetero-bilayer.¹⁸⁸ Panels (a–c) are reprinted by permission from Springer Nature from ref. 188. (d) Experimental ILE energies and DFT-calculated transition energies for MoS₂/WSe₂ hetero-bilayers with different twist angles, showing the quantitative agreement of Γ -K with experiment.¹⁸⁷ (e) Room-temperature PL spectra for isolated MoS₂ (orange) and WSe₂ (blue) monolayers, and crystallographically aligned (twist angle near 0°) hetero-bilayer (green).¹⁸⁷ The momentum-direct K-K ILE can be observed for the heterostructure near 1.0 eV. (f) MoSe₂/WS₂ hetero-bilayers have strong hybridization at 0° and 60° that leads to lower energy emission features at these nearly aligned orientations. Panels (d) and (e) are reprinted with permission from ref. 187. Copyright 2019 by the American Physical Society.

8.3 The role of momentum in charge transfer and recombination

Since photoexcitation of a direct-gap TMDC monolayer produces excitons in the lowest-energy K valleys, the charge transfer and recombination rates should, in theory, be quite sensitive to the degree of lattice registry (twist angle) between the two layers. However, the observation of ILEs for a wide variety of twist angles *via* PL studies such as the ones discussed above makes it clear that there may be mechanism(s) by which crystal momentum mismatch is circumvented to facilitate charge transfer and recombination. In this section, we consider recent experiments that delve into how/why charge transfer and recombination can occur in mis-aligned TMDC/TMDC heterojunctions.

Yu *et al.* made an early observation for MoS₂/WS₂ heterojunctions that the efficiency of interfacial PCT did not depend strongly on lattice (mis)match between the two layers.¹⁹² The authors compared hetero-bilayers created in an epitaxial CVD process, whereby either separate monolayers were grown and mechanically stacked or the two layers were co-deposited into epitaxial heterojunctions. In both cases, PCT was inferred from PL quenching by 2 orders of magnitude relative to the neat monolayers. While the relative crystal orientations were not measured in this study, this initial result suggested that

epitaxial crystal alignment may not correlate strongly with the efficiency of PCT in this model TMDC hetero-bilayer.

Chen *et al.* suggest that hot charge-transfer states provide a mechanism for circumventing momentum mismatch across randomly-stacked TMDC/TMDC hetero-bilayers.¹⁹³ This study utilized pump-probe TA measurements that could probe either excitons in the visible range or free charge carriers in the mid-infrared. They studied a MoS₂/WS₂ heterojunction epitaxially grown in a two-step CVD method, where the relative stacking orientations were 0° (AA stacking, momentum-matched) and 60° (AB stacking, momentum-mismatched). Their results were consistent with a two-step mechanism (Fig. 13a) whereby the initially excited exciton in one TMDC dissociates by charge transfer to produce a hot electron ($\tau \approx 50$ fs) in the other TMDC. This forms weakly-bound hot ILEs that cool over 800 fs. The authors suggest that the excess energy of the intermediate hot ILE allows the state to sample a broader range of momentum space and overcome momentum conservation requirements determined by the CB minima and VB maxima.

Zhu *et al.* studied the effect of the interlayer twist angle ($\Delta\phi$) on PCT and recombination dynamics in WSe₂/MoS₂ hetero-bilayers, where they measured the twist angle of mechanically stacked hetero-bilayers by the angular dependence of second

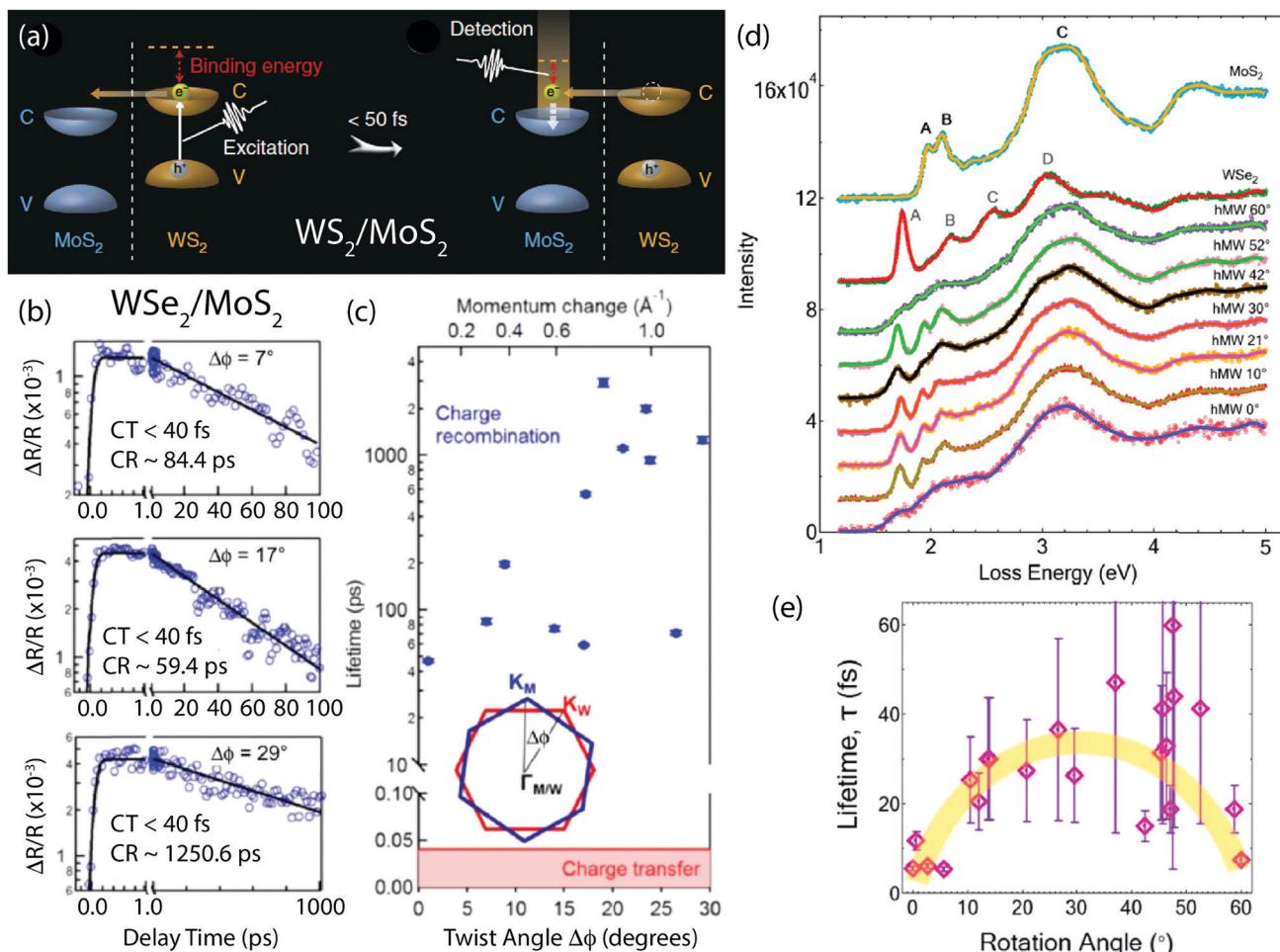


Fig. 13 (a) Proposed hot exciton route for bypassing momentum mismatch in WS₂/MoS₂ heterobilayers. Rapid (<50 fs) electron transfer from WS₂ to MoS₂ initially produces a hot ILE that can be probed in the infrared before relaxing to form a cold ILE.¹⁹³ Reprinted by permission from Springer Nature from ref. 193. (b) Transient reflectance probing of photoinduced charge transfer (CT) and charge recombination (CR) for a WSe₂/MoS₂ bilayer, at varying twist angles ($\Delta\phi$).¹⁹⁵ (c) CT and CR lifetime as a function of $\Delta\phi$ (bottom axis) or momentum change (top axis) in WSe₂/MoS₂ bilayer. Inset: Schematic depiction of twist angle in momentum space.¹⁹⁵ Panels (b and c) are reprinted with permission from ref. 195. Copyright 2017 American Chemical Society. (d) Rotation-angle-dependent electron energy loss spectra of excitonic transitions in WSe₂/MoS₂ bilayers.¹⁹⁶ (e) Rotation-angle-dependent lifetime (τ) of the WSe₂ A exciton in WSe₂/MoS₂ bilayers, as deduced from Heisenberg uncertainty analysis of EELS spectra shown in panel (d).¹⁹⁶ Panels (d and e) are reprinted with permission from ref. 196. Copyright 2019 American Chemical Society.

harmonic generation (SHG).¹⁹⁵ The authors excited the WSe₂ layer at 710 nm and utilized transient reflectance to track electron transfer from WSe₂ to MoS₂ and subsequent charge recombination. Regardless of $\Delta\phi$, PCT occurred on an ultrafast time scale (<40 fs, Fig. 13b). Although the recombination times varied significantly across the 12 different samples (from 47 ps to 3 ns), there was no clear correlation with $\Delta\phi$ (Fig. 13c). In a conclusion that aligns with the hot exciton model of Chen,¹⁹⁴ the authors suggest that the excess energy available at the Type-II heterojunction allows electrons to circumvent momentum mismatch by sampling a wider range of K -space above the CB minimum, including the M point. Recombination lifetimes were insensitive to temperature, photoexcitation fluence, and gate-controlled carrier density, leading the authors to speculate that carrier recombination was dominated by defect-assisted (Shockley–Read–Hall) non-radiative recombination.

Another recent study took the unique approach of studying the effect of twist angle on the exciton absorption in MoS₂/WSe₂ heterobilayers using low-loss electron energy loss spectroscopy (EELS).¹⁹⁶ They observed that the intralayer absorption peaks were drastically broadened solely for 0° and 60° twist angles (Fig. 13d). Using the analysis introduced by Rigos et al.¹⁷⁰ (Section 8.1, Fig. 9d and e), they interpret this broadening ($\Delta\Gamma$) within the framework of the Heisenberg uncertainty principle, $\tau = \hbar/\Delta\Gamma$, where broadened peaks arise from a shorter exciton lifetimes (τ). Assuming the decrease in exciton lifetime results primarily from PCT across the MoS₂/WSe₂ interface, the analysis shown in Fig. 13e suggests that exceptionally fast charge transfer ($\tau < 10$ fs) occurs for bilayers that are perfectly aligned ($\Delta\phi = 0^\circ$) or anti-aligned ($\Delta\phi = 60^\circ$). These results suggest that, while misaligned TMDC heterobilayers still achieve very fast PCT on sub-100 fs timescales, near-perfect alignment can generate even faster rates (Fig. 13e).

While standard optical studies (absorption, PL, TA, time-resolved PL-TRPL) can observe rapid charge transfer across TMDC heterojunctions, these studies are not always sensitive to the full progression of the exciton and charge carrier population in momentum space. For this reason, Liu and Zhu utilized time-resolved angle-resolved photoelectron spectroscopy (TR-ARPES) to probe the momentum dependence of the excited state population in a MoS₂/WS₂ hetero-bilayer produced by metal-assisted mechanical exfoliation.¹⁹⁷ To maintain valley polarization following PCT (*e.g.* valley-polarized ILEs, see also Section 8.4), interlayer coupling is needed for electron or hole transfer to the spin-polarized *K* or *K'* valley in the other TMDC without losing coherence *via* population transfer to other valleys. However, the wavefunctions at the *K/K'* points are constructed primarily of in-plane metal atom d_{xy} and d_{x²-y²} orbitals with little interlayer electronic interaction.¹⁹⁷ In contrast, first-principles calculations predict that the *Q*, *M*, and *M/2* momentum points are comprised of mixed orbital character from each TMDC layer, resulting in much stronger interlayer interactions. Liu and Zhu show that PCT rates vary from momentum to momentum, where photoexcitation into the WS₂ *K* valley resulted in fast electron transfer to mixed-character *M* and *M/2*, valleys within ~70 fs, followed by slower population transfer to the MoS₂ *K* and mixed-character *Q* valleys over ~400 fs. This occurs because LO (longitudinal optical) phonon scattering is more prominent into *M* and *M/2* than into *Q*, presumably due to the importance of energetic resonance for inter-valley scattering. Their results suggest that interlayer PCT is facilitated by phonon scattering into bands with mixed interlayer character, possibly explaining the general observation that ultrafast electron transfer depends little on the momentum mismatch associated with random twist angle between layers.

These intriguing results¹⁹⁷ suggest an intrinsic constraint to the electron valley polarization lifetime in TMDC/TMDC heterostructures. The near-degeneracy of the electron spin states in the CB at *K/K'* suggests equal probability for scattering into *K* or *K'*, thus mixing the polarization of the resulting electron population in the acceptor. In contrast, the large VB spin-splitting suggests that the hole population is less prone to this phonon-scattering pathway for *K/K'* valley depolarization. Therefore, the valley polarization lifetimes of holes should greatly exceed those of electrons. With this in mind, we turn to discuss the general strategy of using PCT to prolong the valley polarization lifetime.

8.4 Valley polarization in PCT events for TMDC/TMDC heterostructures

PCT across TMDC/TMDC heterojunctions can be an effective strategy for increasing the valley lifetime of valley-polarized carriers.^{24,108,109,198} As discussed in Section 5, spin-valley locking should theoretically produce long valley lifetimes, since inter-valley scattering requires both a large momentum change and a spin flip. For intra-layer excitons in most neat TMDC monolayers, however, valley polarization lifetimes are on the order of picoseconds.^{15,111-115} Thus, a number of recent studies utilize intelligently-designed TMDC/TMDC heterojunctions to facilitate

(1) sustained valley polarization of the carriers residing on either side of the junction, and (2) long valley lifetimes due to spatial separation and reduced Coulomb attraction of the carriers.

For a mechanically stacked MoSe₂/WSe₂ bilayer, Rivera *et al.* utilized circularly polarized PL spectroscopy to determine the retention of initial valley polarization following interfacial PCT (Fig. 14a-c).¹⁰⁹ At zero applied gate voltage, the authors found that 30% of photons emitted by MoSe₂⁻/WSe₂⁺ ILEs retained the pump polarization. The loss of polarization was ascribed to valley depolarization of excitons on the femtosecond to picosecond timescale preceding PCT. The polarization percentage and lifetime were tuned by a gate voltage, with peak values around 40% and 40 ns, respectively, at +60 V and 30 K. The long valley lifetime enabled spatial mapping of ILE drift-diffusion over micron length scales.

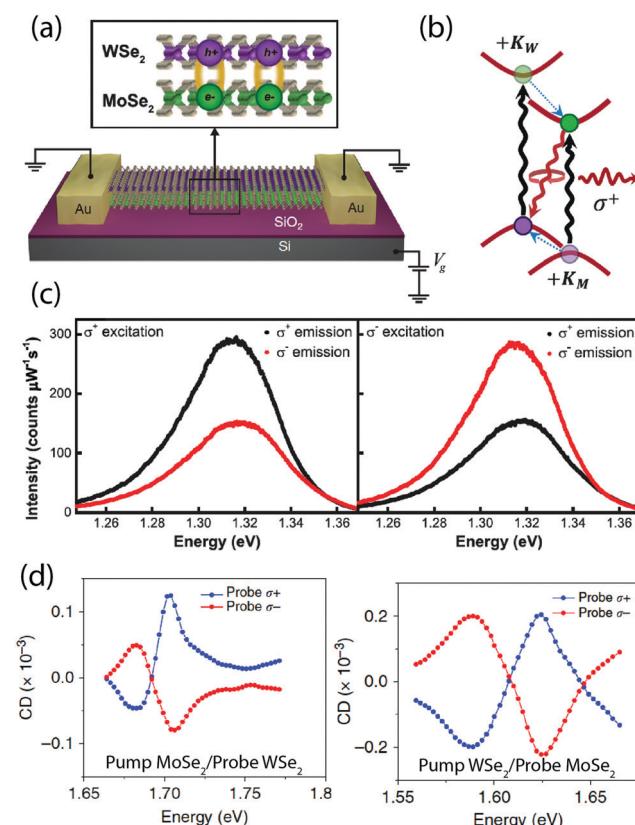


Fig. 14 Valley polarized excitons in MoSe₂/WSe₂ hetero-bilayers. (a) Side view schematic of MoSe₂/WSe₂ heterostructure device, where photo-excitation produces electrons in the MoSe₂ layer and holes in the WSe₂ layer (inset).¹⁰⁹ (b) The resulting ILEs can be valley-polarized when generated with circularly polarized light (black wavy lines).¹⁰⁹ In the example given, fast interlayer charge transfer (blue dotted lines) forms the ILE in the +*K* valley. (c) Optical selection rules in the +*K_W* and +*K_M* valleys produce co-polarized PL for the ILE that can be modulated by the gate voltage (not shown).¹⁰⁹ Panels (a–c) are from ref. 109. © The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (d) Pump-induced circular dichroism (CD) of the WSe₂ A exciton resonance when pumping MoSe₂ at 1.621 eV (left panel), and the MoSe₂ A exciton resonance when pumping WSe₂ at 1.71 eV (right panel).¹⁰⁸ As expected for spin-valley polarization transfer in each charge transfer event, the CD response flips with probe helicity. Reprinted by permission from Springer Nature from ref. 108.

Schaibley *et al.* further studied MoSe₂/WSe₂ heterojunctions using transient reflectance (TR) spectroscopy to probe the retention of valley polarization following PCT.¹⁰⁸ The authors observed strong circular dichroism (CD) in the TR spectrum when pumping and probing with circularly polarized light, where the sign of the CD response flips upon changing the probe helicity (Fig. 14d).¹⁰⁸ To characterize the degree of carrier valley polarization, the authors developed a detailed analysis that was further refined in the study by Kim *et al.* (see discussion below and Fig. 15).²⁴ Based on the TR spectra for the cases of co- and cross-polarized pump-probe pulses, the authors estimated 46% electron spin-valley polarization in the MoSe₂ layer following hole transfer to WSe₂. The retention of spin-valley polarization did not depend on twist angle.

Although Schaibley *et al.* were unable to determine hole polarization yields in their MoSe₂/WSe₂ heterojunctions due to overlapping TR spectral signatures,¹⁰⁸ Kim *et al.* demonstrated near-unity valley polarization and microsecond timescale valley lifetimes for WSe₂ holes in WSe₂/MoS₂ heterojunctions.²⁴ These combined results are consistent with the micro-ARPES study discussed in Section 8.3 that suggested rapid decoherence of the electron valley polarization *via* phonon scattering,¹⁹⁷ which

is not expected to strongly affect the hole population. Kim *et al.* demonstrated that the 50 fs PCT time out-competed intralayer exciton valley depolarization in WSe₂/MoS₂, resulting in generation of perfectly valley-polarized carriers. The authors attributed the ultralong valley lifetimes of holes to carrier separation in real space and momentum space, which increases the recombination time and decreases the propensity of intervalley scattering mechanisms,^{76,199–201} such as the intervalley electron-hole exchange mechanism proposed by Maialle, Silva, and Sham.²⁰² This analysis relied on distinguishing between holes in the *K* versus *K'* valleys, where the authors measured different TA spectra following co-polarized or cross-polarized pump-probe measurements as shown in Fig. 15c–e. The *K*-valley hole quenches and blue-shifts the exciton transition, due to a combination of phase-space filling and the Moss-Burnstein effect (Fig. 15d and g). In contrast, the *K'* valley does not experience phase-space filling and instead the probe pulse predominantly excites intervalley trions (Fig. 15e and f). Using the analysis first demonstrated by Schaibley *et al.*,¹⁰⁸ the authors quantified near-unity *K* valley polarization with a temperature-dependent lifetime exceeding 100 μ s at 10 K (Fig. 15h).

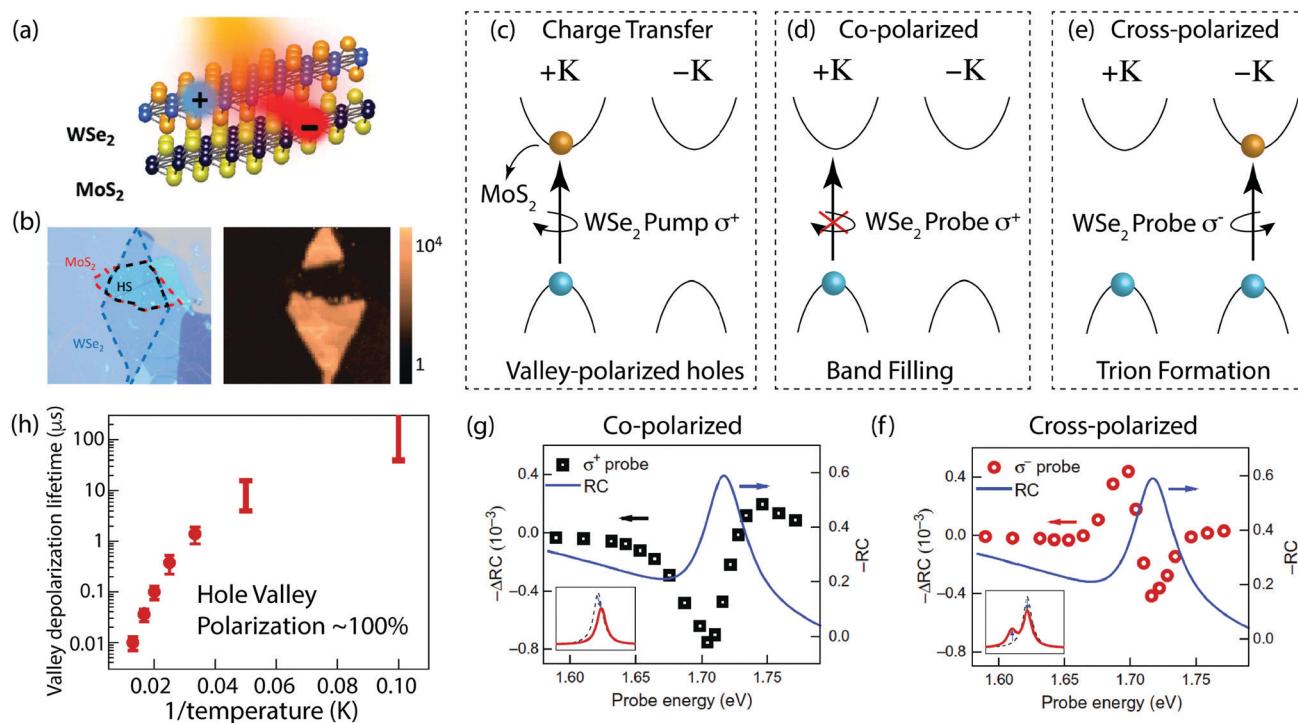


Fig. 15 Long-lived hole valley polarization in WSe₂/MoS₂ hetero-bilayer. (a) Schematic of WSe₂/MoS₂, where photoexcitation produces electrons in MoS₂ and holes in WSe₂.²⁴ (b) Optical microscope image of heterostructure, where MoS₂, WSe₂, and the heterostructure are outlined with red, blue, and black dashed lines, respectively. Panels (c) through (e) summarize the expected sequence of events in the pump–probe measurements. (c) σ^+ photons create valley-polarized excitons in WSe₂. Rapid (<50 fs) electron transfer to MoS₂ leaves valley-polarized holes in WSe₂. (d) For co-polarized probe, holes remaining in the WSe₂ K^+ valley reduce exciton oscillator strength in the K^+ valley (band filling, arrow shown for σ^+ probe photons) and lead to a blue shift of the exciton transition (Moss–Burstein effect, not depicted). (e) For cross-polarized probe, σ^- probe photons create intervalley trions, transferring oscillator strength from the exciton transition to the trion transition. (f and g) Experimental results for the cross-polarized and co-polarized pump–probe configurations, respectively, for the WSe₂/MoS₂ bilayer. The blue lines in each figure show the reflectance contrast (RC) of the heterostructure, for comparison. Insets in panels (f and g) depict the expected spectral responses for these probe configurations, as outlined in panels (d and e). (h) Shows ~100% hole valley polarization for the WSe₂/MoS₂ interface at 10 K. Panels (a, b, f, g, and h) from ref. X. © 2017 The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.

