Direct determination of momentum resolved electron transfer in the photo-excited MoS$_2$/WS$_2$ van der Waals heterobilayer by TR-ARPES

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ABSTRACT

Photo-induced charge separation in transition metal dichalcogenide heterobilayers is being explored for moiré excitons, spin-valley polarization, and quantum phases of excitons/electrons. While the nature of interlayer excitons and the extent of spin-valley polarizations depend on the momentum spaces involved, little is known about this from experiments to date. Here we determine momentum-resolved electron transfer in the WS$_2$/MoS$_2$ heterobilayer using time and angle resolved photoemission spectroscopy (TR-ARPES). Upon photoexcitation in the K valleys, we detect electrons in M/2, M, and Q valleys/points on time scales as short as ~70 fs, followed by population transfer to K and Q valleys in ~400 fs. The interlayer charge transfer is accompanied by momentum specific band renormalization. These findings suggest phonon scattering in interlayer charge transfer, confirm the presence of direct and indirect interlayer excitons, and reveal constraints on achieving long-lived spin-valley polarization.

Monolayer transition metal dichalcogenides (TMDCs) are excellent models for the exploration of semiconductor physics at the two-dimensional (2D) limit, with potential applications in electronics, optoelectronics, and quantum devices. Heterobilayers formed from stacking two TMDC monolayers at controlled angles may bring about new physical properties or processes, such as moiré excitons, long-lived spin valley polarization, exciton condensation, and quantum phases of carriers. For TMDC heterostructures with type-II band alignment, photoexcitation of one monolayer leads to electron or hole transfer to the other

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monolayer on ultrafast time scales, resulting in interlayer excitons with electron and hole spatially separated into the two individual layers\textsuperscript{12–16}. The experimental observations of ultrafast electron transfer ($\leq$100 fs) across TMDC heterobilayers regardless of layer orientations, i.e., momentum mismatch at the K points, are not understood\textsuperscript{15,16,20,21}. While interfacial electron transfer across a TMDC heterobilayer has often been assumed to occur at K/K' points located at the hexagonal Brillouin zone corners, wavefunctions at the K point band edges are predominantly formed by in-plane metal atom $d_{xy}$ and $d_{x^2-y^2}$ orbitals that are strongly confined within each monolayer, with little inter-layer electronic interaction\textsuperscript{17,18}. In contrast, much stronger inter-layer electronic coupling at other momentum spaces, such as Q, M, and M/2, have been predicted from first principles calculations\textsuperscript{18,19}. Figure 1(a) shows band structure calculated at the G0W0 level of theory with spin-orbit coupling by Okada et al. for the angle-aligned WS$_2$/MoS$_2$ heterobilayer\textsuperscript{22}. In contrast to the K points that are localized to each TMDC monolayer, two local minima in the conduction band (CB), M/2 and Q valleys, have mixed characters of both TMDC monolayers and therefore possess strong interlayer electronic coupling. Upon photoexcitation in the K valley in WS$_2$, the conduction band electrons can be scattered by phonons to the layer-mixed Q or M/2 valleys, enabling rapid interlayer charge transfer. Unfortunately, all previous experimental studies on TMDC heterobilayers have relied on optical spectroscopies that predominantly probe optically bright transitions at the K/K' points, with little information on other momentum spaces.

