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Layer Rotation-Angle-Dependent Excitonic Absorption in vdW Heterostructures Revealed by Electron Energy Loss Spectroscopy

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ABBREVIATIONS

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ABSTRACT

Heterostructures comprising van der Waals (vdW) stacked transition metal dichalcogenide (TMDC) monolayers are a fascinating class of two-dimensional (2D) materials with unique properties. The presence of interlayer excitons, where the electron and the hole remain spatially separated in the two layers due to ultrafast charge transfer, is an intriguing feature of these heterostructures. Inevitably, the optoelectronic functionality of 2D heterostructure devices is critically dependent on the relative rotation angle of the layers. However, the role of the relative rotation angle of the constituent layers on intralayer absorption is not clear yet. Here, we investigate MoS₂/WSe₂ vdW heterostructures (hMWs) using monochromated low-loss electron energy loss (EEL) spectroscopy combined with aberration-corrected scanning transmission electron microscopy (STEM), and report that momentum conservation is a critical factor in the intralayer absorption of TMDC vdW heterostructures. The evolution of the intralayer excitonic low-loss EELS peak broadenings as a function of the rotation angle reveal that the interlayer charge transfer rate can be about one order-of-magnitude faster in the aligned (or anti-aligned) case than in the misaligned cases. These results provide a deeper insight into the role of the fundamental principle of momentum conservation in 2D vdW heterostructure charge transfer dynamics.

The advent of 2D materials has been an inflection point both for recent condensed matter physics as well as material science research.¹ Starting with the successful isolation of graphene and subsequent investigations on single and few layer TMDCs, the discovery of a plethora of fundamental phenomena as well as observation of novel properties suitable for diverse potential technological applications, particularly in fields like ultrafast electronics, optoelectronics, have established 2D materials as one of the hottest current research fields.²⁻⁴ One recent topic of focus in this field has been vdW heterostructures made of two or more single atomic layers, which show compelling new properties beyond those of the constituent layers.⁵⁻¹⁶ While the fabrication of heterostructures of high mobility quantum superlattice systems require sophisticated techniques such as molecular beam epitaxy, 2D vdW heterostructures could be made using exfoliation or chemical vapor deposition (CVD) growth of individual layers and then stacking them manually. Direct growth of vertical and lateral heterostructures by CVD with atomically abrupt boundaries have been also demonstrated.^{13, 17} vdW heterostructures comprising constituents such as two layers of graphene,^{18, 19} graphene and boron nitride,²⁰ and various combinations of 2D TMDC materials^{6, 21-24} have been reported. These heterostructures show novel properties such as Hofstadter butterfly states, photo-induced doping, and interlayer excitons with ultrafast charge transfer. These heterostructures possess a new degree-of-freedom, which is expected to critically determine their properties and functionality, i.e., the relative orientation of the individual layers. The fundamental role of the relative orientation of the graphene layers in bilayer graphene Moiré superlattices has been successfully demonstrated recently in the seminal results of observation of superconductivity and correlated insulator behavior at the so-called magic angles.^{25, 26}

In 2D TMDCs, the individual single layers exhibit extremely strong many-body effects in the form of different exciton species with binding energies in the range of ~ 0.4 to 1 eV, due to reduced screening.^{3, 27-29} Heterostructures made of MoS₂ and WSe₂ are known to form a type-II staggered bandstructure.^{11, 23} It has been demonstrated that these kind of heterostructures (e.g., MoS₂/WSe₂ and MoS₂/WS₂) reveal the presence of interlayer excitons which form after ultrafast charge transfer.^{6, 12, 30, 31} The absorption of light occurs in the individual layers, and the holes and electrons move into the adjacent layer forming interlayer excitons, where the holes and electrons are spatially separated. These excitons thereafter emit radiatively as observed in photoluminescence experiments.^{6, 7, 24}

The formation of interlayer excitons are due to ultrafast charge transfer at the time scale of few tens of femtoseconds, and this process competes with other relaxation channels and radiative recombination within the same layer.^{12, 30, 32, 33} The ultrafast charge transfer process is critical for the manifestation of interlayer excitons, which has potential applications in ultrafast photodetectors, photovoltaics, and photocatalysis, and other light detecting and harvesting technologies. Energy and momentum conservation are expected to play a decisive role in the ultrafast charge transfer process and its efficiency. Studies on the fundamental conservation principles of charge transfer dynamics are still lacking, mainly due to the challenge of simultaneously determining the relative orientation of the layers and acquiring (optical excitation) spectra at high spatial resolution, eliminating the possibility of spurious results due to local inhomogeneities.^{34, 35} The relative orientation of the layers incorporates the momentum match or mismatch of the electrons and holes pertaining to the optical excitation of these systems. We exploit this property to investigate how momentum conservation determines or influences the charge transfer rate in a MoS₂/WSe₂ vdW heterostructure.

We employ highly monochromated EEL spectroscopy in the low-loss energy range in an aberration-corrected STEM to determine the optical excitation response of hMWs as a function of the rotation angle between the layers. The low-loss EEL spectra (referred to as EEL spectra hereafter) depend on the complex dielectric function in general, and reflects important features such as the optical band-gap, exciton and interband transitions. The high energy resolution of the monochromated electron beam combined with the high spatial resolution of the aberration-corrected STEM provide unprecedented capability to determine both the optical response and relative orientation (from STEM high angle annular dark field (HAADF) images) of the layers with nanometer resolution. Our main observation is that for the aligned (0°) and anti-aligned (60°) cases, the intralayer absorption peaks are drastically broadened. This increased broadening indicates that interlayer scattering is approximately one order-of-magnitude faster than in the mis-aligned cases (e.g., 30°). The scattering rate is another manifestation of the interlayer charge transfer rate when the electrons and holes move to the adjacent layer. We also observe a small redshift of the absorption peaks in the heterostructure with respect to the peak positions of the individual layers, which we interpret as due to increased screening by the adjacent layer. This is dependent on the interlayer distance, which has local modulations from steric effects.