8.5 TMDC hetero-trilayers

A number of groups have begun exploring complex multi-layer heterostructures to exert greater control over charge transfer directionality and charge separation lifetime. Ceballos and co-workers expanded upon their initial bilayer studies¹⁷¹ by inserting a WS₂ monolayer in between MoS₂ and MoSe₂ monolayers, producing a mechanically exfoliated and stacked tri-layer with a “cascading” band alignment (Fig. 16a).²⁰³ The proposed band alignment should foster electron transfer from MoSe₂ to WS₂ to MoS₂ and hole transfer in the opposite direction, ultimately funneling electrons to MoS₂ and holes to MoSe₂. Indeed, selective excitation of the low-bandgap MoSe₂ layer led to bleaching at the MoS₂ A exciton, with 1.5 ± 0.2 ps electron transfer time (Fig. 16b). Further experiments suggested that hole transfer occurred on a ~ 300 fs time scale.

Following PCT, the lifetimes of separated charges (e^- in MoS₂ and h^+ in MoSe₂, $\tau \approx 920\text{--}950$ ps) was roughly an order of magnitude longer than the excited-state lifetimes in either neat monolayer ($\tau \approx 30\text{--}110$ ps), as shown in Fig. 16c. The authors suggest that the extended lifetimes result from better spatial separation of charges than can be achieved in bilayer TMDC heterojunctions. Interestingly, the authors observed only a weak ground state bleach signal in the central WS₂ layer when MoSe₂ was excited. Based on control experiments on a WS₂

monolayer, the authors concluded that this WS₂ bleach was too weak to arise from electrons temporarily populating the WS₂ conduction band during a stepwise charge transfer from MoSe₂ to WS₂ to MoS₂. The authors suggested coherent electron transfer from MoSe₂ to MoS₂, which they supported with non-adiabatic molecular dynamics simulations.

The same group studied another TMDC tri-layer (MoSe₂/WSe₂/WS₂) in which the band structure did not facilitate a “cascading” electron or hole transfer pathway from one side of the tri-layer to the other, as shown in Fig. 16d.²⁰⁴ In this case, exciting the low-bandgap MoSe₂ layer should transfer holes to the middle WSe₂ layer, while electrons have an energetic barrier for transfer to either WSe₂ or WS₂. Surprisingly, photoexcitation of MoSe₂ at 1.60 eV led to an ultrafast rise of the WS₂ ground-state bleach near 2.0 eV in the TA experiment (Fig. 16e). The rise time of the WS₂ ground-state bleach was similar to the rise time observed in a MoSe₂/WS₂ bilayer, where electron transfer occurs over <350 fs from photoexcited MoSe₂ to the WS₂ layer. Tunneling probability calculations suggested that the ultrafast time scale of electron transfer from MoSe₂ to WS₂ in the tri-layer sample did not correspond to tunneling through the intervening WSe₂ barrier (orange arrow, Fig. 16d). Instead, the authors suggest formation of layer-coupled electronic states (purple dashed line, Fig. 16d) that are lower in energy than the

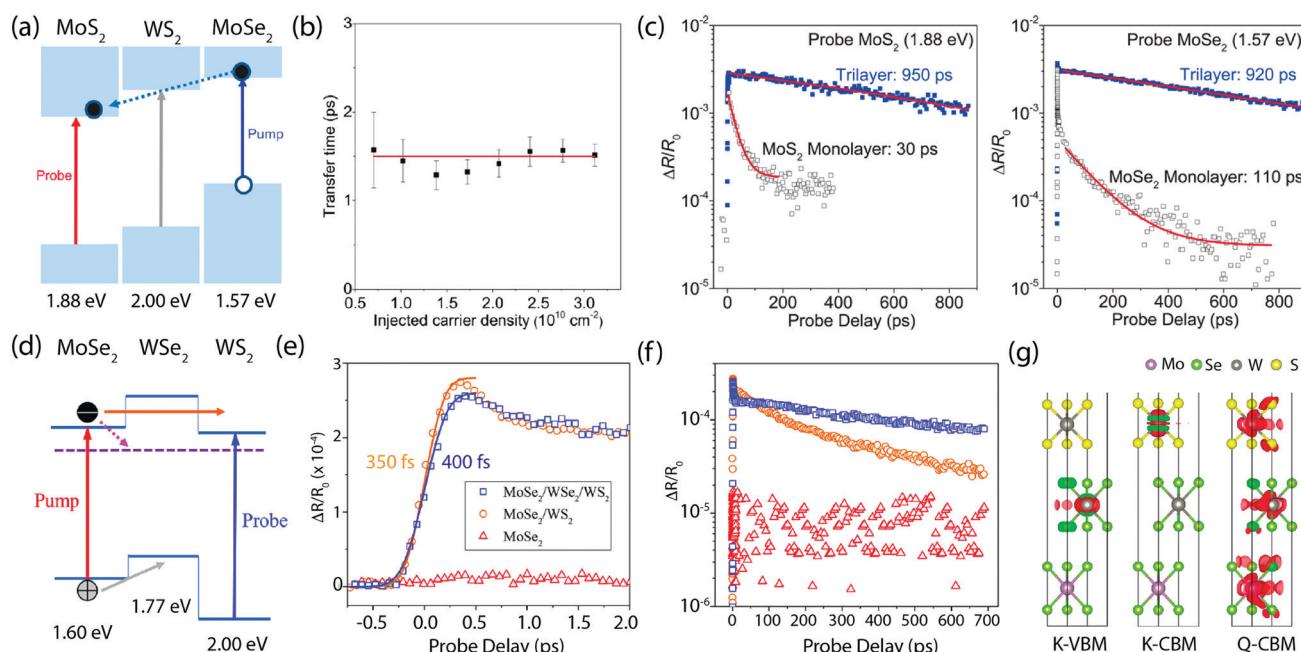


Fig. 16 Photoinduced charge transfer in TMDC hetero-trilayers. (a) Band alignment of a MoSe₂/WSe₂/MoS₂ trilayer, along with pump–probe details for transient reflectance study.²⁰³ (b) Charge transfer time for same trilayer as a function of carrier density injected by pump pulse.²⁰³ (c) Reflectance transients for trilayer sample (blue solid squares), probed at either 1.88 eV (left panel, MoS₂ optical bandgap) or 1.57 eV (right panel, MoSe₂ optical bandgap) after photoexcitation of MoSe₂ at 1.57 eV. Open symbols are transients for a MoS₂ monolayer with same probe energies, but pumped at 3.14 eV.²⁰³ Red curves are exponential fits. Panels (a–c) are reprinted with permission from ref. 203. Copyright 2017 American Chemical Society. (d) Transient reflectance pump–probe configuration for a MoSe₂/WSe₂/WS₂ trilayer. A 1.60 eV pump pulse excites excitons in MoSe₂. Holes are expected to transfer to WSe₂ (gray arrow), while electrons may tunnel to WS₂ (orange arrow) or transfer to (pink arrow) layer-coupled states (dashed line). Electrons making it to WS₂ are probed by a 1.97 eV probe pulse.²⁰⁴ (e and f) Differential reflection signal measured from the trilayer in different sample regions: MoSe₂/WSe₂/WS₂ (blue squares), MoSe₂/WS₂ (orange circles), and MoSe₂ (red triangles).²⁰⁴ (g) Charge densities for trilayer in MoSe₂ (bottom), WSe₂ (middle), and WS₂ (top) for the VBM and CBM at the *K*- and *Q*-points.²⁰⁴ The proposed delocalized layer-coupled states at the *Q*-point are theorized to facilitate ultra-fast charge transfer from MoSe₂ to WS₂. Panels (d–g) are reprinted with permission from ref. 204. Copyright 2018 American Chemical Society.

lowest-energy states at the *K* point that define the optical transitions of the isolated monolayers. The DFT calculations shown in Fig. 16g suggested that the CBM at the *Q*-point (~ 100 meV below the *K*-valley in energy) was delocalized over all three monolayers in the tri-layer system, lending support to layer-coupled states facilitating ultrafast electron transfer from MoSe₂ to WS₂. The lifetimes of the resulting charges (hole in WSe₂ and electron in WS₂ or MoSe₂) were substantially longer than the lifetimes observed for either isolated monolayers or bilayers with the same charge population (Fig. 16f).

8.6 Lateral TMDC/TMDC heterojunctions

All of the TMDC/TMDC heterojunctions discussed so far are vertical heterojunctions where individual TMDC layers are grown or stacked on top of one another. Lateral heterojunctions (Fig. 17) can also be fabricated by vapor phase synthesis routes (Fig. 17a–c), whereby an atomically sharp or more gradual (alloyed) interface is formed between the two TMDCs within the lateral plane of a single crystal structure.^{205–213} The atomic sharpness of the interface can be imaged by aberration-corrected and/or Z-contrast scanning transmission electron microscopy (Fig. 17b), and the individual layers can also be spatially mapped over larger areas using PL (Fig. 17c) and Raman (Fig. 17d) mapping.

An interesting consideration is the degree to which lateral TMDC/TMDC heterojunctions retain the Type-II band alignment that is present in the same vertical heterostructure. Calculated band alignments can deviate significantly between vertical and lateral heterojunctions.^{214–216} This difference results in lateral heterostructures tending to have significantly lower Δ_{CBO} and Δ_{VBO} relative to their vertical counterparts (see Fig. 8).^{208,215,216} Calculations by Gong *et al.* suggest that, for the monolayer MoS₂/WSe₂ lateral heterojunction, Δ_{CBO} is ~ 0 meV and Δ_{VBO} is ~ 70 meV.²⁰⁸ This contrasts with the large Δ_{CBO} (930 meV) and Δ_{VBO} (720 meV) in vertical MoS₂/WS₂ from scanning tunneling spectroscopy (Fig. 8a).¹⁶⁶ Similarly, Guo *et al.* highlight vertical MoS₂/WSe₂ junctions for which theory and experiment suggest very large Δ_{CBO} and Δ_{VBO} (Fig. 18a, ~ 830 meV and ~ 760 meV, respectively),^{165,215} in contrast to <200 meV Δ_{CBO} and Δ_{VBO} in lateral heterojunctions.²¹⁵ Calculations by Yang *et al.* similarly suggest that both Δ_{CBO} and Δ_{VBO} nearly disappear in lateral junctions.²¹⁶

Recent experimental evidence lends credence to the predictions that the Type-II band alignments observed for vertical hetero-bilayers do not necessarily translate to Type-II alignment for lateral junctions. Zhang *et al.* used scanning tunneling spectroscopy/microscopy to directly image the interfacial strain and band alignment in a MoS₂/WSe₂ lateral heterojunction.²¹⁷ Their measurements suggest that interfacial strain imparts significant band bending at the interface, resulting in a Type-I band alignment with large Δ_{CBO} and Δ_{VBO} (Fig. 18b and c). This alignment differs remarkably from the Type-II alignment observed for the MoS₂/WSe₂ vertical heterojunction using the same technique (Fig. 8b).¹⁶⁵

Differences in Δ_{CBO} and Δ_{VBO} between vertical heterojunctions and lateral heterojunctions will likely have significant

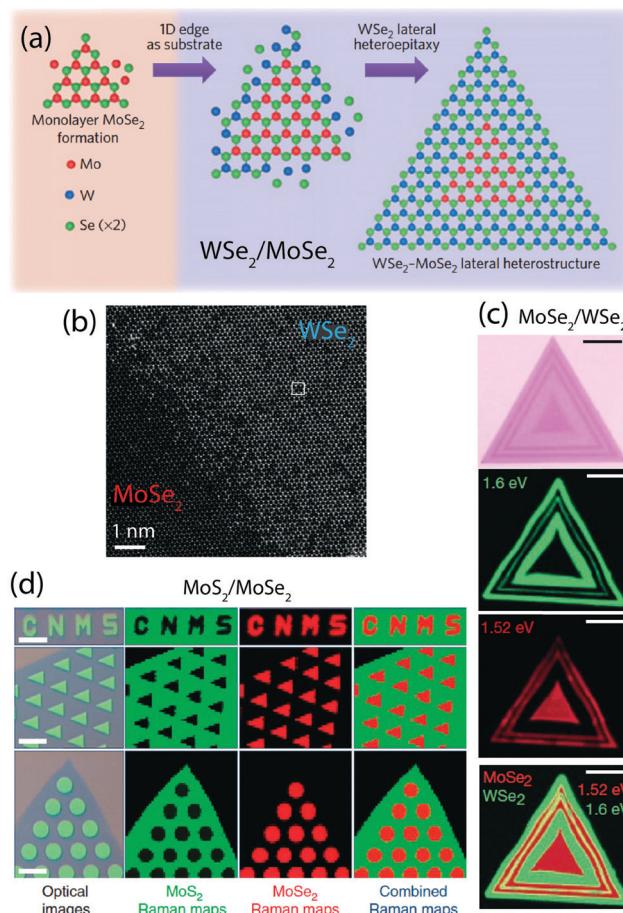


Fig. 17 (a) Schematic illustration of in-plane epitaxial growth process for exemplary lateral WSe₂/MoSe₂ heterostructure.²⁰⁷ (b) High-resolution ADF STEM image of an interface between MoSe₂ (darker) and WSe₂ (lighter). Scale bar, 2 nm.²⁰⁷ Panels (a and b) are reprinted by permission from Springer Nature from ref. 207. (c) Photoluminescence intensity maps for WSe₂ (1.6 eV, top) and MoSe₂ (1.52 eV, middle) domains, and composite PL map (bottom) of a lateral WSe₂/MoSe₂ heterojunction.²¹³ Reprinted by permission from Springer Nature from ref. 213. (d) Optical images (left-most panels) and Raman mapping images (other panels) of lateral MoS₂/MoSe₂ heterojunction arrays formed within monolayer crystals by patterning and selective conversion process. In Raman images, green areas correspond to MoS₂ (403 cm^{-1}) and red areas correspond to MoSe₂ (238 cm^{-1}).²⁰⁹ Reprinted by permission from Springer Nature from ref. 209.

impact on PCT and carrier recombination. For example, theoretical studies suggest that lack of Type-II band alignment in MoS₂/WSe₂ lateral junctions leads to accelerated recombination dynamics compared to vertical heterojunctions (Fig. 19a).²¹⁶ For the lateral junctions, Yang *et al.* found that the electron wave function was localized at the interface region between WSe₂ and MoS₂, and the hole was localized in WSe₂ close to the interface. The authors concluded that the highly localized exciton-like state at the lateral interface recombined significantly faster (191 ps) than in the vertical heterojunction (496 ps).

Experimental studies of PCT across lateral TMDC/TMDC heterojunctions are still sparse. Bellus *et al.* report that the Type-I band alignment at the lateral MoS₂/MoSe₂ interface

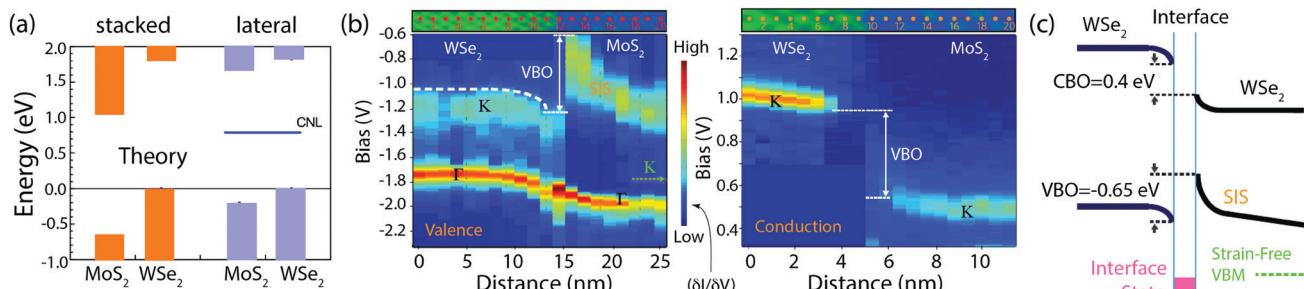


Fig. 18 (a) Comparison of DFT-calculated band alignments for MoS₂/WSe₂ heterojunction, in the stacked (vertical) or lateral configuration.²¹⁵ CNL refers to charge-neutrality level. Reprinted from ref. 215, with the permission of AIP Publishing. (b) Differential current ($\delta I/\delta V$), as measured by scanning tunneling spectroscopy, for the valence band (left) and conduction band (right) of WSe₂/MoS₂ lateral heterojunction. VBO and CBO are the valence band and conduction band offsets, respectively, and SIS denotes strain-induced states.²¹⁷ (c) Type-I band alignment at the lateral WSe₂/MoS₂ interface deduced from scanning tunneling microscopy measurements.²¹⁷ Panels (b and c) are reprinted by permission from Springer Nature from ref. 217.

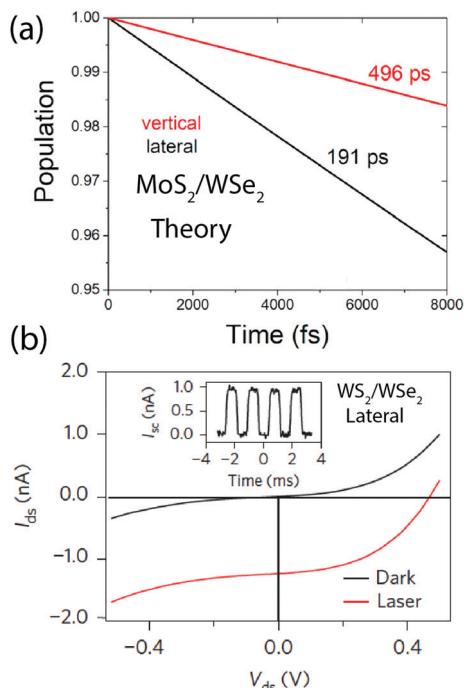


Fig. 19 (a) Calculated electron-hole recombination times for vertical (red) and lateral (black) MoS₂/WSe₂ heterojunctions.²¹⁶ Reprinted with permission from ref. 216. Copyright 2017 American Chemical Society. (b) Current–voltage (I_{ds} – V_{ds}) output of lateral WSe₂/WS₂ heterojunction p–n diode in the dark (black line) and under illumination (red line; 514 nm, 30 nW power).²⁰⁶ Reprinted by permission from Springer Nature from ref. 206.

leads to ultrafast photoinduced energy transfer from MoS₂ to MoSe₂,²¹² as opposed to the evidence of charge transfer and Type-II alignment observed by the same authors for the vertical MoS₂/MoSe₂ heterostructure.¹⁷¹ Spatial PL measurements of lateral MoS₂/WS₂ heterojunctions demonstrated strong interface-localized enhancement of PL at energies intermediate between the MoS₂ and WS₂ monolayer emission peaks, suggesting preferential recombination at the interface. The higher-energy PL near the lateral interfaces is in contrast to the near-infrared ILE observed for the same TMDCs in a vertical heterojunction.²⁰⁸

Despite these possible differences between vertical and lateral heterojunctions, some promising device results have been observed for lateral junctions. Duan *et al.* have shown rectifying p–n diodes for CVD-grown lateral WS₂/WSe₂ heterojunctions with a clear photovoltaic effect (Fig. 19b),²⁰⁶ and others have also observed varying degrees of PV effects in lateral heterostructures.^{208,213,218} Several groups are working towards creating lateral heterostructures with more complex degrees of carrier/exciton localization, such as the lateral WS₂/WSe₂ quantum-well superlattices grown by Zhou *et al.*²¹¹ Looking forward, there is clearly much more to learn about the band alignment within lateral TMDC heterostructures. The exact alignment likely depends on a host of factors, including carrier density and type in each layer, the degree of sharpness or alloying at the junction, the presence and density of interfacial defects, substrate effects, and more. As such, this area is ripe for future exploration, both for understanding and rationally tuning in-plane band alignment and for understanding the effects of this alignment on PCT.

9. TMDC heterojunctions with organic semiconductors

Several complementary relationships exist between organic semiconductors (OSCs) and TMDCs, making heterojunctions between these classes of materials particularly attractive. For example, extensive work on intelligent molecular design has led to an impressive range of OSCs where the band gap, morphology, and the energy level alignment can be tuned by small chemical or processing variations.^{39,219–222} This OSC toolset can be employed to engineer functional TMDC heterojunctions with optimized interfacial charge separation. Additionally, OSCs offer strong optical absorption to increase photon harvesting, surfaces free of dangling bonds, and small spin-orbit coupling that could possibly facilitate retention of selective spin-valley excitations in TMDC-based spintronics. On the other hand, some OSCs tend to have low carrier mobilities, making the higher mobilities in TMDCs particularly beneficial for optimizing carrier separation and collection. Depositing organics onto TMDCs

may also have unique benefits of inducing ordered structure in the organic molecules due to the TMDC-organic surface interactions.^{223,224}

TMDC/organic interfaces have been investigated in several different contexts, such as using organics as TMDC surface treatments to passivate defects,^{225–228} using organics for p-type or n-type doping of TDMCs,^{229–231} or using thicker organic films to form TMDC/organic charge-separating heterojunctions where both the molecular and TMDC layers are active components.^{79,81,232–234} Here, we focus primarily on the case of PCT at TMDC-based heterojunctions, because this is a central component for future device applications including solar fuel generation, photocatalysis, photovoltaics, photodiodes, and phototransistors. We highlight TMDC/organic heterojunctions employing small molecules, carbon nanotubes, or polymers.