Here we apply TR-ARPES to probe interfacial electron transfer dynamics in TMDC heterobilayers with time, energy, and momentum resolutions. We directly determine the dynamic distribution of CB electrons across the Brillouin zone and momentum specific band renormalization. The latter reflects the strong many-body Coulomb interactions in 2D due to quantum confinement and reduced dielectric screening\textsuperscript{23,24}, as we demonstrated recently using TR-ARPES on photo-excited monolayer MoS$_2$\textsuperscript{25}. In the present study, we choose the model system of WS$_2$/MoS$_2$ hetero-bilayer on a dielectric surface (285 nm thick SiO$_2$ on n-doped Si), as shown by an optical image in Figure 1(b). We improve the metal-assisted exfoliation technique\textsuperscript{26–28} for layer-by-layer exfoliation to produce single crystal TMDC monolayers with macroscopic lateral dimensions in the mm-cm range, with yields approaching 100%. To construct the heterobilayer, we first exfoliate a MoS$_2$ monolayer on the SiO$_2$/Si substrate and place a second WS$_2$ monolayer on top with a controlled angle. The lateral size of the resulting heterobilayer region is $> 3$ mm and the crystalline alignment determined by second harmonic generation (SHG, Fig. S1) shows a small
interlayer twist angle of 5°. We deposit gold electrodes on the side of the heterobilayer for grounding. The use of a wide bandgap SiO\textsubscript{2} dielectric substrate minimizes effects on the energetics and dynamics of the TMDC heterobilayer. A schematic of the pump-probe scheme is shown in Figure 1b. The visible pump beam (hv\textsubscript{1} = 2.2 eV, 40 fs pulse width, s-polarized, \(\sim\)10\textsuperscript{13}/cm\textsuperscript{2} absorbed photons per pulse) excites electrons from VB to CB and the extreme UV probe (hv\textsubscript{2} = 22 eV, pulse duration <100 fs, p-polarized, \(\sim\)10\textsuperscript{9} photons/pulse) ionizes the electrons from both

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**Figure 1.** (a) Calculated band structure of WS\textsubscript{2}/MoS\textsubscript{2} heterostructures with A-A stacking (0 degree alignment (Reprinted with permission from Ref. 22. Copyright 2018 American Chemical Society). The color scheme indicates the wavefunction contributions from each layer. The inset is a schematic of the different points in the Brillouin zone. (b) Left: Image of the WS\textsubscript{2}/MoS\textsubscript{2} heterostructure on 285 nm SiO\textsubscript{2}/Si, with blue color from optical contrast. Gold electrodes are deposited on the side (dashed yellow line) for grounding. Right: Schematics of the TR-ARPES experiment. A femtosecond visible pulse serves as pump and the femtosecond EUV pulse probe. The photoelectrons are detected by hemispherical analyzer at various polar angle \(\alpha\) from surface normal for momentum resolution. Shown in the bottom panels are experimental APRES of WS\textsubscript{2}/MoS\textsubscript{2} heterostructure measured along (c) \(\Gamma\)-\(K\) directiona and (d) \(\Gamma\)-\(M\) directions. All TR-ARPES and ARPES measurements are performed at room temperature.
valence and conduction bands. The photoelectrons are collected by a hemispherical analyzer. By varying the pump-probe time delay, we directly record the evolution of CB and VB dynamics. The pump-probe laser cross-correlation (CC) is described by Gaussian fitting to the time dependent rise in the fasted electron signal in our spectra; the variance of the fit is $\sigma = 140 \pm 30$ fs. This gives an estimated experimental time resolution of $\sim 70$ fs ($1/2 \sigma$). Before presenting the TR-ARPES data, we show valence band structures for the WS$_2$/MoS$_2$ heterobilayer along $\Gamma$-K and $\Gamma$-M directions, shown by ARPES without pump in Fig. 1c and 1d. The experimental band structure agrees well with the theoretical predictions in Fig. 1a and differs from the ARPES of WS$_2$ and MoS$_2$ monolayers (Fig. S2).

![Figure 2](image.png)