Experimental procedure

In this work, an aberration-corrected electron microscope operating in the STEM mode at 60 kV is used, as shown schematically in Figure 1(a).³⁶⁻³⁸ Details of the experimental set-up can be found in the Methods section. The hMW samples are fabricated from individual single layers of MoS₂ and WSe₂ grown by CVD (see Methods). The MoS₂ layer is transferred onto the WSe₂ sample (Figure 1(b)). The MoS₂/WSe₂ bilayer is then transferred onto Mo quantifoil grids. One

important aspect of these hMW samples is that the randomly-orientated individual single crystal triangles of MoS₂ are much smaller in size (~1-3 micron sides) than the triangular single crystals of WSe₂ (~10 micron sides). Because of this deliberate choice of sample sizes, there are many MoS₂ triangles with random orientations on a larger single crystalline WSe₂ triangle. This enables us to acquire spectra from a large number of areas with different relative orientations. In this work, we present EEL spectra for hMWs with 29 different orientation angles (see Supporting Information Figure S4). Figure 1(c) and (d) show the STEM HAADF images from hMWs with 29° and 50° misorientations, respectively, as representative cases. The fast Fourier transform (FFT) patterns from these images are used to determine the rotation angles as illustrated in the schematics of Figure 1(e) and (f) (see Supporting Information Section I). The 0° (aligned) case represents the R stacking while 60° (anti-aligned) case represents the H stacking.³⁹

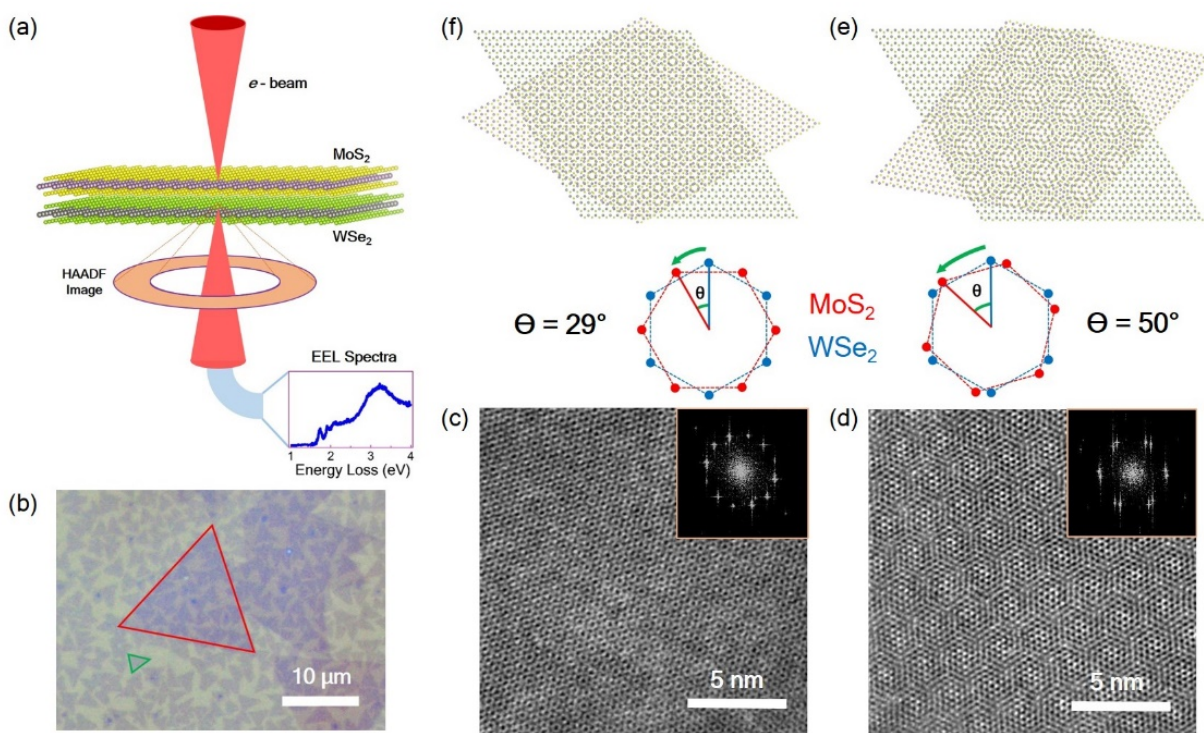


Figure 1. Schematic of the STEM-EEL spectroscopy experimental set-up and hMW sample images. (Anticlockwise from top left) (a) Electron beam converges on the sample plane and scans on the sample giving both high spatial resolution images and high energy resolution EEL spectra. (b) Optical image of a hMW sample. Bigger red triangle indicates one of the monolayer WSe₂ single crystals, while the smaller green triangle indicates one of the many monolayer MoS₂ single crystals. This optical image is taken after the transfer of the MoS₂ to the WSe₂ sample on substrate. (c) STEM HAADF image of the Moiré superlattice of hMW with 29°. The schematic of the two layers in this rotational alignment is shown in (f) above. (d) and (e) represent the case for hMW with 50°. The respective fast Fourier transform (FFT) patterns from the HAADF images are shown in the insets of (c) and (d).

Results and discussion

Layer rotation angle-dependent EEL spectra

In Figure 2(a), the measured EEL spectra is plotted for monolayer MoS₂, WSe₂, and hMWs with different relative orientations as representative cases after zero-loss subtraction using a standard power-law fit (see Supporting Information Figure S2 & S3).⁴⁰ We note that the probe beam size is ~ 1 Å and each presented experimental spectra in this work is integrated from an area of ~ 30 nm X ~ 30 nm or below (see Supporting Information Sections II, IV, and V). This high spatial resolution data acquisition is crucial for avoiding locations with residue, cuts, and edges in the sample, where spectral features change considerably. As a result, we can investigate small peak shifts and line-

shape broadening from intrinsic origin. These effects might be averaged out in optical experiments due to micron scale probe size and potentially the data will have extrinsic contributions.