9.1 Photoinduced charge transfer at TMDC/molecular semiconductor interfaces

PCT has been demonstrated in several TMDC/molecule systems, predominately including heterojunctions with phthalocyanines,^{81,226,235–239} porphyrins,²⁴⁰ acenes,^{79,232,233,241,242} perylenes,^{243–245} and fullerenes.^{246,247} The competitive process of energy transfer has also been studied in heterojunctions with organic dyes.²⁴⁸ While the optimization of carrier generation in TMDC/molecule heterojunctions is still in a nascent stage, small molecule semiconductors are particularly attractive candidates for model systems to enable more detailed understanding of TMDC-based heterostructures. For example, in comparison to polymers, small molecules offer rigid and well-defined molecular units that can pack into lattice structures with potentially less disorder and more easily defined morphologies.²⁴⁹ As we describe here, several examples exist where molecular control has played an important role in elucidating fundamental properties of TMDCs and TMDC/organic interfaces.²³⁶

9.1.1 Charge-transfer driving force and molecular morphology. A crucial initial step for designing TMDC-based heterojunctions that exhibit interfacial charge transfer is proper energy level alignment to achieve sufficient driving force (ΔG) for PCT, as described in Sections 2 and 3 and eqn (4)–(6). As an example of ΔG_{CT} values in organic/TMDC heterojunctions, Table 3 shows estimated driving forces for electron transfer and hole transfer between a range of popular semiconducting molecules that could form a Type-II heterojunction with monolayer MoS₂. In practice, only a few of the molecules in Table 3 have been employed in organic/TMDC heterojunctions, and the actual IP_D, EA_A, and $\Delta G_{ET/HT}$ values will vary depending on the substrate and sample characteristics.

The IP and EA values for molecular semiconductors can depend on molecular orientation, as indicated by the differing ΔG_{CT} values in Table 3 for lying (horizontally stacked) *versus* standing (vertically stacked) CuPc and pentacene. This opens opportunities for tuning the charge transfer yields and rates through modifying molecular packing and morphology. Changing morphology in the organic layer also affects the efficiency of

Table 3 Estimated values for the driving force of electron transfer (ΔG_{ET}) and hole transfer (ΔG_{HT}) for a range of organic molecules that could act as electron donors in Type-II heterojunctions with monolayer MoS₂. References indicate the source of ionization potentials used in eqn (6), and MoS₂ electron affinity values were averaged from ref. 12, 81, 215 and 250 ($EA_{MoS_2} \approx -4.1 \pm 0.1$ eV)

Organic electron donor	ΔG_{ET} (eV)	ΔG_{HT} (eV)
(6,5) SWCNT ^{163,251}	0.02	-0.62
(7,5) SWCNT ⁴⁶	0.02	-0.67
(9,7) SWCNT ⁴⁶	0.14	-0.84
(11,9) SWCNT ⁴⁶	0.20	-0.94
PC ₆₀ BM ²⁵²	-0.29	-0.14
PC ₇₀ BM ²⁵²	-0.38	-0.12
ITIC ²⁵³	0.01	-0.27
Pentacene (lying) ²⁵⁴	-1.73	-1.16
Pentacene (standing) ²⁵⁴	-1.25	-0.68
CuPc (lying) ^{255,256}	-0.48	-0.76
CuPc (standing) ^{255,256}	-1.04	-1.32
ZnPc ²⁵⁷	-0.41	-0.74
SubPc ²⁵⁸	-0.88	-0.45
SubNc ²⁵⁸	-0.67	-0.67
α -T ²⁵⁸	-2.10	-1.17
Ruberene ²⁵²	-1.54	-0.72
DTDCTB ²⁵⁹	-0.27	-0.75
d-DTS(PTT ₂) ₂ ²⁶⁰	-1.04	-1.22
p-DTS(FBT ₂) ₂ ²⁶⁰	-1.04	-1.22

free-carrier generation by varying the extent of carrier delocalization.²³⁶ Indeed, Padgaonkar *et al.* has demonstrated that molecular orientation plays an important role in extending carrier lifetimes in TMDC/phthalocyanine (Pc) heterojunctions.²³⁶ The authors found that face-on stacking of CuPc molecules facilitates hole diffusion away from the interface, extending charge separation up to 70 ns.²³⁶ This long lifetime of separated carriers contrasts with the shorter sub-nanosecond decays in TMDC/H₂Pc heterojunctions, where the mix of edge-on and face-on H₂Pc orientation is suggested to yield inferior charge diffusion.²³⁶ Theoretical calculations also support more efficient charge transfer at TMDC/Pc interfaces with face-on orientation.²³⁷ In perylene systems, it has also been suggested that alkyl chain length can contribute to the molecular tilt angle on MoS₂ surfaces, which could affect charge-transfer dynamics.²⁴⁵ While charge generation and band bending has been investigated in perylene/MoS₂ systems,²⁴³ establishing a link between molecular orientation and charge carrier kinetics in these systems requires additional characterization.

In addition to controlling alignment and stacking orientation when molecules are deposited onto TMDCs, Fig. 20 highlights another promising strategy for optimizing TMDC/organic interfacial contact using a ‘one-pot synthesis’ with self-assembly in solution.²⁴⁶ In this process, rapid injection of a poor solvent (acetonitrile, MeCN) into a good solvent (*N*-methyl-2-pyrrolidone, NMP) containing the TMDCs and fullerenes yields TMDC-C₆₀ aggregates that form due to a combination of the lyophobic effect and strong van der Waals interactions. Interestingly, the authors observed different aggregate formation behavior between MoS₂/C₆₀ and WS₂/C₆₀ structures, as schematically depicted in Fig. 20. They hypothesize that larger WS₂/C₆₀ composites form in the NMP/MeCN solution due to a stronger attractive interaction

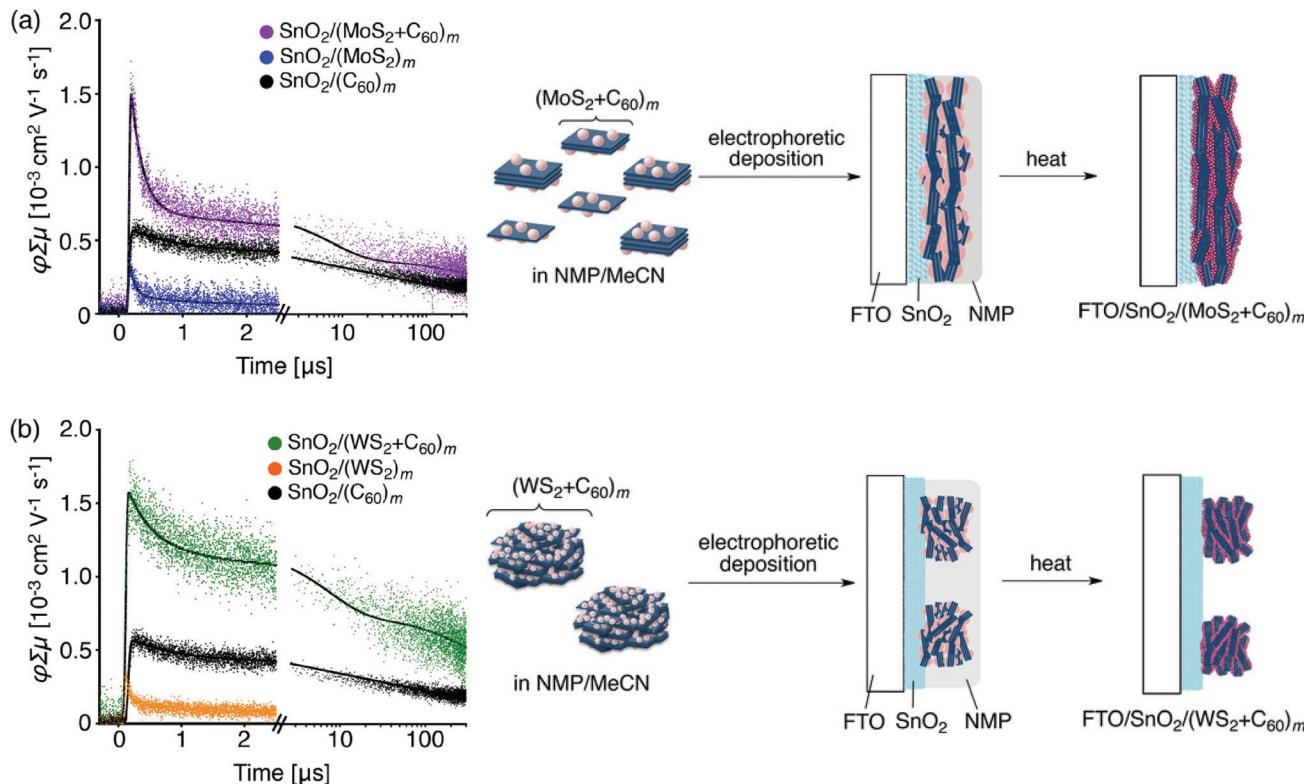


Fig. 20 Transient photoconductivity ($\phi \sum \mu$), in which ϕ is the charge-separation quantum efficiency and $\sum \mu$ is the sum of carrier mobilities measured for (a) $\text{MoS}_2/\text{C}_{60}$ composites on SnO_2 versus (b) $\text{WS}_2/\text{C}_{60}$ composites on SnO_2 , where heterojunction formation via solution self-assembly is schematically illustrated for each material. This figure is modified from ref. 246. Reprinted with permission from ref. 246. Copyright 2018 Wiley.

between WS_2 and C_{60} (calculated as -0.97 eV)²⁶¹ compared to MoS_2 and C_{60} (calculated as -0.84 eV).²⁶¹ The authors observed evidence for free carrier generation in these systems using time-resolved microwave conductivity (TRMC), which showed higher photoconductivity and longer carrier lifetimes for the heterojunctions compared to the neat materials. It should be noted, however, that a significant portion of the TRMC signal in this case is due to interactions with SnO_2 nanoparticles in addition to the TMDC-fullerene hybrid structures. Charge transfer was further evidenced by a photoelectrochemical response in both heterostructures, with an incident photon-to-current efficiency (IPCE) at 400 nm of 35% for FTO/ $\text{SnO}_2/(\text{MoS}_2 + \text{C}_{60})$ and 23% for FTO/ $\text{SnO}_2/(\text{WS}_2 + \text{C}_{60})$, where FTO is fluorine-doped tin oxide.

9.1.2 Charge-transfer states. Even in systems with sufficient driving force for charge generation, opposite charge carriers often remain Coulombically bound at TMDC/organic interfaces due to spatial confinement and low dielectric screening, which can result in interfacial charge-transfer states with binding energies in the range of tens to hundreds of meV.^{79,244} Charge-transfer states at TMDC/organic interfaces have been demonstrated by emergence of sub-gap absorption features, as illustrated in Fig. 21a.²³⁵ In this case, the strong charge-transfer absorption peak is attributable to high oscillator strength for direct excitation of interfacial excitons across CuPc/MoS_2 interfaces, and the authors demonstrated similar sub-gap absorption peaks for a range of metal-center and metal-free

phthalocyanines. The authors found that these charge-transfer states are primarily comprised of the π -character phthalocyanine HOMOs and the TMDC conduction band, so the peak energy of charge-transfer state absorption only weakly depends on the phthalocyanine metal center. However, the small shift observed in the charge-transfer state energy follows a trend based on the phthalocyanine's non-frontier (HOMO-1) metal d-orbitals, suggesting enhanced orbital mixing occurs with closer energy alignment between the HOMO-1 and the MoS_2 valence band. This example demonstrates the promise of small variations in molecular structure for tuning interactions at organic/TMDC interfaces.

Similar to the ILEs at TMDC/TMDC heterojunctions, interfacial charge-transfer states at TMDC/organic heterojunctions can be characterized by emission peaks at lower energies compared to the neat materials' photoluminescence. Fig. 21b shows sub-gap luminescence at 1.7 eV from charge-transfer states in a 1L- WS_2 /tetracene heterojunction.⁷⁹ The charge-transfer emission was longer-lived than the exciton lifetimes of either separate neat material, with a stretched-exponential decay giving an average lifetime of 2.1 ns. The authors attributed the dispersion of the decay time constant (*i.e.* the stretching exponent in their fit of the charge-transfer lifetime) to a distribution of different charge-transfer state configurations. Using transient absorption microscopy, the authors measured diffusion of charge-transfer states away from the optical excitation.

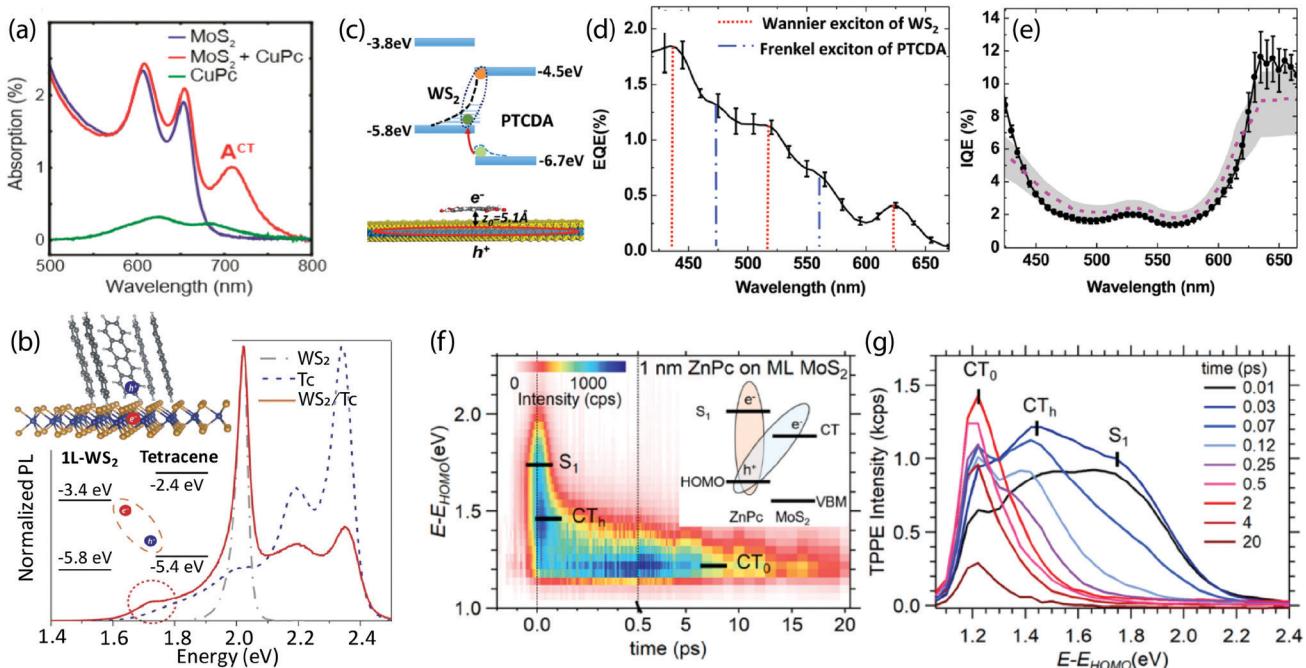


Fig. 21 (a) Strong sub-gap charge-transfer state absorption in MoS₂/CuPc heterojunctions,²³⁵ reprinted with permission from ref. 235. Copyright 2019 American Chemical Society. (b) Evidence of charge-transfer state photoluminescence (PL) around 1.7 eV in WSe₂/tetracene heterojunctions;⁷⁹ From ref. 79. © The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (c) Illustration of energy level offsets, charge transfer, and delocalization at PTCDA/WS₂ heterojunctions;²⁴⁴ (d) external quantum efficiency (EQE) for PTCDA/WS₂ where vertical lines indicate excitation of predominately WS₂ (red) or PTCDA (blue);²⁴⁴ (e) internal quantum efficiency (IQE) for PTCDA/WS₂;²⁴⁴ panels (c–e) are reprinted with permission from ref. 244. Copyright 2017 American Chemical Society. (f and g) Time-resolved two-photon photoemission (TPPE) showing evolution of photoluminescence from ZnPc singlet exciton (S₁) to hot charge-transfer states (CT_h) to relaxed charge-transfer states (CT₀) in ZnPc/monolayer-MoS₂ heterojunctions.⁸¹ Panels (f and g) are reprinted with permission from ref. 81. Copyright 2019 American Chemical Society.

They fit their data to two diffusion constants of $\sim 1 \text{ cm}^2 \text{ s}^{-1}$ and $\sim 0.4 \text{ cm}^2 \text{ s}^{-1}$, and they attributed the slower-moving population to trapped, low-energy charge-transfer states. They estimate these localized charge-transfer states to be $\sim 10 \text{ meV}$ lower energy than the delocalized states, suggesting that trapping/de-trapping at room temperature likely contributes to the stretched-exponential lifetime and broad emission profile for charge-transfer states at these heterojunctions.

As demonstrated by this WSe₂/tetracene study,⁷⁹ as well as by extensive investigations of this topic in organic heterojunction systems,^{39,178,179} understanding the equilibrium between localized and delocalized charge-transfer states is essential for optimizing free-carrier generation. However, the spatial nature of charge-transfer states at organic/TMDC interfaces differs from organic-only heterojunctions, particularly due to the significant asymmetry of carrier polarizability and delocalization on either side of the heterojunction. For example, Liu *et al.* addressed the implications of more confined Frenkel excitons generated in the organic layer *versus* Wannier-Mott excitons generated in the 2D TMDC layer for a perylene (PTCDA)/WSe₂ system (Fig. 21c–e).²⁴⁴ They found that the differing degree of delocalization between the two layers results in an asymmetric charge-transfer state that can be modeled as a point charge in the organic that is bound to a hole with high in-plane delocalization in the TMDC (Fig. 21c). They calculated 38.2 meV binding energy for the charge-transfer state, suggesting

that it is stable at room temperature. Using this heterojunction in a device, the authors observed higher internal quantum efficiency (IQE) upon TMDC excitation as shown in Fig. 21e. They attributed the higher IQE to greater exciton dissociation when exciting delocalized states in the TMDC layer ($\sim 80\%$, from PL quenching) in comparison to the organic layer ($\sim 12\%$) that relies on exciton diffusion to the interface. Since the IQE is equal to the exciton quenching efficiency (from PL) multiplied by the charge-transfer state dissociation at the interface (η_{diss}) and subsequent charge collection (η_{CC}), the authors attribute low IQE values of 1–10% to low $\eta_{\text{diss}}\eta_{\text{CC}}$ of only $10.6 \pm 2.2\%$ (Fig. 21e).

Kafle *et al.* further addressed delocalization by suggesting that charge separation at ZnPc/MoS₂ interfaces proceeds through delocalized hot charge transfer states (CT_h).⁸¹ The authors used time-resolved two photon photoemission (TR-TPPE, Fig. 21f and g) to track the processes that they attributed to ZnPc singlet exciton (S₁) quenching *via* charge transfer to MoS₂, followed by cooling within the charge-transfer state manifold.⁸¹ They ascribed a time constant of 40 fs to PCT from ZnPc to MoS₂, after which CT_h at intermediate energy rose and decayed with a time constant of 120 fs. The authors suggested that this 120 fs decay of CT_h then gave rise to the relaxed, localized CT₀ state. This value is consistent with general charge-transfer time constants in organic/TMDC systems, which are reported in the range of sub-instrument-response to 10 ps. The value can be affected by factors such as

the CT driving force, carrier delocalization, dielectric environment, and electronic coupling.^{79,232}

9.1.3 Effect of TMDC thickness. TMDC thickness also plays an important role in the energy level alignment, charge transfer driving force, and prominence of energy transfer at TMDC/organic interfaces. For example, Fig. 22a and b demonstrates the thickness dependence in WS₂/tetracene heterojunctions, where going from 1-layer to 2-layer WS₂ increases the valence band minimum and blocks hole transfer to the tetracene layer.⁷⁹ For the 1L-WS₂/tetracene Type-II junction, charge transfer

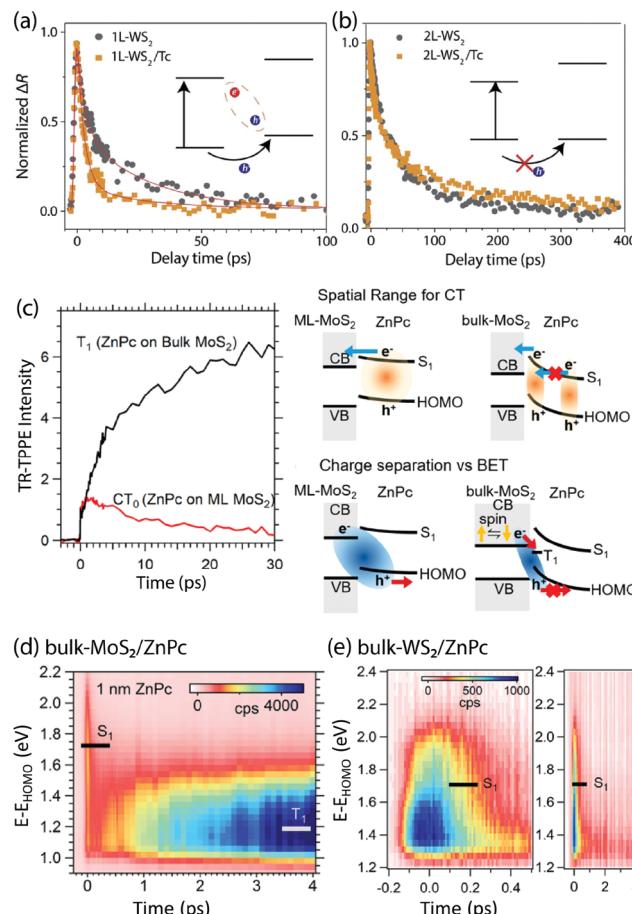


Fig. 22 (a) Transient reflectance for neat 1L-WS₂ (grey circles) compared to 1L-WS₂/tetracene Type-II heterojunctions (yellow squares) where charge-transfer occurs versus (b) 2L-WS₂/tetracene Type-I heterojunctions where hole transfer is blocked and energy transfer occurs.⁷⁹ Panels (a and b) are from ref. 79. © The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (c) TR-TPPE intensity for the ZnPc triplet (T_1 , black) in ZnPc/bulk-MoS₂ heterojunctions compared to the relaxed charge-transfer state (CT_0 , red) in ZnPc/monolayer-MoS₂ along with a schematic illustration of greater spatial range for the ZnPc singlet excitons near the interface in ZnPc/monolayer-MoS₂ compared to the bulk case, which results in charge separation in monolayer-MoS₂ heterojunctions versus back electron transfer (BET) that populates triplets in ZnPc for bulk-MoS₂ heterojunctions.⁸¹ Reprinted with permission from ref. 81. Copyright 2019 American Chemical Society. (d) TR-TPPE shows triplet formation in ZnPc/bulk-MoS₂ heterojunctions.⁸⁰ (e) TR-TPPE shows singlet exciton decay and avoided ZnPc triplet formation in ZnPc/bulk-WSe₂ Type-I heterojunctions.⁸⁰ Panels (d and e) are reprinted with permission from ref. 80. Copyright 2017 American Chemical Society.

occurs with a time constant of ~ 2.2 ps and out-competes energy transfer. As the WS₂ layer number (*i.e.* nL) increases, the interface transitions from Type-II to Type-I, and energy transfer occurs upon selective tetracene excitation. The authors observed slower energy transfer with increasing thickness, ranging from 44 ± 5 ps for 2L-WS₂/Tc to 84.8 ± 4.4 ps for 7L-WS₂/Tc.