**Figure 2.** TR-ARPES of the WS$_2$/MoS$_2$ heterostructure (a) without ($\Delta t<0$) and (b) with the visible pump excitation ($\Delta t=0$), respectively. The ARPES spectra are collected at $M$, $M/2$, $\Gamma$, $Q$, $K$ positions in the momentum space. The color scheme is scaled to show weak signal in the CB. (c) The corresponding electron energy distribution curve (EDC) near the CB edge, collected without ($\Delta t<0$, red) and with ($\Delta t=0$, green) the visible pump excitation, and the difference with and without pump (black). The EDCs are integrated within a 0.3 Å$^{-1}$ window of the center momentum at each point. The visible pump is fixed at a photon energy of 2.2 eV and the probe at 22 eV. The sample is at room temperature.
We carry out TR-ARPES measurements around five representative positions in the momentum space, including the Brillouin zone center Γ, corner K (K’), edge M and the halfway positions of Q and M/2. The corresponding ARPES of conduction band without (Δt < 0) and with (Δt = 0) visible pump excitation are shown in Fig. 2, with the energy distribution curves (EDCs) in the bottom panels. The monolayers are intrinsically n-doped and, as a result, the CBM is very close to the Fermi level (E_F). Similar intrinsic n-type doping has been reported in other mechanically exfoliated TMDC monolayers25,29–31. The intrinsic electron doping is reflected in the electron population at Δt < 0 predominantly near the K point, which is predicted to be the global minimum of the CB. When the pump pulse overlaps with the probe pulse at Δt = 0, the increases in conduction band electron population appear at K, Q, M and M/2 positions within the pump-probe cross correlation. The CB electrons are not observable at Γ, as expected from its predicted higher energetic location than those of the K, Q, M and M/2 positions.

The rates of ultrafast interlayer electron transfer vary from momentum to momentum, as shown by energy-integrated CB electron intensities at the K, Q, M, and M/2 positions as a function of pump-probe delay, Fig. 3. The corresponding TR-ARPES spectra in 2D pseudo-color plots are shown in Fig. S3. The initial pump pulse induces direct transition in the K valleys of both WS₂ and MoS₂ monolayers, as known from the much larger oscillator strength of intralayer excitons than that of the interlayer32. Based on the band structure in Fig. 1a, we expect the initial excitations to be followed by electron transfer from WS₂ to MoS₂ in the CBs and hole transfer from photo-excited MoS₂ to WS₂ in the VBs. The initial excitation is directly detected in the rise in CB populations at Δt=0, as is shown in Fig. 3a-d. At the M and M/2 positions, Fig. 3c & 3d, the rise times are not resolvable within experimental time resolution, as shown by comparisons to the pump-probe laser CCs (blue curves). We conclude that interlayer electron transfer from the K valley of WS₂ to the mixed M and M/2 momentum positions occur with a time constant of τ_M ≤ 70 fs, the experimental time resolution. This can be understood from the strong interlayer electronic coupling at the M/2 point and that M/2 is energetically close to the K valleys of WS₂. The population at the M point can by mediated by the M/2 point and both processes require the participation of a phonon, likely a longitudinal optical (LO) phonon33, for momentum conservation. Following the ultrafast rise, the electron populations decay with a single exponential lifetime of τ_Md = 0.7±0.1 ps at both M and M/2 points; black curves are single exponentials convoluted with Gaussian cross correlations. As we discuss below, this decay can be attributed to the transfer of

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electron population to the lower-lying Q (mixed WS$_2$ and MoS$_2$) and K (MoS$_2$) valleys, as well as Auger recombination at the initial high excitation densities.

Figure 3. CB electron dynamics at K, Q, M/2, and M points as a function of pump probe delay. The integrated conduction band photoelectron intensities are shown as grey curves, with intensity at $\Delta t < 0$ set to zero. The solid black curves are kinetic fits and the blue curves (scaled to experimental peak intensity) are Gaussians ($\sigma = 140$ fs) representing laser pump-probe cross correlation. The dashed lines show zero intensity levels.