The loss-function is given by the imaginary part of $[-1/\epsilon(q, E)]$, where $\epsilon(q, E)$ is the dielectric response function, q is momentum, and E is energy. In the case of optical probes, q is negligible, and hence we observe the signatures of dipole-allowed transitions in the optical dielectric function spectra, which can be mimicked in an EEL experiment performed in the TEM mode. In our case, the experiment is performed in the STEM mode which incorporates nonzero momentum changes to the charge carriers during excitations, due to the finite convergence and collection angles used. However, as can be seen in the monolayer EEL spectra of MoS₂ and WSe₂, the overall shape and peak positions are remarkably close to the optical case (see Supporting Information Figure S8). In particular, the so called A, B, C peaks of MoS₂, and A, B, C, D peaks for WSe₂ observed in optical experiments and discussed in the literature are also found to be the most prominent features of the EEL spectra as can be seen in Figure 2(a).^{12, 41, 42} There are a couple of small peaks after the B exciton peak in MoS₂ EEL spectra, which could be due to transitions with finite momentum change. Overall, the close resemblance of the EEL spectra acquired in the current STEM-EEL spectroscopy setting with that of optical absorption features (specifically, with ϵ_2) emphasize the fact that these spectra could be used directly for understanding processes and extracting physically meaningful parameters as a first approximation, without invoking the complex and computationally challenging finite momentum change in the analysis. We take a similar

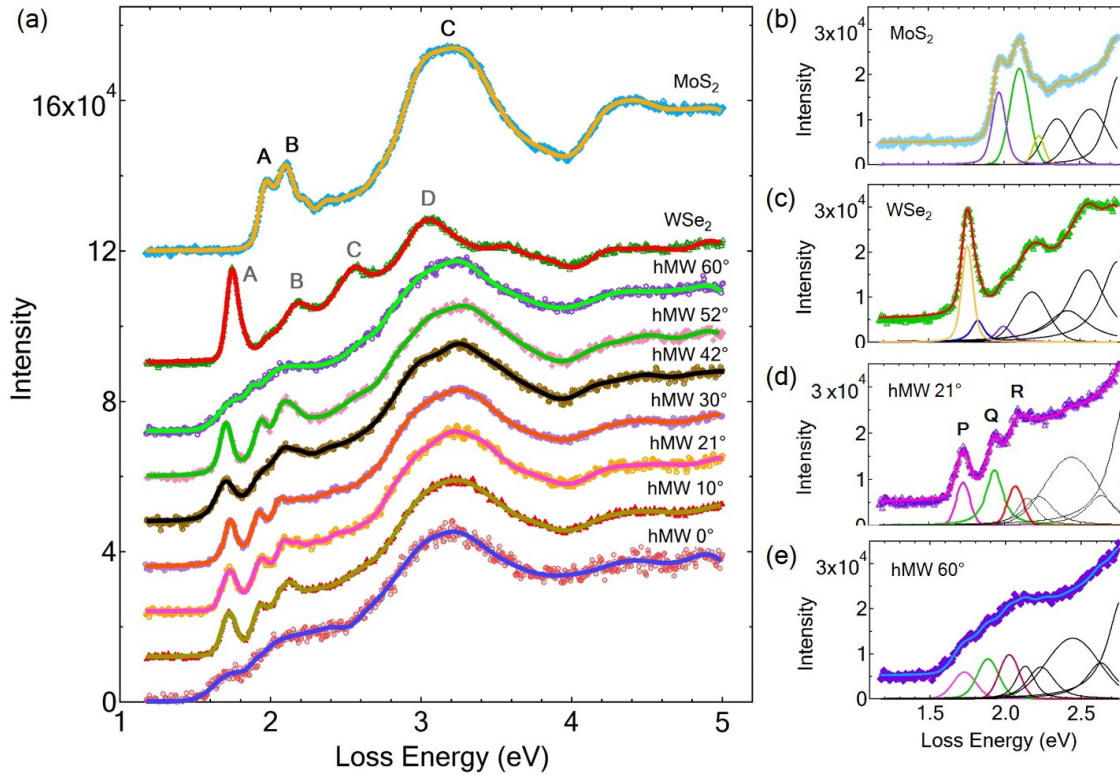


Figure 2. Relative orientation-dependent EEL spectra of hMW. (a) Comparison of the EEL spectra of monolayer MoS₂ and WSe₂ with that of aligned (ant-aligned) and misaligned hMW. (b) EEL spectrum of monolayer MoS₂ upto 2.75 eV, showing the Gaussian-Lorentzian oscillators used to fit the spectrum. (c), (d), and (e) represent the similar cases (as for (b)) for WSe₂ monolayer, hMW with 21°, and hMW with 60°, respectively, as representative cases.

approach and base our analysis and interpretation in this work on the EEL spectra and unravel some important results.