TMDC thickness variations can still affect heterojunction photophysics even when the energy level alignment remains favorable for charge transfer. For example, Kafle *et al.* addressed thickness dependence of the TMDC layer using MoS₂/ZnPc interfaces (Fig. 22c).⁸¹ In this case, both 1L-MoS₂/ZnPc and nL -MoS₂/ZnPc interfaces have Type-II band alignment, despite the increase in MoS₂ valence band minimum with increasing thickness. The authors suggested that bulk-MoS₂/ZnPc heterojunctions are less efficient at free charge generation, which they attributed to strong band-bending in the ZnPc layer caused by HOMO energy pinning when ZnPc is deposited onto the bulk TMDC. The origin of this VB-HOMO pinning is still unclear, and further studies into such thickness-dependent interfacial interactions would be beneficial to the community. As depicted in Fig. 22c, the authors suggest that this uneven energy landscape within the bulk TMDC causes (1) more localization of ZnPc excitons that suppresses singlet exciton dissociation, in addition to (2) more localization of interfacial charge-transfer states, where spin flipping on the TMDC side of the heterojunction results in triplet charge-transfer states that relax to low-energy ZnPc triplet excitons. Bulk-WSe₂/ZnPc heterojunctions were also investigated (Fig. 22e) and found to form a Type-I junction, where singlet energy transfer from ZnPc to WSe₂ prevents low-energy ZnPc triplet formation by avoiding spin flipping within the charge-transfer manifold.⁸⁰

9.1.4 Triplet excitons. Similar to the studies of recombination to triplets in ZnPc/TMDC heterojunctions by Kafel *et al.*, the kinetic competition between charge separation/delocalization *versus* photocurrent loss to localized triplet excitons has long been important for optimizing organic electronics.^{262–264} However, TMDC-containing heterojunctions offer additional challenges for avoiding low-energy triplet excitons compared to organic-only systems. That is, the strong spin-orbit coupling associated with heavy metal atoms in TMDCs can expedite a spin flip to picosecond timescales in comparison to the nanosecond intersystem crossing times typical for neat organics. Indeed, the heavy-atom effect in the TMDC layer likely contributes to the fast (< 4 ps) conversion to triplets in TMDC/ZnPc heterojunctions, while intersystem crossing in neat ZnPc has been reported to proceed with > 100 ps to nanosecond time constants.⁸⁰ In addition to exploring the effects of band bending as done by Kafle *et al.*,⁸⁰ translating strategies from the OSC toolset to TMDC/organic heterojunctions may offer promise for future device optimization. For example, factors such as aggregation, functionalization, and molecular orientation have been found to alter the prevailing photophysical pathways in organic heterojunctions (*i.e.* charge separation *versus* loss to triplet states).^{262–264}

We note that in some strategies envisioned for photovoltaics or solar fuels, triplet formation is desirable. In particular,

singlet fission (SF) is a process by which one singlet exciton splits into two lower-energy triplet excitons, enabling greater than 100% photon-to-electron conversion.²⁶⁵ High-efficiency SF has been demonstrated in a few molecular systems, most notably pentacene and tetracene.²⁶⁶ Incorporating TMDCs as charge acceptors in SF devices requires proper energy level alignment to separate triplet excitons (produced by SF) into free carriers. While several studies have demonstrated photoactive pentacene/TMDC²³² or tetracene/TMDC⁷⁹ heterostructures, to our knowledge these heterojunctions generate carriers from TMDC exciton dissociation and do not make use of SF or triplet dissociation. For example, Homan *et al.* showed that pentacene excitations in pentacene/MoS₂ systems do not contribute to photocurrent, which decreases the utility of this system as pentacene would be the primary light absorber in the active layer. Despite the Type-II energy alignment, dissociation of pentacene singlet excitons is out-competed by sub-picosecond SF, which rapidly produces two low-energy triplet excitons that are not extractable at the MoS₂ band energies.²³² Instead, the authors found that photocurrent generation is due to MoS₂ exciton dissociation occurring on the time scale of 6.7 ps with 50% hole transfer yield to pentacene.²³² Computational studies provide further insight, suggesting ultrafast hole transfer from MoS₂ to pentacene followed by carrier cooling and eventual slow interfacial charge recombination.²⁴² Further efforts to pair SF materials with different TMDCs may open new avenues for possible > 100% charge generation yields if proper band alignment can be achieved to extract the SF-generated triplets that form on ultrafast timescales.

9.2 Photoinduced charge transfer at TMDC/polymer interfaces

Organic/TMDC heterojunctions that utilize semiconducting polymers rather than small molecules are promising due to the facile solution processing and scalability of polymer materials as well as benefits for exciton and charge transport offered by longer chain lengths. The organic photovoltaic community has explored charge generation in an extensive range of polymer structures, and Fig. 23 demonstrates the transfer of this knowledge to organic/TMDC systems where heterojunctions were created using three common polymers from polymer:fullerene photovoltaics.²⁶⁷ These polymers include P3HT

(regioregular poly(3-hexylthiophene-2,5-diyl)), PCDTBT (poly[N-9-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]), and PTB7 (poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)-carbonyl]-thieno[3,4-*b*]thiophenediyl]). All three polymers form Type-II heterojunctions with MoS₂ (Fig. 23), suggesting that interfacial charge transfer is thermodynamically favorable. Using transient absorption spectroscopy, the authors suggested that charge transfer was faster from MoS₂ to PTB7 or PCDTBT (~120 fs) in comparison to P3HT (9 ps). Despite a slower charge-transfer time for P3HT/MoS₂ heterojunctions, the authors concluded that their MoS₂/P3HT samples were the most efficient due to increased carrier lifetime. Interestingly, the P3HT exciton luminescence increased three-fold in the heterojunction, which is not typically a sign of exciton dissociation to produce free carriers. Other studies have shown quenched PL at MoS₂/P3HT interfaces, which has been attributed to charge transfer in these other samples.^{268–270} The authors reported accelerated excited-state recombination in MoS₂/PTB7 and MoS₂/PCDTBT heterojunctions compared to the neat materials, suggesting the heterojunctions fabricated for this study require additional optimization to sustain free charge.

Studies by Zhong *et al.* provide further details on the photophysical mechanisms for ultrafast carrier generation and recombination at PTB7/MoS₂ heterojunctions, which are summarized in Fig. 24a.²⁷¹ Similar to Petoukhoff *et al.*,²⁶⁷ the authors also observed charge transfer at timescales < 250 fs, but Zhong *et al.* attributed the ultrafast process to a different origin, namely electron transfer from PTB7 to hot states in the MoS₂ conduction band (MoS₂^{*}, Fig. 24a).²⁷¹ Theoretical calculations support this assignment by showing ~10 fs electron transfer facilitated by delocalization across the PTB7 LUMO and MoS₂ conduction band (Fig. 24b).²⁷² The different timescales between theory and experiment are likely due to the “perfect” nature of simulated interfaces that do not include disorder and defect sites. However, it is interesting to note that Garcia-Basabe *et al.* propose faster charge generation timescales in organic/TMDC systems than the timescales typically reported in studies using pump-probe spectroscopy.²⁶⁸ They note that ultrafast processes may be masked by the instrument response function (IRF) in these laser-based characterization methods, and they used synchrotron-based spectroscopy (*i.e.* the core-hole clock method) to measure charge transfer on femtosecond and sub-femtosecond timescales in P3HT/MoS₂ heterojunctions.²⁶⁸

After the ultrafast, sub-IRF charge generation process, Zhong *et al.* further observe additional charge formation with a slower time constant (1–5 ps), which they attribute to both an exciton diffusion-limited electron transfer from PTB7 to MoS₂ as well as hole transfer from MoS₂ to PTB7.²⁷¹ Theoretical studies similarly suggest that the hole-transfer process proceeds on a slower timescale, ranging from 1 ps to 70 ps depending on the PTB7 thickness. As shown in Fig. 24b, the calculations suggest accelerated hole transfer with increasing PTB7 thickness, which originates from a greater density of states in thicker PTB7 layers that can couple to the MoS₂ valence band.²⁷¹ This was suggested as

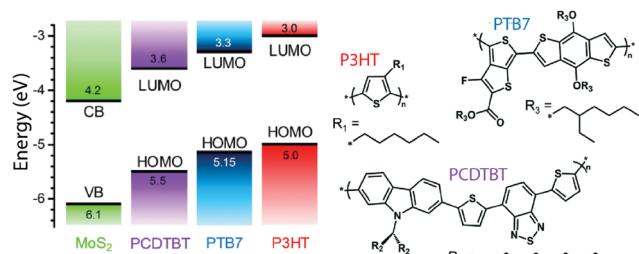


Fig. 23 Energy levels for MoS₂ and polymers that were studied in heterojunctions with MoS₂ from ref. 267. Republished with permission of Royal Society of Chemistry, from ref. 267; permission conveyed through Copyright Clearance Center, Inc.

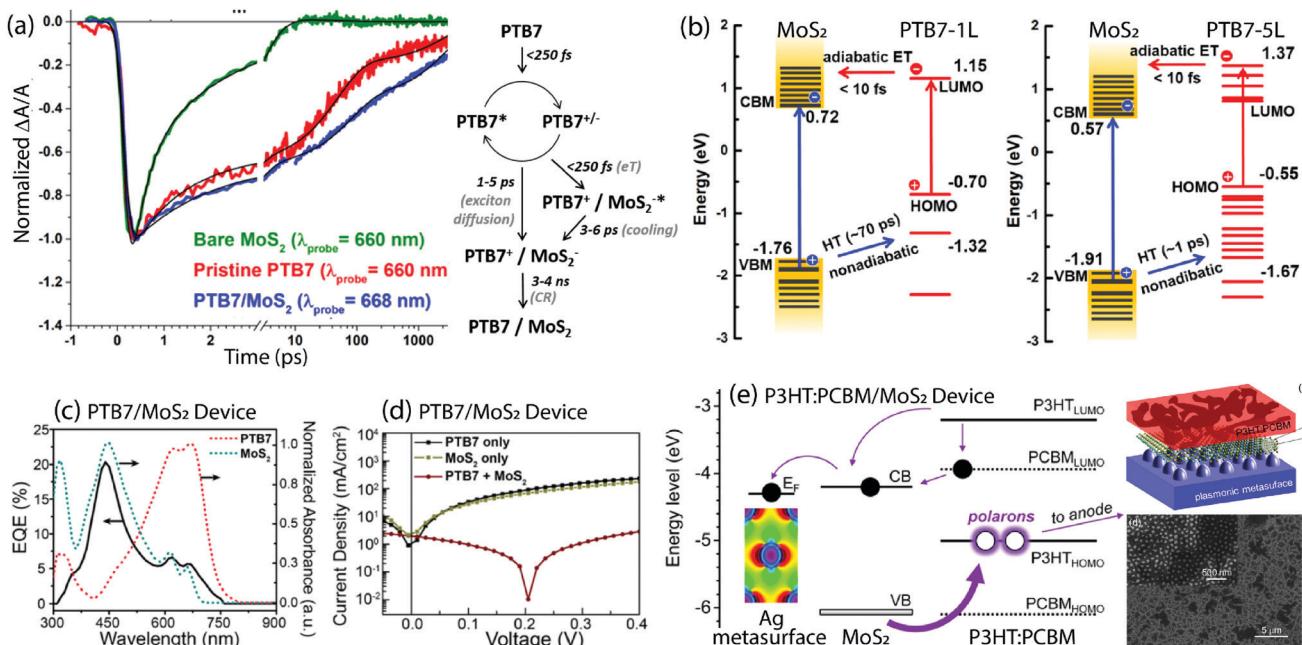


Fig. 24 (a) Transient absorption showing longer-lived kinetics MoS_2 /PTB7 heterojunctions compared to pristine MoS_2 or PTB7 along with the proposed photophysical pathways following excitation of PTB7 in the heterojunction.²⁷¹ Reprinted with permission from ref. 271. Copyright 2018 American Chemical Society. (b) Calculated energy alignment and photophysical processes in MoS_2 /1L-PTB7 versus MoS_2 /5L-PTB7.²⁷² MoS₂/PTB7 device data showing Reprinted with permission from ref. 272. Copyright 2019 American Chemical Society. (c) External quantum efficiency (EQE) and (d) current–voltage curves.²⁷³ Panels (c and d) are reprinted with permission from ref. 273. Copyright 2016 American Chemical Society. (e) Photophysical pathways for charge generation in P3HT:PCBM/MoS₂ devices employing Ag metasurfaces, along with schematic illustration and scanning electron microscope image.²⁷⁴ Reprinted with permission from ref. 274. Copyright 2016 American Chemical Society.

a possible explanation for greater quenching of MoS_2 photoluminescence, which has been experimentally observed with increasing PTB7 thickness.²⁷³

In contrast to the studies of Petoukhoff *et al.*,²⁶⁷ Zhong *et al.* did observe an increase in the excited-state lifetime in PTB7/ MoS_2 heterojunctions compared to the neat materials (Fig. 24a).²⁷¹ This contrast possibly stems from sample-to-sample variability and suggests room for better fundamental understanding of TMDC/organic interfaces. Zhong *et al.* attributed the longer lifetimes in the heterojunctions to free carrier formation at the interface and to a shift in the PTB7 equilibrium between excitons and polaron pairs. Shastry *et al.* similarly saw evidence for charge generation in PTB7/ MoS_2 heterojunctions, including mutual PL quenching in the heterojunction and functional photovoltaic devices with 0.1% efficiency (Fig. 24c and d). However, despite the charge generation observed in this system *via* spectroscopy, the PTB7/ MoS_2 devices showed minimal photocurrent originating from PTB7 light absorption (Fig. 24c).²⁷³ Zhong *et al.* suggest this may be caused by charge trapping at interfacial MoS_2 defects and recombination in PTB7 *via* polaron pair or triplet states.

Strategies to enhance light absorption in thin TMDC/organic device have been employed to increase charge photogeneration and power conversion efficiencies. For example, Petoukhoff *et al.* fabricated TMDC/polymer devices with plasmonic metasurfaces by patterning monolayer MoS_2 onto Ag nanoparticles and coating these surfaces with 1:1 P3HT:PCBM (Fig. 24e).²⁷⁴ The authors observed the greatest absorptance enhancement from the MoS_2 component, with 10-fold enhancement from

550–900 nm. MoS_2 to P3HT hole transfer was investigated with TR spectroscopy probing P3HT polaron and exciton states. The PCT processes are summarized in Fig. 24e, where the enhanced MoS_2 absorptance led to greater PCT and higher P3HT polaron yields. Although the authors did not employ this structure in a device, other photovoltaic devices employing P3HT/PCBM/ MoS_2 in various configurations show power conversion efficiencies (PCE) in the range of 1–4%, slightly lower than PTB7/PCBM/ MoS_2 devices with PCEs up to ~8%.²⁷⁵ P3HT/PCBM/ MoS_2 structures have also been employed in photocathodes for hydrogen evolution with photocurrent of 1.21 mA cm^{-2} at 0 V vs. RHE under 1 sun illumination.²⁷⁶

9.3 Photoinduced charge transfer at TMDC/SWCNT interfaces

Beyond polymers and molecular semiconductors, semiconducting single-walled carbon nanotubes (s-SWCNTs) are another class of promising components for TMDC/organic heterojunctions. SWCNTs are intriguing for their very large aspect ratios with a rigid periodic lattice along the length of the tubes. These structures support features such as high carrier mobilities, low reorganization energies, sharp optical transitions, and diameter-dependent tunability of the energy landscape, while offering high photochemical stability.^{277,278} Both photocurrent generation and hydrogen evolution have been demonstrated in TMDC/SWCNT heterojunctions.^{279–282} For example, Fig. 25a shows photocurrent generation in a heterojunction between monolayer MoS_2 and 1.4 nm diameter s-SWCNTs, where excitation of both MoS_2 (500–600 nm) and the SWCNT S_{22} (900–1100 nm) produce photocurrent.²⁷⁹

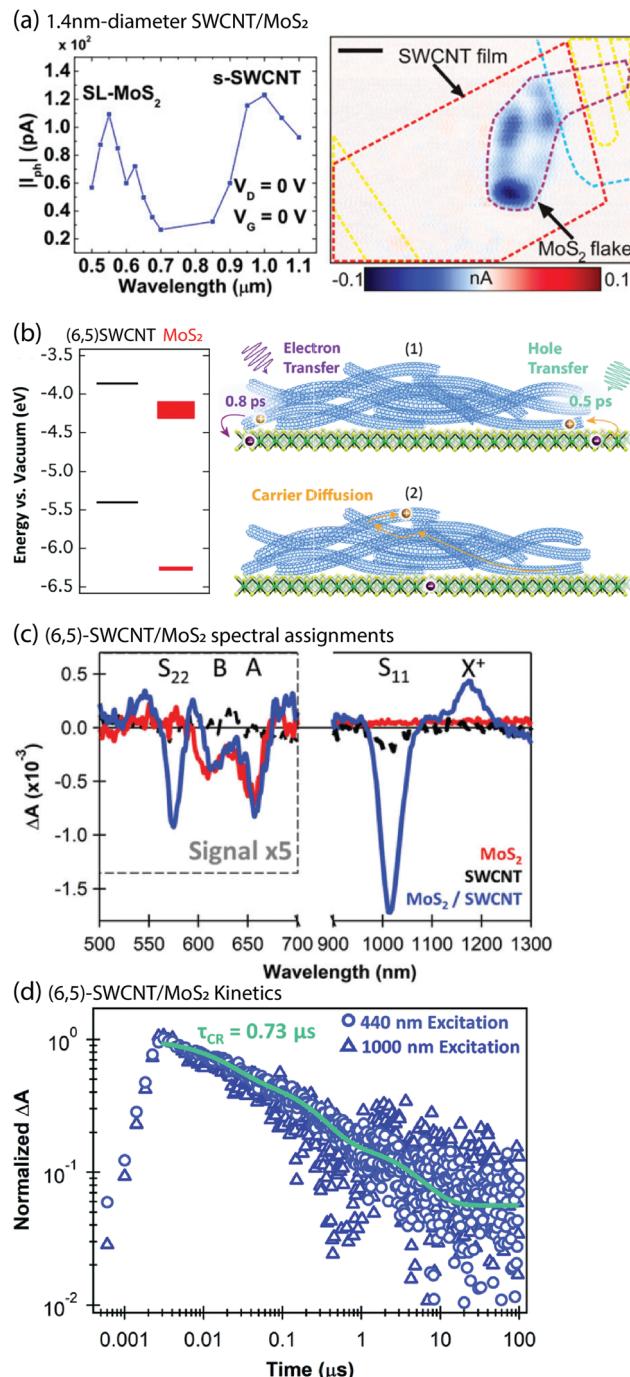


Fig. 25 (a) Wavelength-dependent photocurrent (I_{ph}) and photocurrent map for 1.4 nm-diameter SWCNT/MoS₂ devices.²⁷⁹ Republished with permission of Royal Society of Chemistry, from ref. 279; permission conveyed through Copyright Clearance Center, Inc. (b) Type II energy-level offsets and schematic illustration of charge transfer in (6,5) SWCNT/MoS₂ heterojunctions along with (c) assignment of spectral features in TA spectra and (d) demonstration of exceptionally long-lived charge carriers with charge recombination time constant (τ_{CR}) of 0.73 μs .¹⁶³ Panels (b–d) are republished with permission of Royal Society of Chemistry, from ref. 163; permission conveyed through Copyright Clearance Center, Inc.

However, it's important to note that there is still significant room for improvement through more systematic understanding

of the charge generation, charge transfer, and recombination mechanisms.

Fig. 25b–d shows recent investigations on the photophysics at interfaces between monolayer MoS₂ and highly-enriched 0.76 nm diameter (6,5) s-SWCNTs using transient absorption spectroscopy.¹⁶³ Sub-picosecond charge transfer at these Type-II interfaces was characterized by the SWCNT trion (X^+) induced-absorption signature shown in Fig. 25b. Fig. 25e shows exceptionally long carrier lifetimes in these heterojunctions, with an amplitude-averaged lifetime of 0.73 μs from components of 17.5 ns (43%), 233 ns (43%), and 4.4 μs (14%). These carrier lifetimes significantly exceed those observed for the TMDC/TMDC, TMDC/molecule, and TMDC/polymer heterojunctions discussed above. The high carrier mobilities in SWCNT networks are suggested to facilitate charge motion away from SWCNT/TMDC interfaces and support these exceptionally long carrier lifetimes.¹⁶³ Despite the long carrier lifetimes, these heterojunctions could be further optimized by improving the charge-transfer yields, which were estimated as ~23% for electron transfer from the SWCNTs to MoS₂ and ~39% for hole transfer from MoS₂ to the SWCNTs.