In contrast to the prompt formation of M/2 and M electrons, there is a delay component in the rise in either K or Q electron signal, as is obvious from the comparison between experimental kinetic profiles (grey) and laser CCs (blue) in Fig. 3a& 3b. Kinetic fits (black curves) give effective rise time constants of $\tau = 0.4 \pm 0.2$ ps the K and Q points, respectively. Here $\tau$ reflects an average of the prompt formation of electron population at K from optical excitation, the ultrafast transfer from K to Q, and/or the delayed formation due to inter-valley scattering from M and M/2. Following the rise, the decay in either case can be described by bi-exponentials, with time constants for the fast and slow channels of $\tau_{d1} = 0.7 \pm 0.3$ ps and $\tau_{d2} \geq 40$ ps, respectively. The fast channel dominates initially and is likely a result of many-body scattering, such as Auger recombination, at the initial high excitation density. While the K point is predicted to be the global conduction band minimum (CBM), the Q point lies close in energy (see Fig. 1a). Thus, the similarity in the kinetic profiles at the K and Q points suggests a dynamic equilibrium. Assuming
the same photoionization cross sections from the two points and neglecting the difference in density-of-states, we estimate the energy difference between these two points from the photoelectron intensity ratio at long times (~10 ps) based on the Fermi-Dirac distribution. This estimation gives a difference of $\Delta \text{CBM}_{Q-K} \sim 20$ meV, which is smaller than the predicted value of 130 meV without carriers\(^2\). The accumulation of electrons in different CB valleys will renormalize and shift the CB positions relative to each other. In each monolayer, the $\Sigma$ point, akin to the $Q$ point in a heterobilayer, is predicted to shift more significantly than $K$ upon electron doping\(^3\), resulting in a reduction in energy difference. The slow decay channel at $\tau_{d2} \geq 40$ ps is assigned to the radiative and nonradiative recombination of direct and indirect interlayer excitons.

In addition to the energy integrated electron intensities, we show energy-resolved dynamics in the K and the Q valleys in Fig. S4 for early time energy relaxation. Within ~200 fs, the average energy at the K point decreases by ~ 300 meV, which is reflective of CB electron population relaxation from WS\(_2\) to MoS\(_2\). In contrast, the energy distribution of electrons in the Q valley stays mostly constant on the ultrafast time scale. This suggests that the initial transfer from the photo-excited K valley in WS\(_2\) to form hot electrons in the mixed Q valley is negligible.

![Figure 4](image.png)

**Figure 4.** Dynamics of VBM renormalization at different momentums at a function of pump probe delay time $\Delta t$. The shift of VBM position is obtained from linear extraction at the band edge at each momentum position. The band gap renormalization ($\Delta \text{VBM}$) is the largest at $\Delta t \sim 0$ and decreases as carrier recombination proceeds with time.
Concurrent with CB dynamics, we probe the VBs from the EDCs at different momentum positions, illustrating the dynamics of band renormalization from charge carriers at each valley. While we are not able to determine the photoinduced hole populations due to small changes in VB signal, we clearly resolve shifts in the VB edges attributed to band renormalization from photoinduced charge carriers. The shift of the VBM can be obtained by linear extrapolation near the high energy cutoff, showing the relative change in the VBM upon photoexcitation (EDC in 2D pseudo color plots are shown in Fig. S5). The monolayers and the heterobilayer are highly n-doped and the n-doping pins the CBM to the Fermi energy. As a result, the band renormalization appears almost exclusively as upshifts in the VBM\textsuperscript{25}. Band renormalization in 2D semiconductor systems is a strong function of momentum and depends specifically on carrier population in each valley\textsuperscript{35}. Fig. 4 shows the time-dependent relative shifts ($\Delta$VBM) at $\Gamma$, K, Q, M/2, and M positions. Following optical excitation of the heterobilayer, band renormalization is clearly observed at the K, Q, M/2 and M, and there are long-lived $\Delta$VBM at K and Q points only. Such momentum-specific band renormalization is consistent with the observation of CB electrons at the same momentum spaces. Surprisingly, band renormalization is negligible at the $\Gamma$ point (grey circles in Fig. 4a), despite the fact that the $\Gamma$ point is predicted to be the global VBM in the WS$_2$/MoS$_2$ heterobilayer, confirmed by ARPES spectra in Fig. 1c &1d\textsuperscript{19}. The absence of band renormalization at the $\Gamma$ point suggests inefficient scattering of holes from the K to the $\Gamma$ valleys. At high excitation densities used here ($10^{12-13}$/cm$^2$), the larger band renormalization of VB at K than that at $\Gamma$ may change the energy ordering between $\Gamma$ and K, leading to the accumulation of holes in the K/K’ valley. This emphasizes the necessity of viewing the band structure of a photo-excited 2D semiconductor from a dynamic perspective. This issue deserves further theoretical investigation.