For the hMWs, the EEL spectra is different from both the monolayer MoS₂ and WSe₂. However, as can be seen from Figure 2(a), particularly for the misaligned cases ($\sim 10^\circ$ - 52°), the spectra can

be interpreted as originating from the effective dielectric response of the two layers together with weighted average contributions (see Supporting Information Figure S8).¹² Three relatively well separated peaks (P, Q, and R as labelled in Figure 2(d)) are observed for the misaligned cases until ~ 2.4 eV in energy. More importantly, these peaks are strongly broadened for the aligned (0°) and anti-aligned (60°) cases. This observation is the key evidence of the enhancement of the charge transfer rate, as will be discussed later. For determining the peak shifts and broadening accurately for quantitative analysis, we perform fitting of the EEL spectra using multiple physically meaningful Gaussian-Lorentzian line-shapes corresponding to each structure (or peak) in the spectra. Since our focus is on the first two peaks and their lineshapes, we perform data fitting up to 2.75 eV for all the hMWs with 29 different orientation angles. The results from these fittings are used for subsequent analysis and discussion in this work. The representative cases of the fit results and the constituent line-shapes are shown in Figure 2(b)-(e) for MoS₂, WSe₂, and hMWs with 21° and 60° relative orientations, respectively. We note that eight Gaussian-Lorentzian line-shapes are used for the data fitting of hMWs as shown in Fig. 2(d)-(e). The lineshapes beyond the first two peaks (P, Q) have considerable overlap among themselves even in the misaligned cases. As discussed hereafter, the origin of the P peak can be interpreted as from the A peak of WSe₂, and the origins of Q and R peaks can be interpreted as from the A, B peaks of MoS₂. However, the unambiguous determination of the origin of the rest of the peaks in terms of the energy bands of WSe₂ and MoS₂ is nontrivial. In general, these peaks originate from intralayer transitions involving deeper valence and higher conduction bands of WSe₂ and MoS₂.

Redshift and broadening of heterostructure peaks

In Figure 3(a), lineshapes of the A peak of WSe₂ and the P peak of hMW at 21° and 60° as representative cases are compared. Two distinct features are observed - there is a small redshift

of the P peak with respect to the A peak of WSe_2 , and the P peak is drastically broadened for the 60° case. The peak shift ($\Delta_1 = A - P$) is plotted as a function of the rotation angle in Figure 3(b). We note that variations of the A peak position is observed for even single layers of WSe_2 in different holes in the grid (see Supporting Information Figure S6). This can be attributed to unintentional local doping variations and strain effects.^{43,44} To eliminate systematic errors and to accurately estimate the shift relevant to a particular sample location, WSe_2 and hMW EEL spectra are

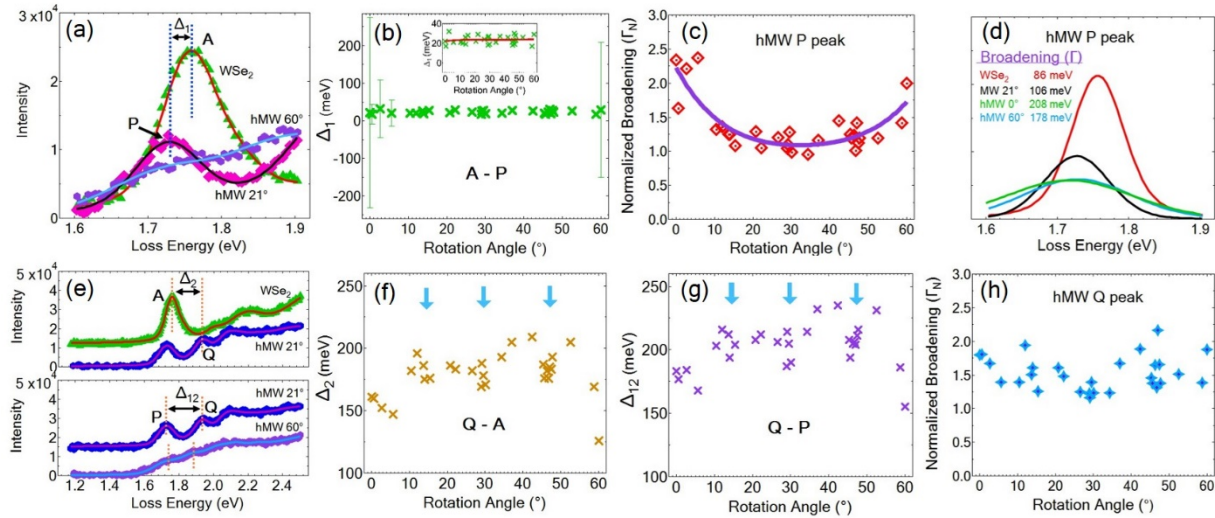


Figure 3. Peak-position and broadening of the P, Q peaks of hMW and their comparison to the A peak of monolayer WSe_2 . (a) Comparison of the lineshape of the P peak of hMW with 21° and 60° with that of the A peak of monolayer WSe_2 . (b) Plot of Δ_1 as a function of rotation angle. (c) Plot of the normalized broadening (Γ_N) of the P peak with respect to the broadening of the A peak of monolayer WSe_2 as a function of rotation angle. (d) Plot of the lineshape of the Gaussian-Lorentzian oscillator corresponding to the A peak of WSe_2 and P peak of hMW with 21° , 0° , and 60° showing their respective broadening (Γ). (e) Top panel shows Δ_2 , the difference of the peak position between the A peak of WSe_2 and the Q peak of hMW (with 21°). Bottom

panel shows Δ_{12} , the peak position difference between the P and Q peaks of hMW (with 21° and 60°). (f) and (g) are plots of Δ_2 and Δ_{12} , respectively, as functions of rotation angle. (h) Plot of the normalized broadening (Γ_N) of the Q peak with respect to the broadening of the A peak of monolayer WSe₂ as a function of rotation angle.

collected from adjacent positions in every location during a single scan. Δ_1 is calculated from these spectra by subtracting the respective peak positions of WSe₂ and hMW. We observe that Δ_1 is almost constant with no perceivable difference with rotation angle of the layers. For aligned (and anti-aligned) cases and close to these, the error bars are rather large due to the large broadening and hence no definitive conclusions can be drawn for those cases. However, for all other misaligned cases, the error bars are reasonable, and we estimate Δ_1 as 22 ± 10 meV. We interpret this shift as due to increased screening by the adjacent layer as reported previously.^{6, 12, 45} Importantly, the broadening of the P peak of hMW shows distinct rotation angle dependence (Figure 3(c)), where the broadening becomes approximately more than double for the aligned and anti-aligned cases in comparison to the misaligned cases. In Figure 3(d) the broadening of the A peak of WSe₂ and the P peak of hMW are shown for the aligned, anti-aligned, and misaligned cases.