With a goal of achieving controlled, clean interfaces and strong electronic coupling in TMDC/SWCNT hybrid systems, recent studies have begun to explore CVD-based methods for conformal TMDC growth.^{283,284} Fig. 26a–c shows a study by Xiang *et al.*²⁸³ where low-pressure CVD or metal-organic CVD was used to conformally grow MoS₂ single-walled nanotubes around SWCNTs within a free-standing network. MoS₂ only grew on SWCNTs with diameters >3 nm, and the MoS₂ nanotube yield was very low (<1%) in this procedure due to the strain associated with MoS₂ nanotubes <4 nm. A CVD-grown BN coating around the initial SWCNT enabled higher yield of MoS₂ nanotube growth due to a reduction in the strain. Liu *et al.* recently demonstrated the CVD growth of MoS₂ single crystals on SWCNTs that were grown prior on a quartz substrate.²⁸⁴ The authors found that MoS₂ flakes grew over top of the SWCNTs instead of underneath the SWCNTs (Fig. 26d). Identical polarized second harmonic generation (SHG) patterns were observed in multiple spots of the interfaced MoS₂ flakes (Fig. 26f), indicating that the whole MoS₂ domains were single crystal. While both of these studies demonstrated PL quenching of the CVD-grown MoS₂ by proximal SWCNTs, there is a large degree of polydispersity in interface energetics due to the uncontrolled electronic structure of these SWCNTs (*i.e.* metallic and semiconducting SWCNTs both present). The quenching likely originated from energy transfer in both studies due to the large SWCNT diameters. Looking forward, such growth techniques may be useful for creating Type-II TMDC/SWCNT heterojunctions if the starting SWCNTs are small-diameter highly enriched s-SWCNTs.

10. TMDC/quantum dot interfaces

Semiconductor nanocrystals (quantum dots, QDs) are an interesting class of 0D excitonic nanomaterials, where the optical band gap can be synthetically tuned across a wide spectral

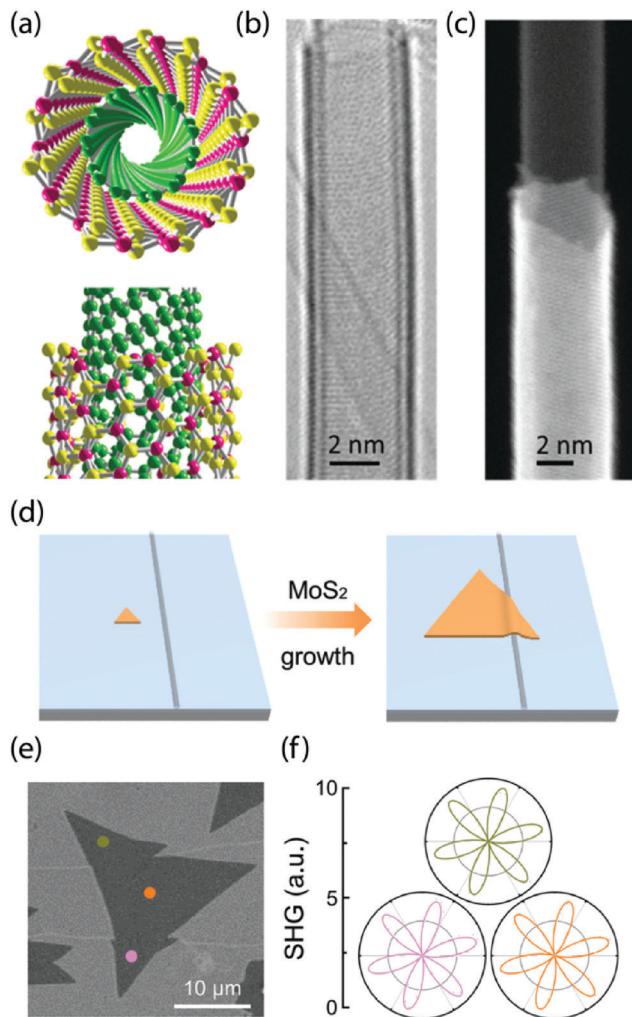


Fig. 26 CVD-grown MoS₂/SWCNT heterojunctions. (a) Atomic model, (b) high-resolution TEM image, and (c) high-angle annular dark field STEM image of single-walled MoS₂ nanotube grown on a SWCNT.²⁸³ Panels (a–c) are ref. 283. © The authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (d) Schematic of MoS₂ growing over top of SWCNT where the CVD MoS₂ growth occurs on pre-grown SWCNTs on a quartz substrate.²⁸⁴ (e) SEM image MoS₂ monolayer grown across SWCNTs where discontinuous edges are formed at two sides of the nanotubes. (f) Polarized SHG patterns taken at positions labeled in panel (e) indicate the MoS₂ domain is a single crystal. Panels (d–f) are republished with permission of Royal Society of Chemistry, from ref. 284; permission conveyed through Copyright Clearance Center, Inc.

range (*e.g.* UV to IR) through appropriate material selection and QD size. The size-tunable bandgap has made QDs versatile components in commercialized light-emitting diode (QLED) displays, a wide spectral range of photodetectors, PV applications, and photocatalysis.^{36,285–289} Here, we discuss the unique photo-physics that occur in 0D/2D QD/TMDC structures.

Because the photophysical processes at semiconductor interfaces determine their best-suited device applications, it is important to differentiate between various interfacial charge-transfer and energy-transfer pathways that may take place. Li *et al.* addressed this in 2L-MoS₂/QD devices, where charge transfer dominated in heterojunctions with core-only CdSe

QDs, and nonradiative energy transfer (FRET) dominated when using core/shell CdSe/ZnS QDs (Fig. 27a–c).²⁹⁰ In both cases, the authors observed significant interfacial interactions resulting in >95% quenching of the QD PL lifetimes when used in heterojunctions (from 15 ns to 430 ps in core-only and from 19 ns to 320 ps in core/shell). While a driving force for PCT would exist between 2L-MoS₂ and CdSe in both cases, the ZnS shell blocks charge transfer in the heterojunction with core–shell QDs, which enables the competitive FRET process to dominate. Interestingly, the authors observed different trends in photocurrent response with increasing photoexcitation power between the two heterojunctions (Fig. 27d). In the case of PCT (MoS₂/CdSe heterojunction), the authors attributed decreasing photocurrent with fluence to a photogating effect where accumulation of negative charge on the QD decreases MoS₂ band bending to inhibit hole collection. Such charge accumulation and resulting photogating does not occur in the 2L-MoS₂/CdSe/ZnS system where energy transfer dominates. Based on the differences in fluence dependence, the authors suggest that the 2L-MoS₂/CdSe/ZnS system would be useful for photovoltaic applications, which operate under higher fluences, and MoS₂/CdSe heterojunctions can be used for photodetectors under lower light intensities.

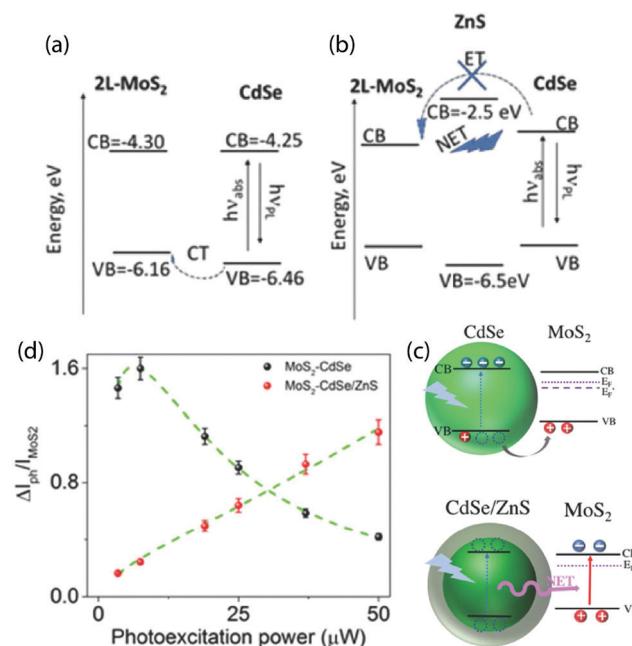


Fig. 27 Interfacial transfer of bilayer MoS₂ with CdSe (core only) or CdSe/ZnS (core/shell) QDs. (a) Energy level diagram for MoS₂/CdSe where photoexcited CdSe transfer holes to MoS₂ and can have excess negative charge accumulate on CdSe at higher photoexcitation powers (photogating). (b) Energy level diagram of MoS₂/CdSe/ZnS systems where nonradiative energy transfer (NET) occurs. (c) Illustration of the charge transfer and NET processes. (d) Photocurrent as a function of laser power, where the positive slope versus photoexcitation power in MoS₂-CdSe₂/ZnS is better for photovoltaics and the negative slope due to photogating from electron accumulation in MoS₂/CdSe₂ system is better for photodetectors at low light exposure.²⁹⁰ All panels reprinted with permission from ref. 290. Copyright 2018 Wiley.

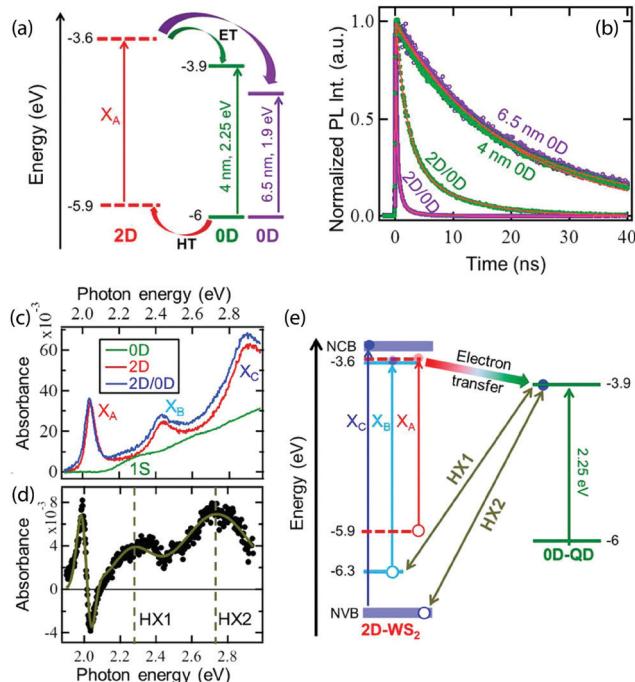


Fig. 28 Monolayer WS_2 and CdSe/ZnS (core/shell) QDs dynamics. (a) Energy schematic showing increased driving force for electron transfer (ET) from WS_2 (labeled as 2D) to 0D QDs with larger core diameter while hole transfer (HT) is unaffected. (b) The heterojunction with larger driving force shows faster PL decay compared to neat QDs. (c) Comparison of steady-state absorption spectra of the heterojunction with the separate WS_2 and QD layers where (d) the difference shows new absorption features labeled as hybrid excitons HX1 and HX2. (e) Illustration of the HX states in the 2D/0D hybrid system, showing the single-particle states making up the A (red), B (cyan), and C (purple) excitons (X_i) of WS_2 . QD states are shown in green.²⁹¹ All panels reprinted with permission from ref. 291. Copyright 2016 American Chemical Society.

Boulesbaa *et al.* studied interfacial charge transfer between monolayer WS_2 and CdSe/ZnS (core/shell) QDs (Fig. 28).²⁹¹ The authors demonstrated mutual PL quenching in this system, suggesting that charge transfer (rather than energy transfer) takes place. To highlight the effect of driving force for electron transfer from photoexcited WS_2 to the QD, the authors increased the QD core diameter, which lowers the EA while keeping the IP constant (Fig. 28a). The higher driving force for electron transfer resulted in a greater quenching of the PL lifetime (Fig. 28b), consistent with eqn (6) (Marcus theory). Using TA spectroscopy, the authors showed WS_2 to QD electron transfer in <45 fs to yield an interfacial exciton (HX) with ~ 140 meV binding energy that decays on picosecond time scales. Interestingly, based on the change in ground-state absorption spectrum (Fig. 28c and d), the authors postulate the formation of two HXs, where the lower-energy HX1 involves a hole in WS_2 band that gives rise to B excitons, and the higher-energy HX2 involves a hole in WS_2 band that gives rise to C excitons (Fig. 28e).

Similar to the studies of PCT driving force by varying QD diameter in Fig. 28a and b, Chen *et al.*⁴⁴ varied the PCT driving force in two ways – (1) by pairing a single size of PbS/CdS QDs with MoS_2 having variable numbers of layers (Fig. 29a), where

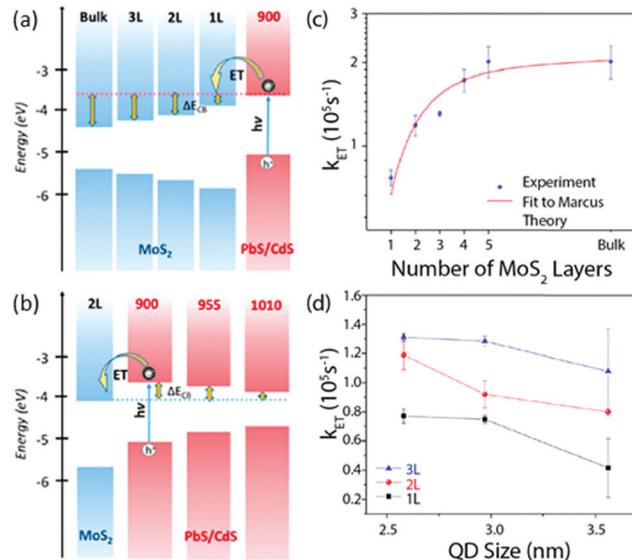


Fig. 29 (a) Interfacial charge transfer kinetics are tied to the thermodynamic driving force for photoexcited electron transfer from PbS/CdS QD to MoS_2 .⁴⁴ The energetics of (a) MoS_2 with variable numbers of layers interfaced with PbS/CdS QDs at a single diameter or (b) bilayer MoS_2 interfaced with variable diameters of PbS/CdS QDs. (c) The photoinduced electron transfer rate increases with the number of MoS_2 layers due to an increase in the driving force. (d) The photoinduced electron transfer rate decreases with QD size due to a decrease in the driving force. Reprinted with permission from ref. 44. Copyright 2019 American Chemical Society.

the driving force increases with increasing layer number, and (2) by pairing MoS_2 bilayers with PbS/CdS QDs having variable diameters (Fig. 29b), where the driving force increases with decreasing QD diameter. In both cases, the authors used TRPL to demonstrate that the PCT rate (k_{ET}) increased with increasing thermodynamic driving force (Fig. 29c and d). These results can be understood within the Marcus formulation of charge transfer, as discussed in Section 1 (eqn (6)).

Monolayer WS_2 interfaced with InGaN QDs (Fig. 30a) has unique emission properties that are attributed to an interfacially-bound negative trion, where Coulombically-bound WS_2 excitons couple to electrons accumulated at the QD surface (Fig. 30b).²⁸⁵ This interfacial state (X, Fig. 30) is lower in energy than the WS_2 exciton (A) and higher in energy than the WS_2 trion (T). Interestingly, the WS_2 spin-valley physics are transferred to the electrons of the QD. Specifically, the emission from both the WS_2 exciton (A) and interfacial trion (X) are influenced by circularly polarized light (Fig. 30c). That is, the emission intensity depends on the detection polarization (*i.e.* left-left: LL or left-right: LR) with circularly polarized emission intensity ratios ($(I_{\text{LL}} - I_{\text{LR}})/(I_{\text{LL}} + I_{\text{LR}})$) of 16% for both X and A.

TMDC/QD interfaces have recently been commissioned for infrared (IR) photodetectors. These have benefits over graphene/QD systems because the dark current is reduced by the TMDC band gap and devices can be switched on/off with gating.²⁹² In 2015, Kufer *et al.* reported on a few-layer MoS_2 /p-type PbS QD phototransistor, that exhibited photo-excited electron transfer from the PbS QDs to TMDC with a

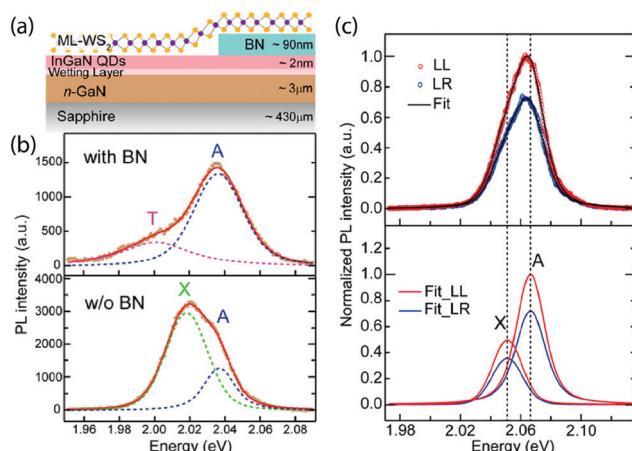


Fig. 30 Interfacially-bound negative trion between monolayer WS₂ and InGaN QDs. (a) Schematic of the WS₂/InGaN device design where BN is boron nitride. (b) PL from the WS₂/BN/InGaN QD region showing WS₂ exciton (A) and trion (T) emission. PL in the WS₂/InGaN QD region without BN shows quenched WS₂ T emission with additional interfacial negative trion (X) emission. (c) Left circularly polarized excitation with left/right circularly polarized emission detection (LL or LR, respectively) for WS₂/InGaN interfaces. The circular polarization is 16% for both X and A.²⁸⁵ Reprinted with permission from ref. 285. Copyright 2018 American Chemical Society.

photoresponse up to $\sim 1.2 \mu\text{m}$ (Fig. 31a and b).²⁹² The responsivity of the phototransistor was greatly improved by interfacing PbS QDs with MoS₂ compared to PbS QDs only, where the responsivity improved to $6 \times 10^5 \text{ A W}^{-1}$ from $4.3 \times 10^2 \text{ A W}^{-1}$. Moreover, the spectral range extended much further into the IR compared to the MoS₂ only (Fig. 31b), and the hybrid system had a typical decay time of 350 ms and a detectivity of 5×10^{11} Jones (detectivity figure of merit). Similarly, PbS QDs have also been coupled with 2D WSe₂ to be a broadband transistor with high performance. Hu *et al.* demonstrated this 2D TMDC/PbS QD interface also gives good responsivity (Fig. 31c, $2 \times 10^5 \text{ A W}^{-1}$) and can be used in the IR with a respectable decay time of 480 ms and detectivity of 10^{13} Jones.²⁹³

In 2019, Özdemir *et al.* demonstrated TMDC/QD interfaces with photodetection up to $2 \mu\text{m}$. The authors found that

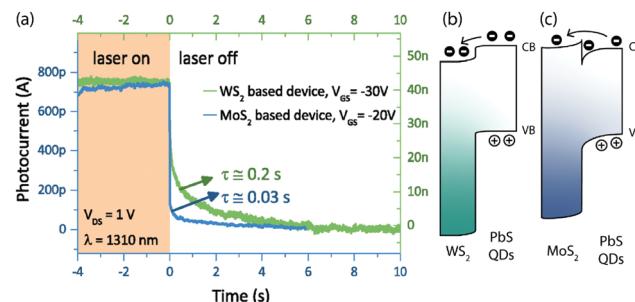


Fig. 32 TMDC/QD infrared detectors. (a) Few-layered WS₂/PbS QD system has longer photocurrent lifetimes than few-layered MoS₂/PbS QD systems. (b and c) Band energetics and charge transfer in WS₂ and MoS₂-based hybrid devices, respectively.²⁹⁴ All panels are reprinted with permission from ref. 294. Copyright 2019 American Chemical Society.

few-layered WS₂/PbS QD detectors outperformed few-layered MoS₂/PbS QD detectors due to a greater driving force for electron transfer from PbS to WS₂.²⁹⁴ The WS₂/QD system showed responsivity of 1400 A W^{-1} at $1.8 \mu\text{m}$ and 1 V bias with 10^{12} Jones at room temperature. Moreover, the WS₂/PbS QD device decay time was improved by an order of magnitude compared to the MoS₂-based device (Fig. 32a). The authors suggested that band bending at the MoS₂/QD interface results in a barrier for electron transfer, enhancing interfacial recombination for this system and a poorer photoresponse (Fig. 32b).

MoS₂ has also been explored for photodetector applications in heterojunctions with ZnCdSe/ZnS core/shell QDs.²⁸⁷ These photodetectors showed improved response over MoS₂ by 3 orders of magnitude, with 10^4 A W^{-1} and detectivity of 10^{12} Jones at wavelengths $> 700 \text{ nm}$. Interestingly, the inner ZnCdSe core of the QD would form a Type-II band offset with MoS₂, but the wide-gap ZnS shell forms a Type-I junction with both ZnCdSe and MoS₂ components. For this reason, electron transfer from photo-excited QDs to MoS₂ occurs via tunneling, and simultaneous exciton energy transfer from the ZnCdSe core to MoS₂ is also proposed. The authors find that photocurrent improves when going from few-layer to monolayer MoS₂, consistent with a report by Prins *et al.* showing greater nonradiative energy transfer from photoexcited CdSe QDs to monolayer *versus* few layer MoS₂.²⁹⁵

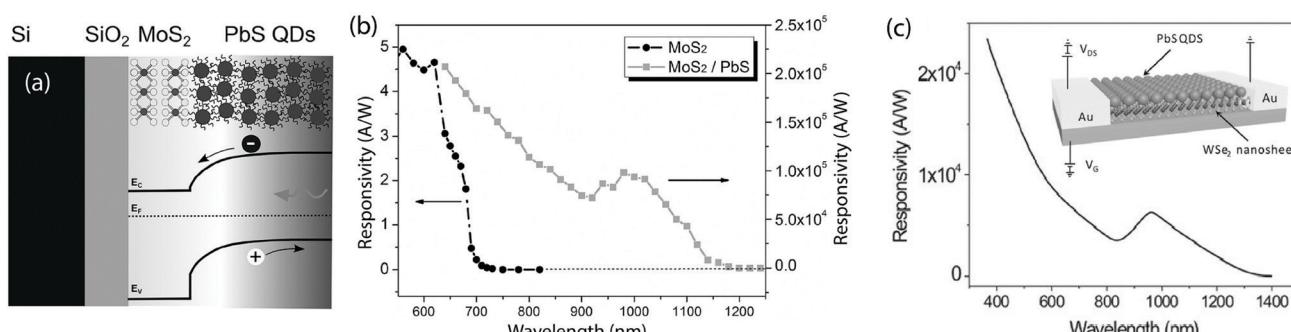


Fig. 31 Photodetectors using few-layered MoS₂ with n-type PbS quantum dots (QDs). (a) Energetic depiction of the MoS₂/PbS interface.²⁹² (b) Responsivity of the MoS₂-only or MoS₂/PbS QDs.²⁹² Panels (a and b) are reprinted with permission from ref. 292. Copyright 2015 Wiley. (c) Responsivity of WSe₂/PbSQD.²⁹³ Reprinted with permission from ref. 293. Copyright 2017 Wiley.