Figure 5 summarizes the dominant dynamic pathways following across-gap excitation in the K valleys in both WS$_2$ and MoS$_2$ in the WS$_2$/MoS$_2$ heterobilayer. Interlayer electronic coupling strength in the WS$_2$/MoS$_2$ heterobilayers at both the M/2 and the Q positions are of the order of hundreds meV, more than one order of magnitude larger than that in the K valley.\textsuperscript{18} The initial ultrafast transfer on the $\leq$ 70 fs time scale is more prominent to M/2 and M than that to the Q valley, suggesting the importance of excitation energy resonant condition in addition to electronic coupling and phonon participation\textsuperscript{36}. The strong interlayer electronic coupling at Q and M/2 valleys and the ubiquitous involvement of LO phonon scattering may explain the ultrafast charge transfer in TMDC heterobilayers regardless of twist angles\textsuperscript{12}. The CB electrons at the M/2 and M
positions are subsequently scattered to the K and Q valleys on time scales of $\tau \sim 0.4$ ps. The CB electrons in the K and Q valleys undergo recombination with VB holes on time scales $\geq 40$ ps. Thus, the bright K-K (K’-K’) exciton is in dynamic equilibrium with the dark K(K’)-Q exciton.

The result presented above suggest that valley polarization of CB electrons is lost on ultrafast time scales. Valley/spin polarization has been discussed as one of the most exciting properties of TMDC monolayers and heterobilayers$^{37,38}$. Due to strong spin-orbital coupling and the optical selection rule, spin-valley specific polarization can be optically prepared in monolayer TMDC with circularly polarized light.$^{39,40}$ The lifetimes of spin-valley polarized excitons in the K or -K valleys in a TMDC monolayer are short, one the order of picoseconds$^{41,42}$, but can be lengthened by many orders of magnitudes for the charge separated interlayer exciton in a TMDC hetero-bilayer$^7$. While spin-valley polarization for TMDC heterobilayers has been observed in optical absorption/reflection$^8$ and emission spectra$^7,43$, the quantitative measure of spin-valley polarization as determined by the purity of circularly polarized light emission/absorption/reflection is far from perfect. The CB energy splitting of opposite spins at K/K’ points are negligible, resulting in approximately equal probability of electron scattering from the M/2 and M valleys/position to K and K’ valleys. The dynamic equilibrium between Q and K/K’ further scrambles the CB spin-valley polarization. The ultrafast depolarization of CB electrons in the K or K’ valleys is confirmed in our TR-ARPES experiments on the WS$_2$/MoS$_2$ heterobilayer with circularly polarized excitation (Fig. S6). A recent TR-ARPES study with circular polarized pump excitation of bulk WSe$_2$ also reveals that CB valley polarization is lost in $\sim$100fs$^4$. In contrast to the CB, hole transfer in the VB between MoS$_2$ and WS$_2$ may maintain a high degree of spin-valley polarization. Similar to the CB, VB wavefunctions at the K and K’

Figure 5. Schematics of intervalley electron scattering in the CB. The visible pump beam excites the electron from VB to CB in the K valleys (green arrows), followed by ultrafast scattering ($\leq 70$ fs) of electron from K to M/2 and, to a lesser extent, the Q valleys (black arrows). The dashed arrows represent subsequent electron scattering ($\sim 0.4$ ps) from M/2 and M to K and Q. The double-ended and dashed arrows represent dynamic equilibria.
points are confined within each monolayer\textsuperscript{17–19} and hole transfer between MoS\textsubscript{2} and WS\textsubscript{2} may be assisted through the layer-mixed $\Gamma$ valley. The large spin-orbit splitting at the K/K’ points ensures that the K/K’ $\rightarrow$ $\Gamma$ $\rightarrow$ K/K’ hole transfer process may maintain a high degree of spin valley polarization. Moreover, the differentia band renormalization (Fig. 4) changes the energetic order between K/K’ and $\Gamma$ under photo-excitation, moving the latter out of energy range for efficient hole scattering.