We also observe a distinct shift of the Q peak of hMW for different rotation angles (Figure 3(e)). To quantify this shift, we plot both $\Delta_2 = Q - A$, the energy difference of the Q peak of hMW with respect to the A peak of WSe₂, as well as $\Delta_{12} = Q - P$, the energy difference of the P and Q peaks of hMW, in Figure 3(f) and Figure 3(g), respectively. Intriguingly, both Δ_2 and Δ_{12} show variations in the range of 50 ± 10 meV which are much larger than for Δ_1 . Also, we observe weak signatures of interesting dips in the plots of Δ_2 and Δ_{12} near 15°, 30°, and 45°

(indicated by ↓) . We further note that Δ_{12} is the sum of Δ_1 and Δ_2 . As Δ_1 is more or less constant, Δ_{12} appears to be a trivial offset of Δ_2 . Hence, Δ_2 depends almost linearly on the shift of the Q peak of hMW with respect to the A peak of MoS₂. As we interpret the Q peak of hMW as the shifted intralayer A peak of MoS₂ due to screening, it is inferred that the screening effect is larger on the excitonic absorption of MoS₂ in comparison to WSe₂. However, the broadening of the Q peak of hMW shows nontrivial rotation angle dependence with no distinct trend (unlike the P peak) as can be seen from Figure 3(h). We propose this to be a result of the different band arrangements and available diverse relaxation pathways in the valance bands of hMW.^{7, 46, 47}

Ultrafast charge transfer induced broadening of P peak

To understand the important observation of the rotation-angle-dependent broadening of the P peak, we look deeper into the charge carrier dynamics process during the intra- and interlayer exciton formation due to excitation of quasiparticles. Due to the work function difference and the different positions of the valence and conduction bands, the hMW band structure is known to form a staggered type-II band alignment as shown in Figure 4(a) (see Supporting Information Section X). Favourable energetics pushes the excited electron from the conduction band of WSe₂ to the conduction band of MoS₂, while the hole in the valence band of MoS₂ moves to the valence band of WSe₂. These electrons and holes in separate layers form interlayer excitons. The charge transfer occurs extremely fast within a timescale of 20 - 50 fs for the MoS₂/WS₂ heterostructure.^{12, 30, 31} One distinct feature of these heterostructures is the momentum space indirect character, which can be tuned by changing the rotation angle of the layers. This feature is shown schematically in Figure 4(b) for hMW, where the K (K') valleys of the Brillouin zones of MoS₂ and WSe₂ in the conduction and valence bands, respectively, are separated by a finite

momentum difference for misaligned cases. However, for the aligned and anti-aligned cases, these valleys become direct in nature, which dramatically enhances the charge transfer process leading to the efficient formation of the interlayer exciton.

As shown in Figure 4(c), the broadening of the A peak of WSe₂ has various contributions. Γ_{exp} is the experimental broadening due to the energy spread and instability of the electron beam, spectrometer aberrations etc. (30 ± 5 meV), $\Gamma_{rad+phonon}$ is the radiative recombination lifetime and phonon assisted intra and intervalley scattering (in the same layer) induced broadening (~ 40 meV), and $\Gamma_{dop+inhomog}$ is the doping and inhomogeneity induced broadening (~ 10 meV).^{12, 44}