They attribute higher energy transfer efficiency to lower dielectric screening as the MoS_2 layer thickness decreases. Another example of MoS_2 /QD hybrids is dodecanethiol-functionalized MoS_2 nanosheets coupled to dodecanethiol-functionalized CuInS_2 QDs. Ahmad *et al.* showed improved photocurrent response of $\text{MoS}_2/\text{CuInS}_2$ QD hybrids compared to the QD or nanosheet only, which they attribute to charge transfer at the Type-II heterojunction.²⁹⁶

A recent study by Wang *et al.* suggests that heterostructures between exfoliated few-layer MoS_2 and PbS nanoplatelets can enable long-lived infrared-responsive photoconductivity.²⁹⁷ In this case, phototransistors made from the heterostructures generated photocurrent upon NIR excitation of the PbS nanosheets, driven by photoinduced electron transfer from PbS to MoS_2 . Band bending at the interface produced a small recombination barrier, so that cooling the system to 180 K or lower led to a persistent photoconductivity that showed little decay over the $\sim 10^4$ second experimental time frame. Such results demonstrate the potential applicability of TMDC-based heterostructures to optical information processing applications such as nonvolatile memory or neuromorphic computing.

11. TMDC/perovskite heterojunctions

Metal-halide based perovskites are a fascinating class of solution-processable semiconductors that are being explored for a variety of optoelectronic and energy applications. Perovskite is a general crystal structure with ABX_3 stoichiometry. In metal-halide perovskites, A is an organic (*e.g.* methyl ammonium, MA) or inorganic (*e.g.* cesium) cation, B is a transition metal (most typically lead) cation, and X is a halide anion. Based in part on exceptionally high free carrier yields and diffusion lengths, solar cells based on these materials have rapidly increased in efficiency over the past decade, with certified power conversion efficiencies now surpassing 25%.^{298,299} High PL quantum

yields enable efficient light-emitting diodes (LEDs) across widely tunable ranges of emission energy.^{300,301} In addition to these more traditional optoelectronic applications, the existence of strong spin-orbit coupling, long spin coherence lifetimes,³⁰² and Rashba spin-splitting³⁰³ has spurred interest in perovskites for spintronic applications.³⁰⁴

Thus far, TMDC/perovskite interfaces have been studied primarily in the context of photovoltaics^{305–308} and photodetectors,^{309–312} with $\text{MoS}_2/\text{MAPbI}_3$ interfaces receiving the most attention (Fig. 33a). Perovskite solar cells use an electron transport layer (ETL) and hole transport layer (HTL) to extract electrons and holes, respectively.^{313–316} Interestingly, despite MoS_2 typically serving as an n-type material and electron acceptor,³¹⁰ these perovskite PV studies have primarily (but not exclusively)³⁰⁶ utilized MoS_2 as an HTL.^{305,307,308} This brings up important questions about the energetics of this interface, since the typically reported range for the VBM of MoS_2 (-6.2 to -6.3 eV *vs.* vacuum) would not appear to favor hole transfer from the valence band of MAPbI_3 , which is typically reported in the range of -5.4 to -5.8 eV *vs.* vacuum.³¹⁴ Indeed, using ultraviolet photoelectron spectroscopy, Peng *et al.* concluded that a pristine MoS_2 monolayer forms a Type-I band alignment with MAPbI_3 (Fig. 33b), consistent with transient absorption results that suggest negligible hole transfer from the perovskite to the TMDC.³¹⁷

To determine the degree to which interfacial atomic structure may impact the thermodynamics and kinetics, the same authors used a mild O_2 plasma treatment to create sulfur vacancies in MoS_2 .³¹⁷ First-principles calculations indicated that S vacancies produce mid-gap states, making the “vacancy-engineered” MoS_2 monolayer p-type, consistent with the experimental observation of a large (~ 1.1 eV) increase in the MoS_2 work function (Fig. 33c). This significantly larger work function changed the interfacial band alignment at the vacancy-engineered $\text{MoS}_2/\text{MAPbI}_3$ to Type-II. TA measurements showed a delayed rise time of the perovskite bleach that was interpreted as arising

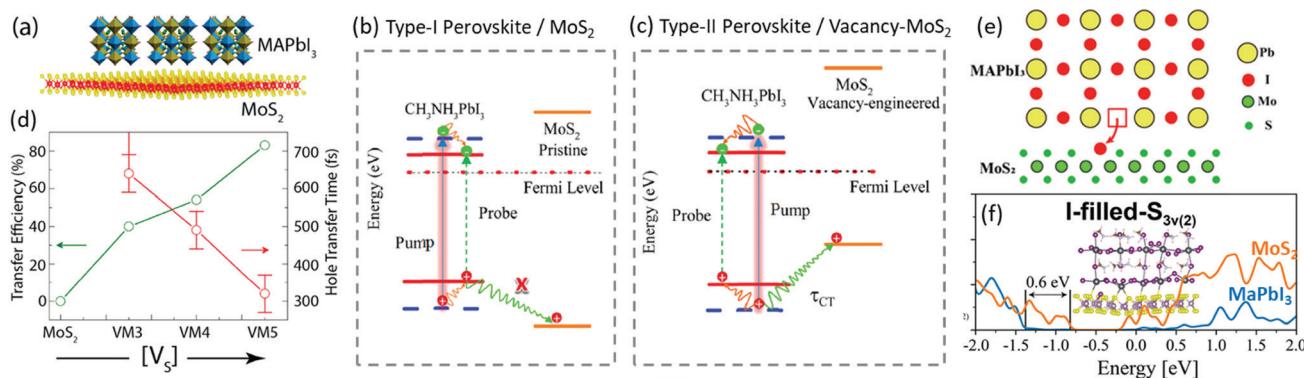


Fig. 33 (a) Schematic of $\text{MoS}_2/\text{MAPbI}_3$ heterojunction.³¹⁷ (b) Schematic of $\text{MoS}_2/\text{MAPbI}_3$ interfacial energetics that result in Type-I offset in comparison to (c) Type-II offset when MoS_2 is treated by O_2 plasma to create sulfur vacancies. (d) Hole transfer efficiency (left axis) and hole transfer time (right axis) from MAPbI_3 to MoS_2 , measured by transient absorbance spectroscopy, for MoS_2 with varying sulfur vacancy density $[V_s]$.³¹⁷ Panels (a–d) are reprinted with permission from ref. 317. Copyright 2016 American Chemical Society. (e) Schematic of $\text{MoS}_2/\text{MAPbI}_3$ interfaces where MoS_2 sulfur vacancies induce MAPbI_3 iodine vacancies at the interface, leading to (f) calculated band offsets with Type-II energy alignment.³² Panels (e and f) are reprinted with permission from ref. 32. Copyright 2020 American Chemical Society.

from ~490 fs hole transfer from the photoexcited MAPbI_3 to the vacancy-engineered MoS_2 . The extracted hole transfer time decreased and the hole transfer efficiency increased with increasing MoS_2 S vacancy density (Fig. 33d),³¹⁷ providing a potential means for improving the efficacy of MoS_2 hole transport layers in perovskite solar cells.³⁰⁷

Shi *et al.* followed up on the impact of vacancies for interfacial alignment with a detailed molecular dynamics study of the monolayer $\text{MoS}_2/\text{MAPbI}_3$ interface (Fig. 33e and f).³² Their simulations suggested that sulfur vacancies alone are not sufficient to reverse the VBM offset to favor hole transfer from perovskite to TMDC. Instead, they find that sulfur vacancies attract iodide anions from the MAPbI_3 , which in turn creates adjacent iodine vacancies at the interface. The resulting interface dipole moment lifts the VBM of MoS_2 above MAPbI_3 by 0.2–0.6 eV, creating a thermodynamic driving force for hole extraction by MoS_2 and a Type-II interface (Fig. 33f). Hole transfer was found to proceed in a biphasic manner, with an adiabatic component (20 fs) and a non-adiabatic component (200–800 fs). These studies suggest that MoS_2 effectiveness as a HTL in perovskite solar cells may depend on the exact atomic structure of each component and the resulting reconstruction upon interface formation.

Recent studies have expanded the initial work on the prototypical $\text{MoS}_2/\text{MAPbI}_3$ interface to a variety of different TMDC/perovskite interfaces. Bauer *et al.* used transient reflectivity to study the interface between CVD-grown monolayer WS_2 and a thin film of bulk MAPbI_3 perovskite.³¹⁸ When exciting this heterojunction at 3.1 eV, higher in energy than the optical gap of both the perovskite (1.6 eV) and the WS_2 (2.0 eV), the perovskite PL was quenched by ~85% and the WS_2 PL was entirely quenched. Since energy transfer is not possible from MAPbI_3 to WS_2 and the MAPbI_3 is quenched instead of enhanced, the authors concluding that quenching occurred primarily *via* charge transfer and not energy transfer. The band alignment suggests electron transfer from WS_2 to MAPbI_3 , with a time constant shorter than the instrument response (<45 fs). Charge separation inhibited recombination, with the slowest recombination time around 2.2 ns.

As with the $\text{MoS}_2/\text{MAPbI}_3$ interfaces discussed above, theoretical studies of TMDC/perovskite nanocrystal interfaces similarly suggest interfacial atomic structure plays an important role in the heterojunction photophysics. Several experimental studies indicate that relatively high bandgap perovskites such as CsPbBr_3 nanocrystals undergo efficient energy transfer to TMDCs like WS_2 , significantly enhancing the TMDC PL quantum yield.^{36,319} Theoretical calculations, however, suggest that the dynamics at this interface depend on the CsPbBr_3 surface termination.³²⁰ In particular, PbBr_2 termination led to a Type-I interface, consistent with the energy transfer observed in experimental studies, while Cs/Br^- terminated surfaces generated Type-II interfaces. Nonadiabatic molecular dynamics simulations of the Type-II heterojunction suggested sub-picosecond PCT, after which the separated charges live for ~2 ns.

Fang *et al.* studied the dynamics of charge separation and recombination in heterojunctions between CsPbBr_3 perovskite

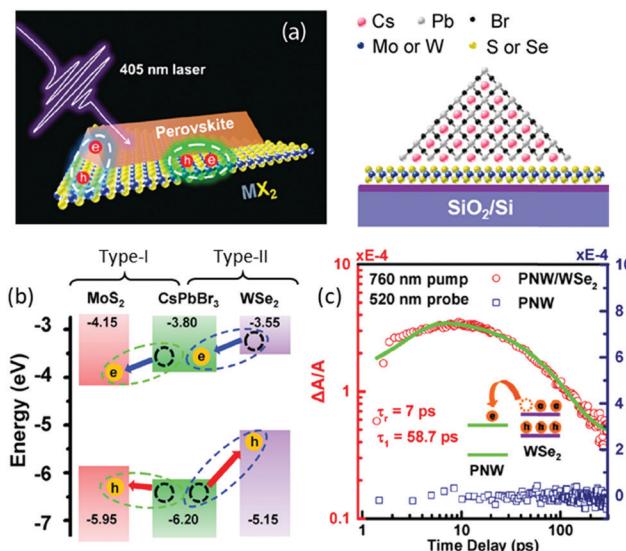


Fig. 34 (a) Schematic of heterojunction between CsPbBr_3 perovskite nanowire (PNW) and MX_2 monolayer. (b) Photoelectron spectroscopy suggests Type-I band alignment for interface with MoS_2 and Type-II alignment for WSe_2 . (c) Transient absorbance dynamics showing 7 ps rise time for photoinduced electron transfer from WSe_2 to CsPbBr_3 NW, followed by 59 ps recombination of separated charges. All panels are reprinted with permission from ref. 321. Copyright 2018 American Chemical Society.

nanowires (PNWs) and either monolayer MoS_2 or monolayer WSe_2 (Fig. 34a).³²¹ X-ray photoelectron spectroscopy suggested Type-I band alignment for $\text{CsPbBr}_3/\text{MoS}_2$ and Type-II alignment for $\text{CsPbBr}_3/\text{WSe}_2$ (Fig. 34b). As such, selective photoexcitation of the CsPbBr_3 NWs initiated energy transfer to MoS_2 with an estimated efficiency of 71% and rate of $1 \times 10^9 \text{ s}^{-1}$. Selective excitation of WSe_2 in $\text{CsPbBr}_3/\text{WSe}_2$ resulted in electron transfer from WSe_2 to CsPbBr_3 at an estimated 70% efficiency. The authors characterized electron transfer *via* the rise in PNW TA signal with a time constant of ~7 ps, followed by decay over ~59 ps representing the recombination of carriers across the interface (Fig. 34c).

12. 2D TMDC hybrid redox systems for water splitting

2D TMDCs have several advantages for use in photoredox systems. In particular, the large surface area and ultrathin nature minimize the distance that an excited carrier must travel to reach the surface, where electrolyte and reactants can be readily available to interact. Interaction between TMDCs with adsorbates and electrolytes is critical for many chemical processes, such as photoactivated H_2 and O_2 generation from water,^{13,14,322–324} CO_2 photoreduction,^{325–328} and N_2 photofixation.^{151,329} To optimize these reactions, it is important to control the catalytic TMDC interface and to generate long-lived charge carriers to drive the desired photochemical reactions. Some strategies for optimizing and extending carrier lifetimes in TMDC-based photoredox systems, which we discuss in this

section, include (i) making hybrid interfaces that separate photoexcited charge carriers through Type-II heterojunctions and Z-schemes, (ii) modifying the TMDC through surface functionalization or internal strain, (iii) employing both semiconducting 2H and metallic 1T TMDCs phases to optimize both light absorption and conductivity, and (iv) utilizing plasmon interactions for band-bending, energy level alignment, or enhancing light absorption. Here, we discuss PCT in several hybrid TMDC-based photoredox systems for water splitting.

In water splitting, the two half reactions of interest are the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which are given by eqn (7) and (8), respectively, in Section 3. For HER to occur, the semiconductor's CBM must be at a more reducing potential (closer to vacuum) than the reduction potential of HER (eqn (7)). For OER to occur, the VBM must be at a more oxidizing potential (further away from vacuum) than the oxidation potential of OER (eqn (8)). For overall water splitting, the semiconductor's CBM and VBM straddle the HER and OER potentials with a bandgap that exceeds 1.23 eV.³³⁰ The relationship between the band energetics of a semiconductor in vacuum and HER/OER stem from a 1986 report by Trasatti.³³¹ Based on this report, 0 V vs. NHE (HER) corresponds to -4.44 eV with respect to vacuum, and therefore, 1.23 V vs. NHE (OER) correlates to -5.67 eV with respect to vacuum.

Experimental and theoretical reports suggest several TMDCs to be good HER and/or OER materials.^{13,14,118,323,324,332,333} For example, one candidate for carrying out overall photoinduced water splitting is monolayer WSe₂. Fig. 35 shows an example in which Wang *et al.* grew wafer-scale WSe₂ monolayers *via* molecular beam epitaxy on SiO₂ substrates.³²² The authors found that at pH 7 the WSe₂ monolayers could be photocatalytic for both HER and OER, which experimentally demonstrated that the VBM and CBM are properly aligned for water splitting. The 1.65 eV band gap of monolayer WSe₂, results in a ~0.1 eV and ~0.3 eV driving force for proton reduction and water oxidation, respectively. The fact that monolayer WSe₂ photocatalytically splits water contradicts some theoretical reports (*e.g.* Fig. 7a). This highlights the need to execute experiments while using the theoretical TMDC band energetics primarily as a guide. Indeed, the band energetics are highly influenced by many factors including experimental conditions, doping, ambient environment, substrate, and strain.

12.1 Hybrid systems

One possible disadvantage for HER and OER reactions both occurring on the same 2D semiconductor is that recombination of opposite charge carriers in close proximity could kinetically out-compete the water-splitting half reactions. Engineering internal electric fields can help separate charges and extend carrier lifetimes. An interesting way to tune the band energetics and achieve some separation of opposite carriers even within a monolayer is to create Janus TMDC monolayers, where the chalcogenides on each side of the transition metal are different. Xia *et al.* calculated the band structure and energetics for such systems.³³⁴ The authors predicted that Janus monolayers would

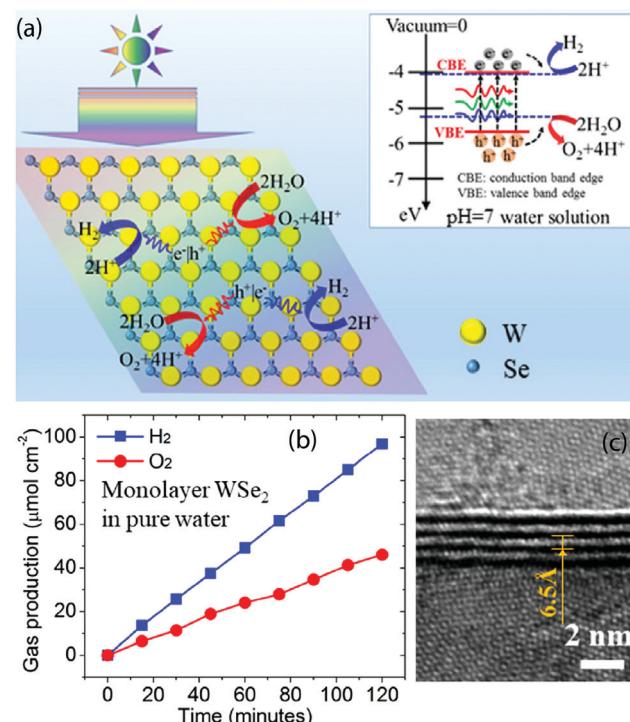


Fig. 35 (a) Schematic representation of monolayer WSe₂ being photoactive for overall water splitting, where the CBM (or conduction band edge – CBE) and VBM (or valence band edge – VBE) are properly aligned. (b) Measured H₂ and O₂ gas production from water splitting by monolayer WSe₂. (c) Lateral view of layer stacking of photoactive WSe₂ samples.³²² Copyright 2018 Elsevier.

have an inherent electric field produced by the asymmetric surfaces, which keeps holes and electrons spatially separated (Fig. 36). They proposed MSTe (M = Mo, W) to be the best

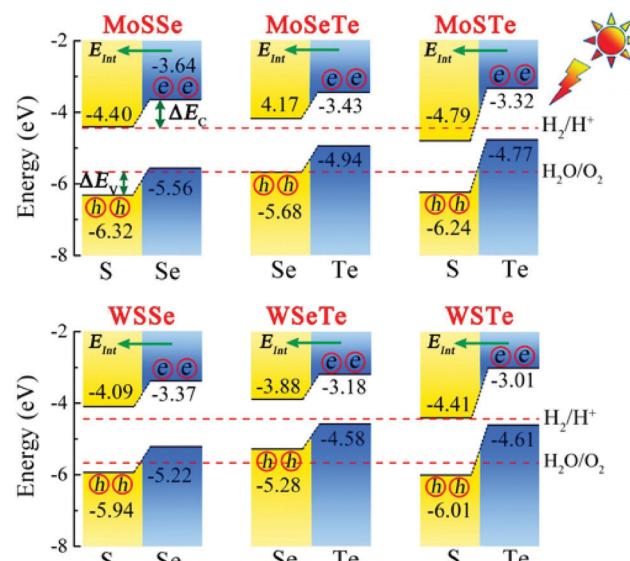


Fig. 36 Calculated band energies for Janus TMDCs with comparison to the HER and OER half reaction energies.³³⁴ Reprinted with permission from ref. 334. Copyright 2018 by the American Physical Society.

photocatalyst for water splitting due to the large driving force for HER and OER along with the large dipole moment caused by the difference in electronegativity between S and Te atoms. The Janus monolayer MoSSe has been experimentally synthesized and found to be good for dark H₂ evolution on the basal sites due to the inherent defects and strain induced by the asymmetry.³³⁵ The MoSSe outperforms MoS₂ or MoSe₂ when using dark electrochemistry. To the best of our knowledge, Janus particles have not been tested for photocatalytic activity.

Another way to suppress carrier recombination is to create heterojunction systems where charge separation results in OER/HER evolution from different components within a hybrid system. This can be accomplished by Type-II band alignment of two semiconductors or creating a “Z-scheme”, where the conduction band of one semiconductor is typically close in energy to the valence band of the other semiconductor. As illustrated in Fig. 37a, Z-schemes offer the advantage of higher oxidation and reduction potentials compared to a

typical Type-II heterojunction. Fig. 37b shows an example of a Z-scheme in which MoS₂ nanosheets on CdS are used for HER, and Co₃O₄/BiVO₄ are used for OER, where the two half reactions are connected by a [Co(bpy)₃]³⁺/[Co(bpy)₃]²⁺ redox couple.³³⁶ This system produced 14.5 and 7.1 $\mu\text{mol h}^{-1}$ of H₂ and O₂, respectively, for 12 h with a quantum yield of 1.04%. This is a noble-metal-free Z-scheme for water splitting, where the CdS and BiVO₄ are the light absorbers and charges are transferred to the MoS₂ and Co₃O₄ catalysts. The large driving force for electron transfer from CdS to MoS₂ (~ 0.77 eV) and hole transfer from BiVO₄ to Co₃O₄ enables the overall water splitting.