In the presence of spin-valley polarized VB holes and unpolarized CB electrons, circularly polarized PL emission results from e-h radiative recombination at the direct K-K (K’-K’) gap. CB electrons at the Q and the spin-opposite K’(K) valleys may act as dark reservoirs. Moreover, the K(K’) points in the CB can be energetically lowered at high symmetry locations on the Moiré potential in a TMDC heterobilayer\textsuperscript{2}, with a possibility of maintaining spin valley polarization for the electron. As a result, confinement of the interlayer exciton to the spin-valley polarized K(K’) valleys may be assisted by the Moiré potential, provided the excitation density and the temperature are both sufficiently low\textsuperscript{3}.

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SUPPLEMENTARY INFORMATION

Direct determination of momentum resolved electron transfer in the photo-excited MoS$_2$/WS$_2$ van der Waals heterobilayer by TR-ARPES

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Supplementary Figures

Figure S1. Determination of WS$_2$/MoS$_2$ crystal orientation via polarization-resolved second harmonic generation (SHG), in which the sample orientation is rotated relative to input laser polarization and collection polarization. The correlation between the phase and Γ-K (zigzag) direction is calibrated by SHG data obtained from CVD grown MoS$_2$ monolayers. The twist angle between MoS$_2$ and WS$_2$ monolayers is determined to be 5±1°.

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Figure S2. EUV-ARPES spectra of monolayer WS$_2$ (left), monolayer MoS$_2$ (right) and WS$_2$/MoS$_2$ heterostructures (middle, reproduced from Figure 1 with adjusted color scale).

Figure S3. 2D pseudo-color (intensity) plots of EDC spectra collected at K, Q, M/2, and M points of the Brillouin zone at different momentums as a function of pump probe delay time $\Delta t$. 
Figure S4. Early time TR-ARPES of K and Q points measured with the polar angle set to collect photoemission from both of them simultaneously. The CB electron energy is relaxed at the K point by approximately 0.3 eV, comparable with the conduction band offset of WS$_2$ and MoS$_2$. In contrast, the energy of Q point stays mostly constant. The dashed lines are guides to the eye.
Figure S5. 2D pseudo-color (intensity) plots of EDC spectra collected at K, Q, M/2, M, and Γ points as a function of pump probe delay time Δt. The photoelectron signals are integrated within a 0.3 Å⁻¹ window of the center momentum.

Figure S6. Time resolved CB electron signal intensities collected at the K point, with right and left circularized pump. The valley polarization cannot be resolved with either 2.2 eV and 1.87 eV pump photon energies.
Experimental Methods

Sample preparation

MoS$_2$ and WS$_2$ monolayers with mm-cm lateral sizes were obtained from a metal mediated exfoliation technique from bulk MoS$_2$ (SPI Supplies) and WS$_2$ (HQ graphene) single crystals.$^1$ For grounding in photoemission experiments, a 150 nm thick gold film is evaporated onto two sides of the heterostructures. The crystal orientations of the MoS$_2$ and WS$_2$ monolayers were determined by second harmonic generation (SHG), as shown in Fig. S1. The heterobilayer sample is annealed at 250 °C in UHV ($10^{-10}$ Torr) for 4h before photoemission measurements.

Time and angle-resolved photoemission spectroscopy (TR-ARPES)

A detailed description of the visible pump - EUV probe TR-ARPES setup was published previously.$^1$ Briefly, The TR-ARPES measurements were carried out in the ultrahigh vacuum chamber ($\sim10^{-10}$ Torr) at room temperature. The EUV probe light at 22 eV was generated with high harmonic generation (KMLabs, XUUS4, modified for 400 nm pump) from the second harmonic of a Ti:sapphire amplifier (Coherent Legend Elite Duo HE+, 10 kHz, 800 nm, 10 W, 35 fs). The visible pump light was obtained from a home-built noncolinear optical parametric amplifier (NOPA, 500-650nm, 35 fs, pumped with the same Ti:sapphire amplifier). The photoemitted electrons are measured on a hemispherical electron energy analyzer equipped with a 2D delay line detector (SPECS Phoibos-100).

References

1. Liu, F., Ziffer, M. E., Hansen, K. R., Wang, J. & Zhu, X. Direct Determination of Band-Gap Renormalization in the Photoexcited Monolayer MoS$_2$. Phys. Rev. Lett. 122, 246803 (2019).