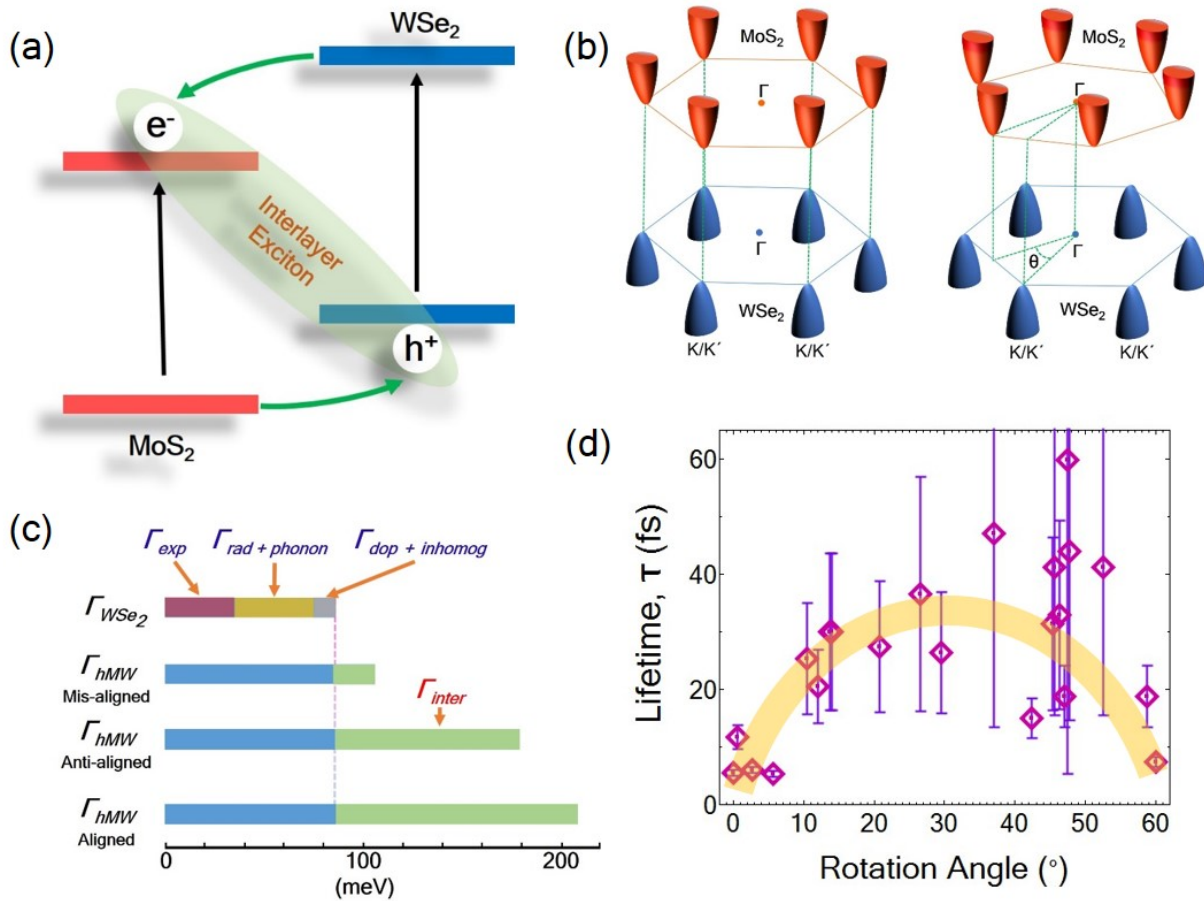


Figure 4. Schematic of the interlayer exciton formation process and the dependence of the lifetime of the excited carriers on the relative alignment of the Brillouin-zones of MoS₂ and WSe₂. (a) Interlayer exciton formation between the respective K-valleys of MoS₂ and WSe₂, after the transfer of the excited electrons in the conduction bands (from WSe₂ to MoS₂) and holes in the valence bands (from MoS₂ to WSe₂). (b) Schematic of the relative positions of the valence band (from WSe₂) K (K') valleys and conduction band (from MoS₂) K (K') valleys for aligned (or ant-aligned) and misaligned orientations. (c) Comparison of the broadening of the A peak of monolayer WSe₂ with that of the broadening of the P peak of hMW in the misaligned, anti-aligned, and aligned cases. (c) Plot of τ , the lifetime of the exciton corresponding to the P peak of hMW as a function of the rotation angle.

These contributions add up consistently to the observed broadening of $(80 - 89) \pm 5$ meV of the A peak of all the WSe₂ samples probed in this work. For the hMW, the P peak originates from the A peak of WSe₂, so inherently, it has the broadening contributions of the isolated monolayer WSe₂. However, the critical difference is the additional broadening channel introduced due to the interlayer charge transfer (or scattering) to the momentum mismatched (or matched) K (K') valley in the conduction band of MoS₂. This additional broadening can dominate the aligned and anti-aligned cases (or cases very close to those) (Figure 4(c)). An estimate of the broadening contribution due to this ultrafast interlayer charge transfer process can be obtained to a good approximation by subtracting the A peak broadening of WSe₂ from the broadening of the P peak of hMW.¹² Using Heisenberg's uncertainty relation, the population lifetime, τ is calculated from this observed broadening, Γ_{inter} due to the interlayer charge transfer process as $\tau = \hbar/\Gamma_{inter}$. Since, the experimental error bar in the estimation of Γ_{inter} is

10 meV, which is equivalent to 60 fs, we plot the lifetime τ until 60 fs as a function of the rotation angle in Figure 4(d) (see Supporting Information Figure S9). Remarkably, we observe the variation of τ in the range of 5 fs to 60 fs, where the smallest values of 5 fs are found for the aligned and anti-aligned cases or angles very close to these. This clearly demonstrates that momentum conservation critically enhances the charge transfer dynamics by about one order-of-magnitude, far beyond that reported previously for interlayer excitons in similar systems.^{12, 30}

Temperature-dependent EEL spectra

To unveil the role of phonon scattering, lattice expansion, and the increase of interlayer separation on the excitonic features and their dynamics in hMW, we further perform temperature-dependent EEL measurements on a typical misaligned hMW from room temperature

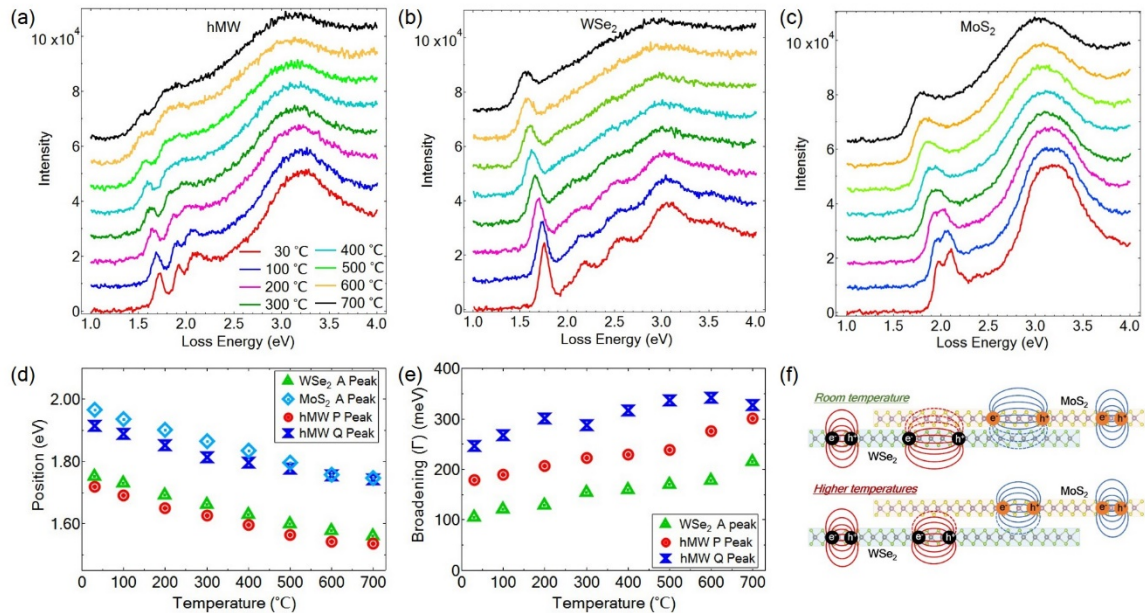


Figure 5. Temperature dependence of the EEL spectra. (a), (b), and (c) represent the temperature-dependent EEL spectra of a misaligned hMW, monolayer WSe₂, and monolayer