While some Z-schemes involve a redox couple between the HER and OER photocatalysts (e.g. Fig. 37b), there is interest in eliminating the redox mediator and creating two-component Z-schemes with the semiconductors in direct contact. For example, Ju *et al.* investigated several GeS/WX₂ systems (X = O, S, Se, Te) and calculated that only GeS/WS₂ has proper

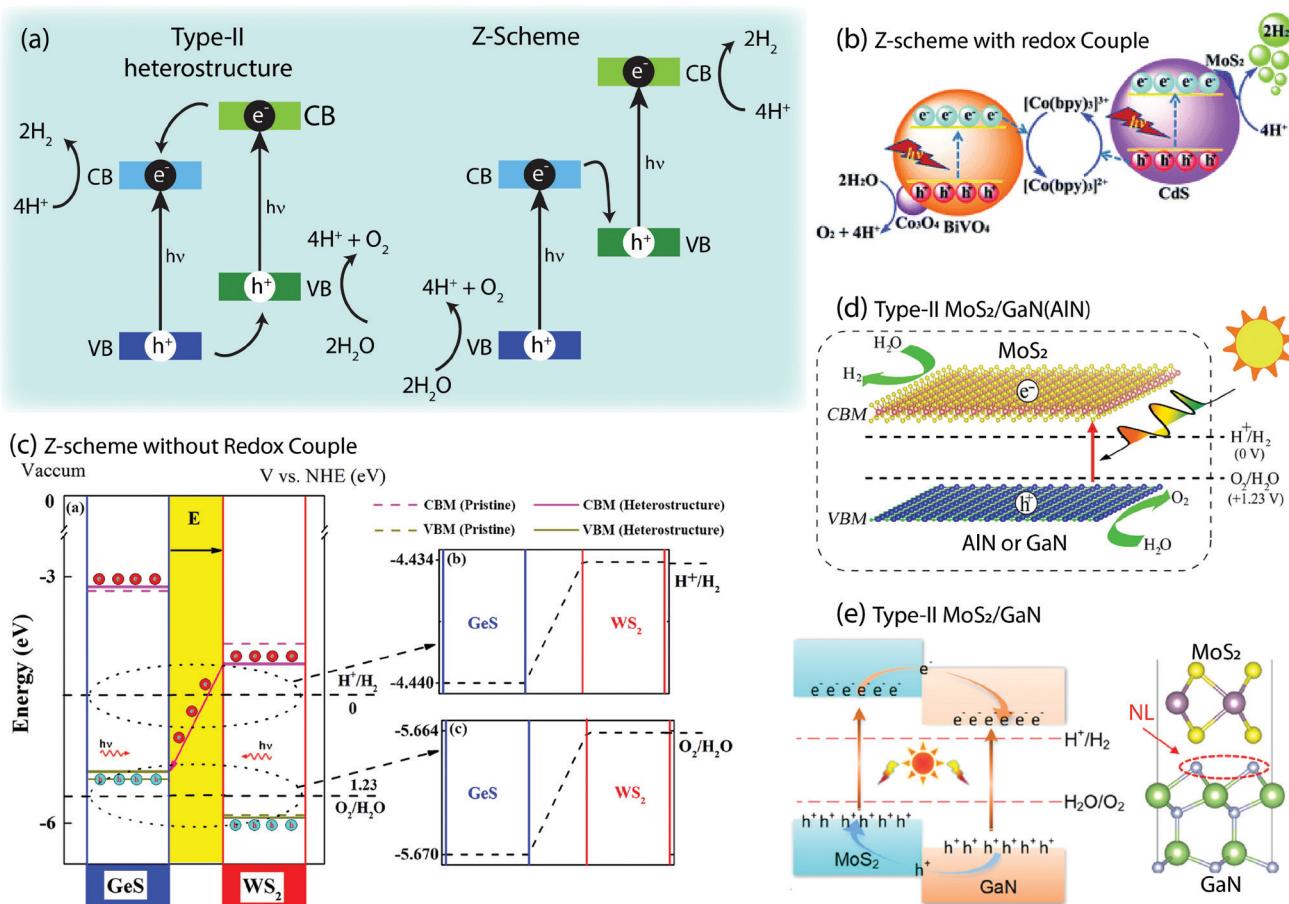


Fig. 37 (a) Schematic showing the difference between a Type-II heterostructure and a Z-scheme.³³⁶ Republished with permission of Royal Society of Chemistry, from ref. 336; permission conveyed through Copyright Clearance Center, Inc. (c) Heterostructure between GeS and WS₂ where the band gap decreases when the 2D layers are interfaced and an internal electric field drives charge separation for HER at GeS and OER at WS₂.³³⁷ Reprinted with permission from ref. 337. Copyright 2018 by Elsevier. (d) Schematic of photocatalytic water splitting for MoS₂/GaN, where HER occurs at the MoS₂ side (top) and OER at the nitride side (bottom).³³⁸ Reprinted with permission from ref. 338. Copyright 2014 American Chemical Society. (e) Contradicting theoretical/experimental work predicts that the MoS₂/GaN would have HER on the GaN side and OER on the MoS₂ side, where the interface is optimized by including a nitridation layer (NIL).³³⁹ Reprinted with permission from ref. 339. Copyright 2018 American Chemical Society.

band alignment for photocatalytic water splitting.³³⁷ The authors suggest that this system forms a Z-scheme as indicated in Fig. 37c, where HER occurs at the GeS CB and OER occurs at the WS₂ VB. Interestingly, the authors suggest that the Z-scheme is possible because ground-state charge transfer across the GeS/WS₂ heterojunction generates an internal electric field perpendicular to the interface that prevents relaxation of photoexcited electrons from the GeS CB to the WS₂ CB and relaxation of photoexcited holes from the WS₂ VB to the GeS VB.

In addition to Z-schemes, Type-II heterojunctions have also been investigated for TMDC-based water splitting systems. For example Liao *et al.* predicted that MoS₂/AlN or MoS₂/GaN would be good photocatalysts for water splitting.³³⁸ The calculated energetics predict that HER would occur on the MoS₂ side and OER on the nitride side (Fig. 37d). However, this 2014 report is contradicted by a 2017 report by Zhang *et al.* that construct MoS₂/GaN band diagrams using X-ray photoelectron spectroscopy data to conclude that HER occurs on the nitride side and OER on the MoS₂ side (Fig. 37e).³³⁹ Zhang *et al.* also suggest that the interface could be optimized by adding a nitridation layer (NIL, Fig. 37e). A recent 2019 report calculated the energetic shifts with the GaN surface termination at the MoS₂ interface and found changes to the band structure where the interface energetics depended on the number of MoS₂ layers.³⁴⁰ However, these theoretical reports have yet to be experimentally verified and photocatalytic experiments should be conducted to verify the charge separation and half reactions at the interface.

Other Type-II TMDC heterostructures are also productive for water splitting. For example, Type-II TMDC/carbon nitride heterostructures take advantage of the high catalytic activity of TMDCs, the abundant active area of carbon nitrides, and the long-term stability of both nanomaterials.^{341–344} Theoretical predictions suggest that C₂N/WS₂ interfaces form Type-II heterostructures with the correct energetics to photocatalytically split water.³⁴² In the photoexcited system, electrons transfer to C₂N and holes to WS₂, enabling water oxidation on the WS₂ side and proton reduction on the C₂N side.

Despite the predicted ability of MoS₂/carbon nitride systems to carry out overall water splitting, experimental demonstrations are thus far focused on the hydrogen evolution half reaction in this hybrid system.^{341,344–346} Indeed, we note that it is often challenging to design one system that performs both HER and OER, so an alternative strategy is to separate the half reactions and optimize each half reaction individually. Several studies have reported photocatalytic hydrogen evolution in WS₂/graphitic carbon nitride (g-C₃N₄)^{345,346} and MoS₂/g-C₃N₄,^{341,344} which has been attributed to charge separation across the interface that suppresses recombination and extends carrier lifetimes. Interestingly, Fig. 38 shows that g-C₃N₄ with 0.01 wt% loading of WS₂ was found to outperform the same loading of Pt catalyst, which suggests that TMDC-based heterojunctions may be a viable route toward avoiding expensive and scarce noble metal photocatalysts.³⁴⁶ Indeed, other TMDC-based systems have also shown improved performance compared to Pt-loaded systems, such as CuInS₂ photocatalysts with 3 wt% MoS₂ loading.³⁴⁷ Photoinduced charge separation is also

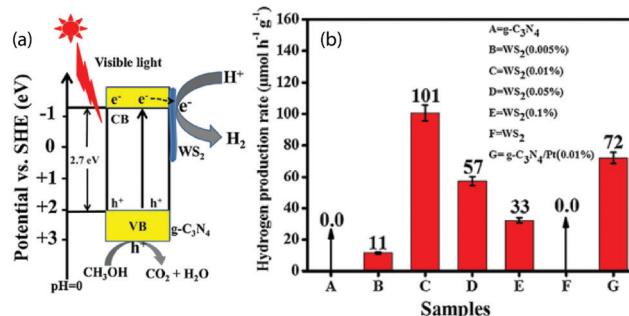


Fig. 38 (a) Schematic of g-C₃N₄ with WS₂ co-catalyst to enhance H₂ evolution. (b) Hydrogen production rates for different samples, where 0.01 wt% loading of WS₂ on g-C₃N₄ gave the highest rate. The samples include A = g-C₃N₄, B = WS₂ (0.005%), C = WS₂ (0.01%), D = WS₂ (0.05%), E = WS₂ (0.1%), F = WS₂, G = g-C₃N₄/Pt (0.01%).³⁴⁶ All panels are reprinted with permission from ref. 346. Copyright 2015 by Elsevier.

suggested to occur in this system based on significant improvement (28×) in HER for hybrid MoS₂/CuInS₂ compared to the separated components.

Photocatalytic HER in TMDC/g-C₃N₄ systems have also been explored using 1T/1T' metallic phase TMDCs. In dark electrochemistry, the metallic (1T/1T') phase of TMDCs have been shown to outperform the semiconducting phase for HER due to an increase in catalytic sites on the basal plane,^{348–350} therefore, the 1T/1T' TMDCs can also contribute to HER in hybrid systems. 1T WS₂/g-C₃N₄ outperformed semiconducting 2H WS₂/g-C₃N₄ due to the lack of active sites on the 2H phase basal plane.²⁵ Photoexcitation of the g-C₃N₄ transfers photogenerated electrons to WS₂, and the high electrical conductivity on the metallic WS₂ improves charge transport and HER. A similar conclusion was reached for MoS₂ on nitrogenated graphene oxide, where the metallic MoS₂ outperformed the semiconducting MoS₂.³⁵¹

The potential advantages of using metallic 1T TMDCs for hybrid reduction systems are not limited to g-C₃N₄. This concept can be leveraged in mixed-phase TMDC layers for solar water splitting. Peng *et al.* exfoliated single-layer MoS₂ and prepared heterostructures containing the semiconducting (2H), metallic (1T), and quasi-metallic (1T')—where the small band gap material still behaves very similar to the metallic phase states and performed photo-initiated HER.¹²⁹ They found that a monolayer heterostructure of semiconducting and quasi-metallic MoS₂ is photoactive for HER. The semiconducting portion of the monolayer absorbs light and the photogenerated electron transfers to the metallic portion (Fig. 39a), where the interface between the two phases drives the charge separation and the basal sites of the metallic MoS₂ enable HER. Alternatively, MoS₂ can be partially converted from the semiconducting to the metallic phase by incorporating supercritical CO₂, after which the metallic phase demonstrated improved photoelectrochemical production of O₂ from H₂O oxidation.¹⁰⁹ These examples demonstrate how sensitive TMDCs are to their environment and how they can be used in various capacities.

Mahler *et al.* also demonstrated increased photocatalytic H₂ evolution of TiO₂ nanoparticles by adding metallic (1T) WS₂

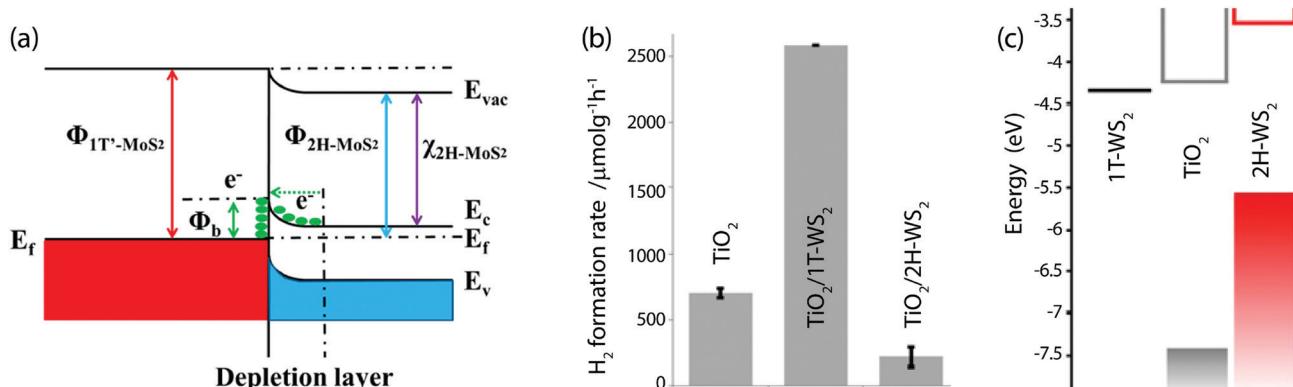


Fig. 39 (a) Band diagram of mixed-phase MoS₂: (left, red) metallic/quasi-metallic and (right, blue) semiconducting. Photoexcited electrons from the semiconducting portion of MoS₂ transfer to the metallic MoS₂ phase and enhance HER.¹²⁹ Reprinted with permission from ref. 129. Copyright 2016 American Chemical Society. (b) The H₂ formation rate and (c) band energetics for TiO₂ with WS₂ co-catalyst in the metallic (1T) or semiconducting (2H) state.³⁵² Panels (b and c) are reprinted with permission from ref. 352. Copyright 2014 American Chemical Society.

nanosheets as a co-catalyst.³⁵² However, when semiconducting (2H) WS₂ nanosheets are added to TiO₂ nanoparticles, the HER activity decreased (Fig. 39b). The authors attributed the difference in co-catalyst performance to the band energetics shown in Fig. 39c. That is, electron transfer from the photoexcited TiO₂ to 1T WS₂ has a favorable driving force for charge separation, while it is unfavorable to transfer electrons to 2H WS₂. The authors further suggest that 2H WS₂ introduces recombination centers for photoexcited TiO₂ electrons and holes.

Given the successful demonstration of PCT in TMDC/QD systems (Section 10), these systems have also been demonstrated for HER and overall water splitting. As an example, HER can be achieved from CdS QDs coupled with WS₂ nanosheets.^{288,353} The QD size can be tuned to create proper band alignment with the TMDC conduction band, which allows for electron transfer from the photoexcited CdS to WS₂. The optimal QD size of 7–8 nm diameter resulted in 14 mmol h⁻¹ H₂ evolved with 58% quantum efficiency at 420 nm excitation (Fig. 40a). Another report similarly coupled TMDCs to CdS for HER by integrating WS₂–MoS₂ nanosheets with CdS nanorods.³⁵⁴ They found superior H₂ generation in the dual-TMDC/CdS nanorods (209.79 mmol g⁻¹ h⁻¹ H₂) in comparison to WS₂/CdS nanorods (169.82 mmol g⁻¹ h⁻¹ H₂) and MoS₂/CdS

nanorods (123.31 mmol g⁻¹ h⁻¹ H₂) (Fig. 40b). Notably, this system outperformed Pt/CdS nanorods (34.98 mmol g⁻¹ h⁻¹ H₂). The authors suggest that the increased H₂ generation was due to photoinduced charge separation within the dual-TMDC co-catalyst (Fig. 40c).

Producing H₂ with near-infrared (NIR) photoexcitation is an exciting avenue because it utilizes a lower energy portion of the solar energy spectrum. For example, 2D black phosphorous (BP) absorbs NIR light (Fig. 41a), and heterojunctions between BP and WS₂ were found to generate 21 and 50 times greater amount of H₂ compared to the bare WS₂ and BP counterparts, respectively (Fig. 41b).³⁵⁵ The increased HER activity is attributed to charge separation at the 2D interface. The photocurrent response is greater, and the interfacial electron transfer is faster with IR irradiation for the black phosphorous/WS₂ interface. The transient absorption spectroscopy of BP only and BP/WS₂ heterojunction had lifetimes of 241 ps and 90.4 ps, respectively, where the faster lifetime of BP/WS₂ is attributed to the electron transfer from BP to WS₂.

Although a greater number of systems have been studied for HER, OER is also challenging and requires attention. Pesci *et al.* studied MoS₂/WS₂ photoanodes for OER,³⁵⁶ observing photo-induced water oxidation to O₂ and an n-type photocurrent

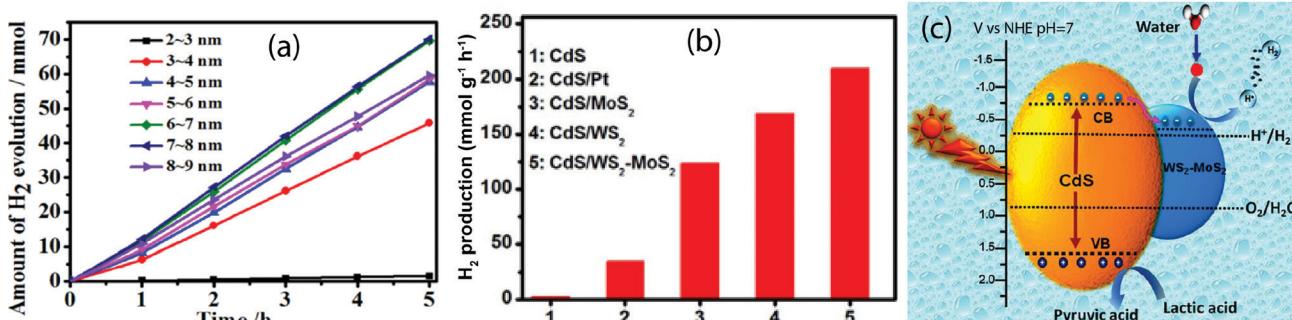


Fig. 40 (a) Amount of H₂ evolved as a function of CdS QD size when coupled to WS₂ nanosheets.²⁸⁸ Reprinted with permission from ref. 288. Copyright 2017 Elsevier. (b) WS₂–MoS₂ co catalysts for CdS nanorods show superior HER activity compared to the other tested configurations.³⁵⁴ Reprinted with permission from ref. 354. Copyright 2017 Wiley.

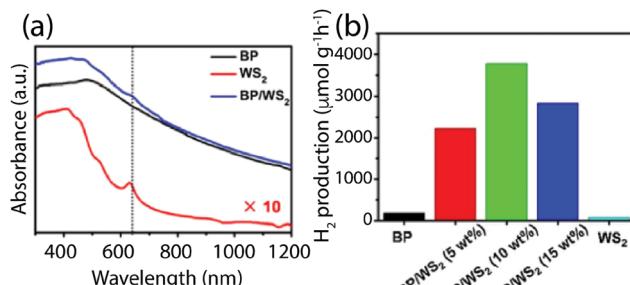


Fig. 41 (a) 2D black phosphorous (BP)/WS₂ can be photoexcited in the near-infrared (NIR) region. (b) NIR excitation leads to significantly increased H₂ production over the isolated 2D materials.³⁵⁵ All panels are reprinted with permission from ref. 355. Copyright 2018 Elsevier.

of 0.45 mA cm⁻². They found a 10-fold increase in IPCE ($\sim 0.1\%$ at 600 nm) in the hybrid system *versus* separate MoS₂ or WS₂ exfoliated nanosheets. The authors attribute this increased performance to improved charge carrier lifetime *via* charge separation at the MoS₂/WS₂ heterojunction. This same group expanded the study in 2019 to include salt-water oxidation using CVD grown large-area MoS₂/WS₂, where they found that reducing defect density improved OER efficiency.³⁵⁷ This interface creates an IPCE of 1.6% and photocurrent density of 1.7 mA cm⁻², an order of magnitude improvement over exfoliated 2D interfaces. The authors attribute the observation of reduced charge recombination and better OER performance for the CVD-grown architecture to lower edge site density and atomically sharp and clean interfaces.

12.2 Functionalization and strain

Methods such as TMDC surface functionalization and modifying internal strain can impact both the ability of the TMDC

system to split water and the interfacial interactions and energetics in hybrid systems that undergo PCT. Adding surface functional groups to TMDCs has been shown to alter the optoelectronic and catalytic properties because the surface energetics can be tuned and/or catalytic sites blocked.²²⁹ Functional groups can be physisorbed to the surface or covalently bound *via* basal and/or edge sites, which affect the properties differently.²²⁹ For example, theoretical studies by Pan *et al.* suggest that C₆H₅CH₂NH₂ functionalized MoS₂ structures are good candidates for photoelectrical water splitting.³⁵⁸ The calculated energetics for bare MoS₂ are not favorable for overall water splitting; however, the energetics can be tuned by putting a dipole on the surface. For most coverages studied, C₆H₅CH₂NH₂ on MoS₂ properly tuned the energetics for water splitting whereas C₆H₅CN was only good for water splitting at 18.75% coverage (Fig. 42a). Suo *et al.* further calculated the band energies of MoS₂ with other physisorbed organics (C₆H₅COOH and C₆H₅OCH₃) in addition to C₆H₅CH₂NH₂ and C₆H₅CN at various coverages.³⁵⁹ They calculated better energetic alignment for overall water splitting (Fig. 42b) along with improved absorption and photoinduced charge separation with the organic layer. Note that in both the Pan and Suo *et al.* calculations,^{358,359} the MoS₂ is calculated to have band energetics that are not favorable for HER or overall water splitting which contradicts other theoretical reports (*e.g.*, Fig. 7).