MoS₂, respectively, from room temperature to 700 °C. (d) Temperature dependence of the peak positions of monolayer WSe₂, monolayer MoS₂, and hMW. (e) Temperature dependence of the broadening of the A peak of monolayer WSe₂ and P, Q peaks of hMW. For clarity, the P and Q peak broadenings are offset by 70 meV and 140 meV, respectively. (f) Schematic of the increase of the interlayer distance at higher temperatures, and its effect on the mutual interlayer screening effect of MoS₂ and WSe₂ layers in hMW. Increase of the interlayer distance at higher temperature reduces the screening.

(30 °C) to 700 °C, and compare the results with those obtained from monolayer WSe₂ and MoS₂. The EEL spectra for hMW, WSe₂, and MoS₂ are shown in Figure 5(a), (b), and (c), respectively. A general redshift is observed for all the peaks at higher temperatures, which can be understood as due to lattice renormalization.⁴⁸⁻⁵⁰ Moreover, the features are broadened at higher temperatures due to enhanced phonon scattering. In Figure 5(d), the positions of the A peaks of WSe₂ and MoS₂, and the P, Q peaks of hMW are plotted as a function of temperature. With increasing temperature, the trend of shift of the P and Q peaks of hMW are similar to the A peaks of WSe₂ and MoS₂, respectively. This supports the interpretation that the P, Q peaks are intrinsically due to intralayer absorption, but redshifted by enhanced screening from the adjacent layer. We note that even at the highest temperature of 700 °C, the P peak shows a screening mediated redshift, which eliminates possibilities of this peak originating from other processes such as trion formation due to charge transfer. As schematically shown in Figure 5(f), higher temperature increases the interlayer distance by fractions of an angstrom, as observed in MoSe₂ for a similar range of temperature increase,⁵¹ and hence the screening effect is observable to up to 700 °C for WSe₂. However, we observe the Q peak position merging with the A peak position of MoS₂ from about 500 °C, which

is non-trivial to understand. This is potentially due to the different excitonic bonding strength and the dynamical nature of the constituent elements at different temperatures (MoS₂ atoms are lighter than WSe₂), but a precise understanding is beyond the scope of this work. Overall, the screening modulation of the Q peak with rotation angle of hMW is most likely due to steric effects, where the interlayer distance changes with rotation angle due to the finite and unequal sizes of the constituent atoms. Such steric effects are responsible for the rotation-dependent band-gap modulation in MoS₂ homobilayers, and for the local modulation of the quasiparticle gap in heterostructures as revealed by scanning tunneling spectroscopy.^{10, 21, 22, 39} The broadening of the A peak of WSe₂, and P, Q peaks of hMW as a function of temperature are plotted in Fig. 5(e), which show that the phonon scattering effects are similar for the three cases with Q peak showing slightly more variation. It is also noted that, for the aligned (or anti-aligned) case, the broadening of the P peak is affected by interlayer scattering to almost the same extent as for thermal phonon scattering at 700 °C, where the broadening reaches ~200 meV.

We note that the broadening of the A peak of monolayer WSe₂ can be tuned using strain.^{43, 44} This strain tuning are possible because the WSe₂ conduction band Q valley minimum is almost degenerate in energy with the K valley minimum. Application of positive or negative strain can change the position of the Q valley minimum, which can help or hinder phonon-assisted scattering of the excited electrons in the conduction band. Thus the A peak becomes broadened or sharpened with strain. Interestingly, various DFT based bandstructure calculations of vdW heterostructures also incorporate such strain effects to various degrees to obtain manageable supercell sizes for computational feasibility^{7, 46, 52}. Such bandstructure calculations of hMW reveal that the valence band in the Γ valley is lifted considerably and the states in the conduction band Q valley are also affected.^{7, 52} These changes are seen due to interlayer interaction

(hybridization) and strain. However, there is no clear consensus on the amount of strain in a real sample and the effects seen in these theoretical results could be affected by the strain introduced artificially.⁴⁶ Moreover, Kunstmann *et al.* has shown that the conduction band Q valley rather shifts upward when the interlayer distance decreases.⁷ These observations indicate that the potential alternative mechanism of the broadening of the P peak of hMW, as we observe experimentally, due to phonon-assisted intralayer and intervalley scattering of electrons is inadequate.

Conclusion

In summary, we have demonstrated that rotational alignment of the constituent layers plays a dominant role in the absorption spectra of vdW heterostructures, which feature strong intralayer absorption peaks. The interlayer charge transfer process, which is responsible for the formation of the interlayer exciton in vdW heterostructures, critically determines the lineshape of these intralayer peaks. There exists an additional relaxation channel for the excited electrons and holes due to interlayer charge scattering, and this manifests as enhanced broadening in the hMW peaks. We estimate the fastest lifetime in the aligned (anti-aligned) case to be about 5 fs, which is one order-of-magnitude faster than the nominal lifetime of ~60 fs for the hMW with largest rotational mismatch (~30°). Our results underline the role of the fundamental principle of momentum conservation in the interlayer exciton dynamics and provide a definitive guideline for the efficient design of functional devices harnessing interlayer excitons. Our results underline the role of the fundamental principle of momentum conservation in the excitonic absorption of vdW heterostructures and provide a definitive guideline for the efficient design of functional devices based on these vdW heterostructures.

Methods

STEM-EEL Spectroscopy

The electron microscope used for imaging and spectroscopy in this work is a JEOL STEM system (3C2), which is operated at the accelerating voltage of 60 kV. This system is equipped with Schottky field emission gun, a double Wein filter monochromator, and delta correctors. EEL spectra, acquired in the STEM mode, are collected by setting the energy resolution to 30 meV at FWHM of the zero-loss peak. The dispersion used is 5 meV/channel. The convergence semiangle α is 40 mrad and the collection semiangle β is 125 mrad. The probe current is 10 pA for the EEL spectroscopy. EEL spectra are acquired in the dual EELS mode to eliminate any systematic error due to zero-loss shift.

For imaging, HAADF detector is used in the same STEM system for each sample location (with different relative orientation of the MoS₂ and WSe₂ layers, as well as for monolayer MoS₂ and WSe₂ regions), immediately after or before the EEL spectra is acquired. The convergence and collection semiangles are 40 mrad and 65 mrad, respectively.

Chemical Vapour Deposition of MoS₂

The MoS₂ monolayer, with triangular shaped single crystals (~1-3 micron sides) with high coverage, is deposited on commercially bought c-plane (0001) sapphire (Al₂O₃) substrate (Namiki Inc) in a quartz tube furnace (planarTECH LLC) with two separate upstream and downstream heating zones. In the downstream region, 4.7 mg of MoO₃ (99.98%, Sigma Aldrich) is placed in a single open-end crucible with a piece of nickel foam (size 3.5 cm x 3 cm, 1 mm

thickness with 400 μm average pore size) placed directly above the MoO_3 powder. The sapphire is placed above the nickel foam, supported by two ceramic pieces. The arrangement of the MoO_3 crucible, nickel foam and sapphire is similar to the work of Lim *et al.*⁵³ 960 mg of sulfur (99.998%, Sigma Aldrich) is placed in the upstream zone, 40 cm away from the MoO_3 precursor. The detailed process flow is as such: the downstream region is first heated at 250 $^\circ\text{C}$ for 10 minutes for degassing purposes with the upstream zone kept at room temperature while an Ar flow of 200 sccm is maintained. The temperature is then ramped to 750 $^\circ\text{C}$ over 12 minutes and is maintained for an additional 10 minutes with an Ar flow of 50 sccm. Following which, the tube is allowed to naturally cool down to 650 $^\circ\text{C}$ prior to opening of the furnace heaters for rapid cooling through ambient exposure while the Ar flow is increased to 200 sccm. Pressure is maintained at 6 Torr during the entire process.

Chemical Vapour Deposition of WSe_2

The WSe_2 monolayer, with larger triangular single crystals (~ 10 micron sides) and high coverage, is deposited on sapphire substrate using CVD as reported in the work of Huang *et al.*⁵² High purity Se and WO_3 powders are used as the precursors, where the selenization of WO_3 is activated by the introduction of hydrogen in the reaction chamber. Ar is used as the carrier gas, where the WO_3 is placed in the center of the furnace on a ceramic boat. The sapphire target substrate is positioned in the downstream side, while the ceramic boat containing Se is placed in the upstream side. For the growth of larger isolated single layers, temperature is maintained at 850 $^\circ\text{C}$.

Sample transfer to TEM grid

The hMW samples on Mo quantifoil grids are prepared by a double transfer method. First, the MoS_2 sample is spincoated with polycarbonate and then, with the help of this polycarbonate

support film, the sapphire substrate is detached from the MoS₂ film in a dilute HF solution. This film is scooped using the sapphire substrate with the WSe₂ monolayer on top. After spincoating polycarbonate for the second time, the sapphire substrate is detached in dilute HF solution like before. The floating heterostructure sample with polycarbonate support film is transferred to beakers with ultrapure water consecutively to get rid of HF residue. Finally, the sample is fetched using the quantifoil grid, and the polycarbonate support film is dissolved in chloroform. After dipping in acetone and isopropyl alcohol, the sample is dried in vacuum.

ASSOCIATED CONTENT

The following Supporting Information file is available free of charge.

File name: *Gogoi_hMW_ACSNANO_SI*

Contents

- I. Determination of the relative rotation angle of the layers
- II. Raw EEL spectra of hMW, WSe₂ and MoS₂
- III. Zero- loss subtraction
- IV. Normalization procedure, and normalized spectra for all 29 hMW
- V. Representative locations (holes) and HAADF images
- VI. Variations of the EEL spectrum of single layer WSe₂ in different holes and near cuts in the same hole
- VII. Composite weighted average EEL spectra
- VIII. Comparison of experimental EEL spectra with loss-function and ϵ_2 of MoS₂ and WSe₂ from optical measurements (ellipsometry and reflectivity)
- IX. Lifetime for all samples
- X. Bandstructure of hMW

AUTHOR CONTRIBUTIONS

K.S. conceived the project. L.Y.C. and P.K.G prepared the TEM grids. P.K.G., R.S., and L.Y.C. performed the STEM imaging and EEL spectroscopy. P.K.G. analyzed the data. S.L.W. performed CVD growth of MoS₂ samples. D.C. supervised MoS₂ growth. L.J.L. supervised WSe₂ CVD growth. H.P.K. and A.V.K. provided theoretical inputs and computational results. All authors discussed the results and related interpretation. P.K.G. wrote the manuscript with contributions from K.S., L.Y.C, and R.S.

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