Similar to the ability to tune band energies with functionalization, strain engineering in both vertical and lateral dimensions has attracted interest as a strategy to alter band positions, improve conductivity, and modify surface interactions.³⁶⁰ For example, bending strain in MoS₂ scrolls fabricated by Hwang *et al.* was suggested to induce a 2H/1T transition that resulted in improved catalytic activity for HER.³⁶¹ Mechanical strain in MoS₂ has been suggested to activate the basal plane

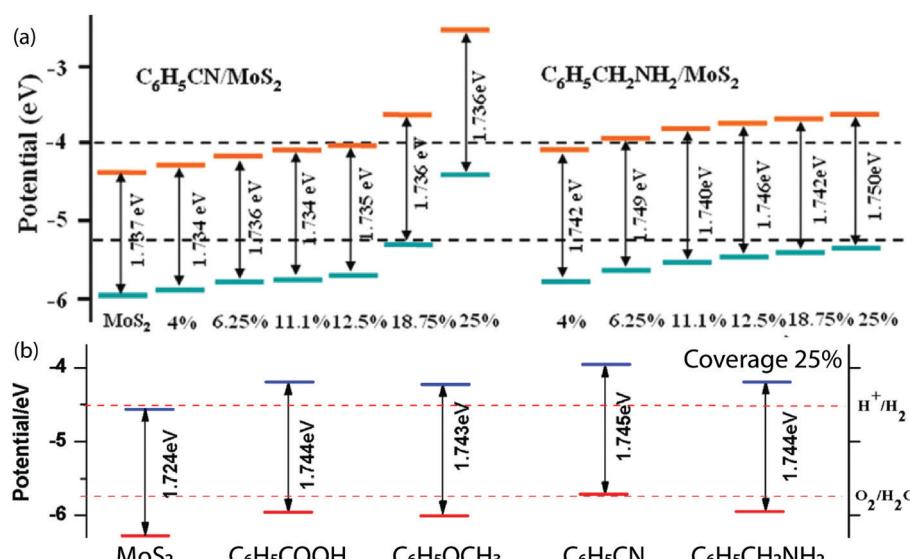


Fig. 42 (a) Band energetics of MoS₂ and MoS₂ functionalized with C₆H₅CN and C₆H₅CH₂NH₂ at various coverages.³⁵⁸ Republished with permission of Royal Society of Chemistry, from ref. 358; permission conveyed through Copyright Clearance Center, Inc. (b) Band energetics for MoS₂ and MoS₂ functionalized with 25% coverage of various organic molecules.³⁵⁹ Reprinted with permission from ref. 359. Copyright 2018 Elsevier.

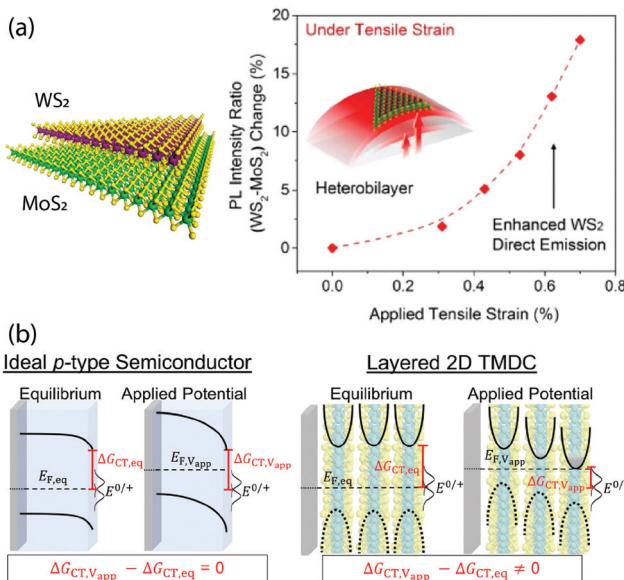


Fig. 43 (a) WS₂/MoS₂ heterojunctions (left) are influenced differently by tensile and compressive strain, where tensile strain enhances WS₂ direct emission compared to MoS₂ (right).³⁶³ Reprinted with permission from ref. 363. Copyright 2017 American Chemical Society. (b) Band energetics for an ideal p-type semiconductor (left) and 2D MoS₂ (right) photoelectrode at equilibrium and while applying a potential. The TMDC photoelectrode shows different PCT driving force with applied potential due to a change in band edge positions.¹³¹ Republished with permission of Royal Society of Chemistry, from ref. 131; permission conveyed through Copyright Clearance Center, Inc.

and improve hydrogen evolution through strained S vacancies.³⁶² Pak *et al.* also suggested that strain can mediate the interlayer coupling between MoS₂ and WS₂ layers, which could have important implications for optimizing carrier generation in heterojunction systems (Fig. 43a).³⁶³

In addition to mechanically-induced strain, Carroll *et al.* suggest that strain in TMDCs can be induced by an external voltage.³⁶⁴ Using *in situ* spectroelectrochemistry, the authors correlated the change in exciton absorption with structural information from Raman spectroscopy, concluding that MoS₂ becomes more strained and transitions to a lower bandgap material under applied potential. This study suggests differences between the dynamic response of an ideal p-type semiconductor electrode *versus* a 2D layered p-type MoS₂ electrode, which is insightful for understanding TMDC electrochemical catalytic reactions (Fig. 43b).

12.3 2D protection layers for photoelectrodes

Protecting Si and other photoelectrodes during catalytic reactions is important for improved and durable catalytic performance, in particular for HER in acidic conditions. For example, few-layer MoSe₂ was shown to protect high-efficiency Si photoanodes, where 3 nm of MoSe₂ was grown by molecular beam epitaxy (MBE) on a p⁺-n Si substrate.³⁶⁵ The applied bias photon-to-current efficiency at ~0.5 V vs. RHE increased from <0.1% to 13.8% with the MoSe₂ layer. The protected photoanode had a stable current density of 2 mA cm⁻² for ~14 hours

at 0.38 V vs. RHE under AM 1.5G one sun illumination. Similarly, Si photoanodes have been protected with MoS₂. By preparing a layering of MoS₂/MoO_x/Mo_xSi/SiO₂ on Si, the Si photoanode was protected for up to 2 months when operating under acidic conditions.³⁶⁶ Eventually the MoS₂ becomes oxidized and no longer present as MoS₂, which likely leads to the failure of the photoanode. These conclusions are in agreement with earlier work by Laursen *et al.* which also demonstrated additional stability of Si photocathodes with a MoS₂ protection layer.³⁶⁷

Metallic MoS₂ has also been shown to enhance HER of p-type Si photoelectrodes by driving electrons to the surface and providing catalytic sites.³⁶⁸ Ding *et al.* achieved 17.6 mA cm⁻² at 0 V vs. RHE under 1 sun illumination and found long term stability (23% decrease in current density over 3 hours).³⁶⁸ They compared CVD-1T MoS₂ *versus* chemically-exfoliated 1T MoS₂ nanosheets and found that CVD-1T MoS₂ was far superior to exfoliated MoS₂ (Fig. 44a). They attribute the difference to lower charge-transfer resistance, both at the interface between CVD-grown 1T MoS₂ and the Si substrate and at the MoS₂-electrolyte interface. Using surface photoresponse spectroscopy, the authors showed slow carrier recombination at the CVD 1T MoS₂/Si interface (Fig. 44b).

Recently, Si nanowires have been improved and stabilized by 2D NbS₂ nanosheets, which are group V TMDCs.³⁶⁹ In addition to >10 000 s stability in strong acid medium, adding NbS₂ co-catalysts to Si nanowires generated a 300 mV anodic shift for photocatalysis and H₂ evolution, where the onset potential is 0.34 eV vs. RHE (Fig. 44c). The improved NbS₂-Si nanowires hybrid PEC performance is 20× and 5× greater than bare Si nanowires and the NbS₂/Si structure, respectively (Fig. 44d). NbS₂ provides a lower energy barrier for HER and increases the carrier separation and transport within the hybrid structure.

CdS nanowires should have the proper band energetics for HER (Fig. 44e), but they do not produce a stable photoanode and corrode by holes accumulating at the surface.³⁷⁰ However, Fu *et al.* have interfaced CdS nanorods with SnS_x nanosheets to improve the HER by reducing hole accumulation.³⁷⁰ The authors explored the effect of tuning SnS_x nanosheet phase from hexagonal SnS₂ (band gap ~2.4 eV) to orthorhombic SnS (band gap ~1.0–1.5 eV) to mixed phases of orthorhombic/zinc blende SnS (band gap ~1.72–1.76 eV). Fig. 44e summarizes how the different phases control the band alignment to decrease hole accumulation in CdS. The SnS orthorhombic phase forms a Type-I band alignment with CdS and does not remove holes from the CdS, but both hexagonal and mixed phase SnS_x have Type-II band alignment that separates charge. Of these two, the authors conclude that the hexagonal phase is the best for water splitting due to a larger driving force for both electron and hole transfer. The hexagonal phase SnS₂/CdS photoanodes demonstrated IPCE of 31.5% at 340 nm and current density of 1.59 mA cm⁻² at 1.23 V vs. RHE, performing stably over 2 hours of testing.

12.4 Plasmon interactions

Plasmon interactions can be used to enhance the local electric field around nanoscale metallic features, with possible

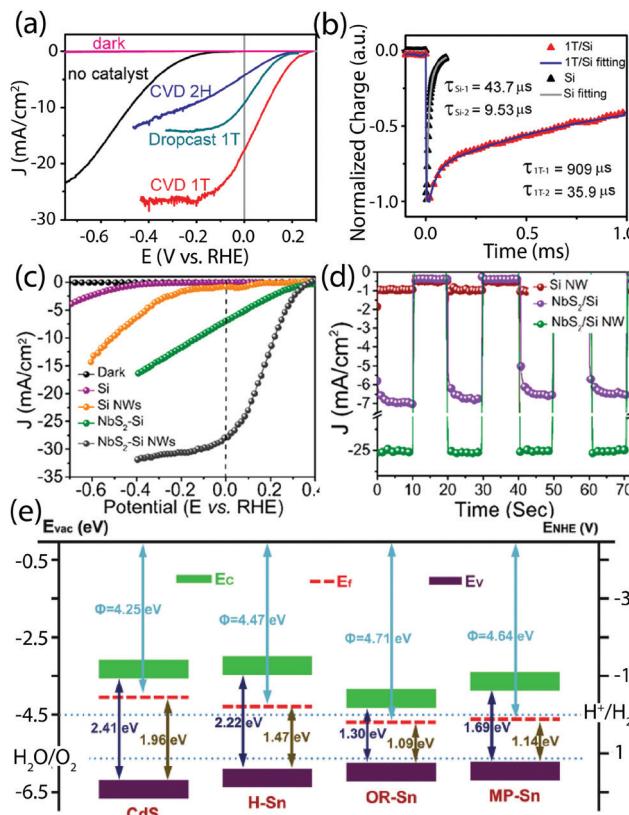


Fig. 44 (a) Metallic (1T) MoS₂ interfaced with p-type Si enhances HER and is more durable than p-type Si only. CVD 1T MoS₂ has better HER performance than chemically exfoliated 1T MoS₂. (b) Time-resolved surface photoresponse spectroscopy yields carrier recombination times that are slower for CVD 1T MoS₂/Si than Si only that leads to better HER performance.³⁶⁸ Panels (a and b) are reprinted with permission from ref. 368. Copyright 2014 American Chemical Society. (c) NbS₂/Si nanowires for improved photoelectrochemistry. Linear sweep voltammetry curves for photoinduced HER show that the NbS₂/Si nanowires give the lowest overpotential. (d) Photoresponse of the NbS₂/Si nanowires gives the highest current density and is stable over many cycles.³⁶⁹ Panels (c and d) are reprinted with permission from ref. 369. Copyright 2019 American Chemical Society. (e) Measured band energies of CdS nanowires and different phases of SnS_x, where H is hexagonal SnS₂, OR is orthorhombic SnS, and MP is mixed phases of orthorhombic and zinc blende.³⁷⁰ Reprinted with permission from ref. 370. Copyright 2018 Wiley.

implications for improving photocatalysis. For example, Chen and Cronin *et al.* found enhanced photocatalysis in a system of WSe₂ coupled to 5 nm Au nanoislands.³⁷¹ They observed 7× enhancement of the photocurrent (20 nA to 140 nA) over bare WSe₂ and large charge-separating fields over the monolayer. The surface area of WSe₂ decreased by 70%, but the overall photoconversion efficiency improved from 3.5 to 24.7% due to effective coupling of incident light by the Au plasmons.

Plasmons have also been shown to enhance OER for MoS₂ photoanodes.^{372–374} Fig. 45a shows an example of Au plasmons enabling electron transfer and charge separation.³⁷⁴ In this study, Xu *et al.* showed that Au plasmons improved OER in MoS₂ nanosheets on carbon fiber cloth. The Au plasmons modified band bending at the interface between MoS₂ and the carbon fiber cloth, eliminating the barrier for electron

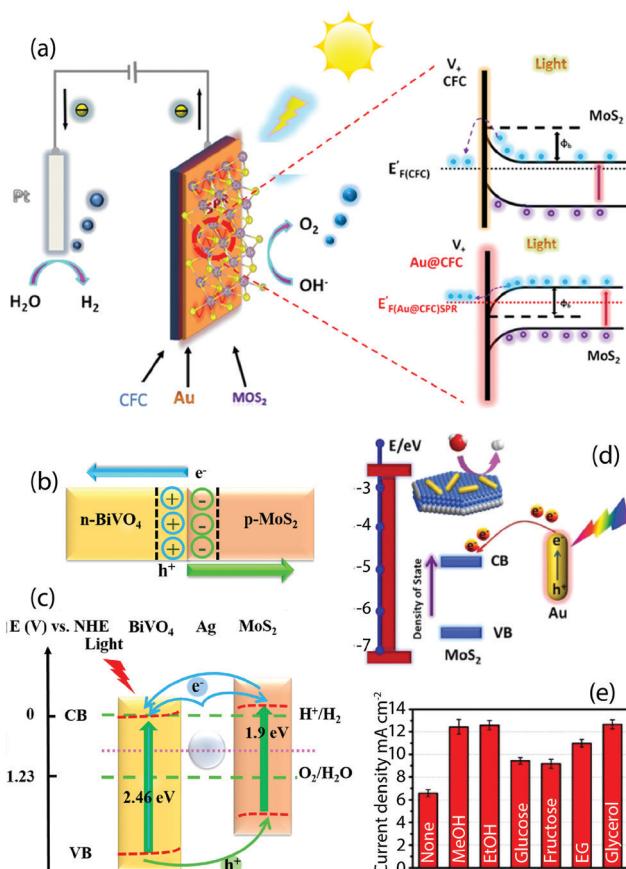


Fig. 45 (a) Au plasmons coupled to MoS₂ nanosheets enhance OER compared to MoS₂ without Au plasmons due to better electron transfer to the carbon fiber cloth (CFC) and charge separation at the electrode/electrolyte interface.³⁷⁴ Reprinted with permission from ref. 374. Copyright 2017 American Chemical Society. (b) Schematic of charge separation at BiVO₄/MoS₂ heterojunctions with Ag plasmons. (c) The band alignment enables OER at the MoS₂ side and electron transfer to the electrode assembly through BiVO₄, with Ag plasmons enhancing OER activity.³⁷⁵ Panels (b and c) are reprinted with permission from ref. 375. Copyright 2018 American Chemical Society. (d) MoS₂ coupling to Au nanorods improves HER performance and photocurrent density. (e) The MoS₂ photocurrent can be further enhanced if a hole scavenger is used.³⁷⁶ Panels (d and e) are reprinted with permission from ref. 376. Copyright 2015 American Chemical Society.

transfer from MoS₂ to the electrode (Fig. 45a). Photoconversion efficiency improved up to 1.27%, with 10 mA cm^{-2} at 1.23 V vs. RHE. Pan *et al.* showed plasmon-enhanced OER in MoS₂ using a p-n heterojunction photoelectrode with MoS₂/BiVO₄ coupled to Ag plasmons (Fig. 45b and c).³⁷⁵ This system produced 2.72 (4.02) mA cm^{-2} photocurrent at 0.6 V (1.23 V) vs. RHE, with IPCE of 51% at 420 nm. The BiVO₄-Ag-MoS₂ configuration outperformed all other tested configurations, where the next best performing configuration was BiVO₄-Ag (~1.7 mA cm^{-2} at 0.6 vs. RHE and 32% IPCE at 420 nm).

Researchers have also coupled plasmons to TMDCs for HER. For example, Fig. 45d shows enhanced HER for MoS₂ nanosheets attributed to hot electron injection from Au nanorods.³⁷⁶ The MoS₂/Au nanorods show ~3-fold increase in current density at 808 nm illumination (~6 mA cm^{-2}) compared to

the dark current ($\sim 2 \text{ mA cm}^{-2}$), whereas the MoS₂ produces very little photocurrent at 808 nm. The authors showed that hole scavengers further increase HER activity (Fig. 45e), where the current density nearly doubles when using methanol, ethanol, or glycerol hole scavengers. They attributed this enhanced photocurrent generation to decreased charge recombination and increased photogenerated electron lifetimes.

13. Future prospects

In this review, we highlighted PCT properties at TMDC heterointerfaces that can enable TMDCs to be used in quantum computers, photodetectors, photovoltaics, and water splitting. However, practical TMDC-based devices are still in nascent stages of development, and additional lengths will have to be taken to effectively harness their unique photophysics on larger scales. Here, we have discussed how the fundamental properties of TMDCs—such as band energetics, the types and lifetimes of quasi particles, spin and valley degrees of freedom, and crystal structure—must be leveraged to improve photoinduced charge generation at interfaces with a goal of enabling functional devices. We further identified interfacial PCT driving force and kinetics as important factors for optimizing carrier separation, which can be achieved by changing the components on each side of the interface. To this end, we discussed various promising TMDC heterojunctions: TMDCs coupled to other TMDCs, organic semiconductors (small organic molecules, polymers, and single-walled carbon nanotubes), quantum dots, perovskites, and electrolyte solutions. While each class of materials has unique challenges and target applications, in all cases researchers strive to optimize the interface to achieve performance metrics such as high photocurrent response, suitable voltages, long-lived carriers, wavelength-specific photoresponse, durable operation, and spin selectivity.

At this early stage of development, practical challenges remain for the future prospects of TMDCs in device applications. Most studies thus far investigate photophysical processes on small spatial scales and under well-controlled environmental conditions. In reality, the developing state of synthetic methods often results in spatial variations in active material properties (*e.g.* defect states, doping, layer thickness, crystal structure, and band gap), where many of these factors can simultaneously affect performance as device sizes increase. Fabrication of heterojunctions further complicates syntheses, especially when the device geometry requires TMDCs to be grown on top of the heterojunction material rather than onto a standard substrate. External environment and atmospheric conditions also drastically affect photophysics and the resulting performance metrics of ultrathin TMDCs.^{230,377} In some cases, this environmental sensitivity can be harnessed to create gas detectors and humidity sensors,^{230,377} but in other cases it may have less-desirable effects for energy conversion. Furthermore, differing dielectric properties of device-relevant layers like electrodes or encapsulants may impact the mix of TMDC excited states, phase, and conductivity.²³⁰ While fundamental studies are important to benchmark the

impacts of TMDC inhomogeneities, heterojunction material interactions, and atmospheric or chemical exposure, development of real-world devices will depend on long-term strategies for controlling their fabrication, stabilization, encapsulation, and operating environment/temperature.

Despite these challenges, the studies outlined in this review have shown great strides toward functional photoresponsive TMDC-based heterojunction devices on the lab scale. As outlined in Section 12, both photocatalytic hydrogen and oxygen evolution from water splitting have been achieved with visible light at reasonable over-potentials for a wide range of different TMDC nanostructures and heterojunctions. TMDC heterojunctions have similarly shown promise in photocatalytic CO₂ reduction,^{326–328,378,379} and N₂ reduction.^{380,381} These results promise cost-saving advantages if efficiencies are improved and TMDCs can be used as effective photocatalysts (for example to overcome the scarcity and high cost of Pt that currently limits the spread of water splitting technology). However, further development based on the fundamental principles identified in this review is needed to design efficient TMDC-based Type-II or Z-scheme systems for overall water splitting without the use of sacrificial agents.

In photovoltaics, the use of 2D TMDCs as active absorber layers has thus far been limited to low overall efficiencies ($\sim 0.1\text{--}10\%$), though these devices offer advantages worth further pursuing such as the ultrathin, semi-transparent nature, high thickness-normalized performance, and good stability. While some studies in this review have shown that texturing and plasmonic effects can enhance absorption even in ultrathin layers,²⁷⁴ lower current densities in semi-transparent devices are to some extent acceptable. However, significant effort is still needed to increase voltages and improve charge collection from the lower percentage of photons that are absorbed. Creating heterojunctions to decrease recombination and extend carrier lifetimes is an important step toward these goals. While several heterojunctions have been tested for photovoltaics and photodetectors (Sections 8–11), further effort is needed to address the fundamental phenomena behind the wide variation in literature results that can be obtained even for nominally similar heterostructures.

The properties outlined in this review also suggest 2D TMDCs as promising candidates for the rapidly emerging fields of neuromorphic and quantum computing. Neuromorphic computing attempts to emulate the nonlinear dynamical functions of the brain by using materials that can transform small electrical or optical inputs into large conductance modulations with fast switching speeds and tunable conductance lifetimes (volatility). While TMDCs have been explored for a broad variety of electrically-induced switching behaviors, recent studies have begun exploring ways in which optical switching in TMDC-based heterojunctions can enable synaptic or neuronal emulation.^{297,382} It will be critical to understand and manipulate dynamic excited-state processes in TMDC heterojunctions to fully exploit the rapid switching and persistent photoconductivity needed to enable complex neuromorphic functions, and the field is just beginning to take on these challenges. Quantum information

processing relies upon the manipulation of quantum-mechanical phenomena to perform computations, communication, encryption, and simulations. A critical component for quantum information processing is the spin–photon interface where quantum information can be transformed between these two degrees of freedom.³⁸³ Such interfaces are attractive applications for TMDCs, due to the inherent spin-valley locking of TMDCs, whereby the valley pseudo-spin is directly tied to the photon circular polarization (Sections 8.3 and 8.4). Heterojunctions are viewed as particularly promising for achieving the long valley coherence lifetimes needed to enable practical quantum information applications such as quantum logic gates and quantum repeaters.³⁸⁴ As the field moves forward, some key advances will be to improve valley coherence lifetimes *via* efficient photoinduced charge separation and to further increase operation temperatures to avoid the energy impact of cryogenic operation.

Overall, 2D TMDC-based heterojunctions are proving to be promising components in future energy harvesting, energy storage, and computational applications, where photogenerated charges need to be directed through a device to perform work or retain memory. The strategy of engineering PCT from a standpoint of controlling the fundamental photophysics in TMDC-based heterostructures will continue to serve an important role in the rational design of high-performance quantum-confined systems.

Conflicts of interest

There are no conflicts of interest to declare.

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