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Mapping modified electronic levels in the moiré patterns in MoS₂/WSe₂ using low-loss EELS

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ABSTRACT

Hybrid/moiré interlayer and intralayer excitons have been realized in twisted two-dimensional transition metal chalcogenides (2D-TMD) due to variation in local moiré potential within a moiré supercell. Though, moiré excitons have been detected in TMD heterostructures by macroscopic spectroscopic techniques, their spatial distribution is experimentally unknown. In the present work, using high-resolution scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS), we explore the effect of the twist angle in MoS₂/WSe₂ heterostructures. We observe weak interaction between the layers at higher twist

angles ($> 5^\circ$) and stronger interaction for lower twist angles. The optical response of the heterostructure varies within the moiré supercell, with a lower energy absorption peak appearing in regions with the *AA* stacking.

TEXT

“Twistronics” has emerged as an upcoming and promising way to manipulate two-dimensional (2D) materials for applications in quantum computing.¹⁻⁶ Stacking two monolayer 2D materials with deliberate rotational misalignment generates a new periodic arrangement known as a moiré pattern. In materials like graphene and hexagonal boron nitride (h-BN), moiré patterns introduce controllable periodic potentials resulting in the generation of flat electronic bands, for example with Hofstadter’s butterfly spectral signatures,⁷ or at the origin of Mott insulator states in graphene-h-BN heterostructures⁸ or emergent properties like superconductivity in magic twist angle in bi-layer graphene.²

Similarly, moiré patterns have created interesting effects in transition metal dichalcogenides (TMDs) which are MX_2 type compounds where $\text{M} = \text{Mo/W}$, $\text{X} = \text{S/Se/Te}$, etc.^{1,3,4,6,9-15} Semiconducting monolayer TMDs have large excitonic binding energies, making them observable even at room temperature.¹⁴ Additionally, TMDs heterostructures could have lower energy interlayer excitons arising from bands having the same spin characters at different layers.¹⁵ Artificial stacking of such TMDs gives an additional degree of freedom to control these interlayer excitons by changing the twist angle.⁴ However, given the typical exciton radius of TMDs (~ 1 nm scale), the moiré effects can only be observed when their periodicity is large. It has been demonstrated both theoretically and experimentally that at specific twist angles ($< 5^\circ$) moiré mini bands are generated that result in the formation of moiré/hybridized excitons in

vertical TMD heterostructures.^{1,4,11,13,16-18} These moiré/hybridized excitons can be controlled by circularly polarized light, electrical biasing and magnetic field.^{3,4}

Most experiments probing such excitons are based on optical absorption, reflectivity or photoluminescence, with a lower limit for spatial resolution defined by diffraction and typically of the $\lambda/2$ scale (above 500 nm). Therefore, up to now, local effects of the moiré periodicity have only been probed indirectly. On the other hand, scanning probe techniques, such as STS (scanning tunneling spectroscopy) or EELS (electron energy loss spectroscopy) using a focused electron probe in a STEM (scanning transmission electron microscope) can measure spectral information with sub-nanometer spatial resolution. EELS measures the inelastic electron scattering giving information about different neutral excitations in materials, such as excitons, plasmons and core-level excitations.¹⁹ Recent advances in electron optics have made it possible to achieve spectral resolution in the tens of meV scale²⁰⁻²⁴ in conjunction to high spatial resolution (sub-1 nm), making it a one of a kind technique to obtain spectral information at the atomic scale.²² Very recently, Gogoi et. al. have understood the interlayer couplings in moiré MoS₂/WSe₂ heterostructures above room temperatures using EELS spectroscopy.²⁵ Similarly, using STS, Pan et. al.¹⁸ and Zhang et. al.¹⁶ has measured the additional electronic states at the top (bottom) of the valence (conduction) band at the Γ (K) points in the moiré MoS₂/WSe₂ heterostructure.

In this letter, we have utilized the advantageous spatial and spectral resolution in EELS to image the interlayers excitons in MoS₂/WSe₂ moiré heterostructure at low temperatures (~120 K). We have observed that the MoS₂/WSe₂ heterostructure EELS spectra are dependent on twist angles. High angle structures (close to 30° rotation) show spectra that resemble pure MoS₂ and WSe₂ (with substantial damping of the WSe₂ contribution). Low angle structures (close to 0°

rotation) are very different, probably due to strong hybridization between the two layers. In these low angle structures, we observe indications of a low energy interlayer exciton at specific points of the moiré pattern.

Results and discussion:

MoS₂ and WSe₂ were individually grown by chemical vapor deposition (CVD). Heterostructures of MoS₂/WSe₂ were formed by stacking the individual layers by PDMS dry transfer and subsequently transferring the heterostructure assembly on Mo quantifoil TEM grids by wet transfer. Details are given in the supplementary information. Figure 1a (inset) shows the low magnification scanning transmission electron microscope (STEM) image of the MoS₂/WSe₂ heterostructure with hexagonal flakes being WSe₂ and the remaining large area being MoS₂. The different twist angles of as-transferred heterostructures were determined by nano-diffraction (Figure S2, Figure 1b,c). All the EELS experiments were performed at low temperatures (~120 K) to study low temperature interlayer excitations. Figure 1a displays the EELS spectra of monolayer MoS₂ and WSe₂ and their heterostructures with aligned (0.3° degree twist) and anti-aligned (30° degree twist) configurations. For a thin material, low-loss EELS measures the imaginary part of the dielectric function²⁶ and can be directly compared to optical absorption. In the present experiment, MoS₂ monolayer displays two spin-split exciton peaks ($X_{A,Mo}$ and $X_{B,Mo}$) at 1.96 eV and 2.15 eV whereas the intralayer exciton for WSe₂ ($X_{A,W}$ and $X_{B,W}$) were found at 1.75 eV and 2.3 eV. We found that the intralayer exciton peak for MoS₂ or WSe₂ were above or below the reported optical absorption values at 150 K.²⁷⁻²⁹ We suspect that this variation could result from local strain or presence of defects.^{30,31} However, the exciton peaks of intrinsic MoS₂ and WSe₂ monolayers match with the ones measured by earlier EELS studies.²⁴ The linewidth of

WSe₂ is significantly larger than that of MoS₂, possibly due to a higher defect concentration in the WSe₂ layer.

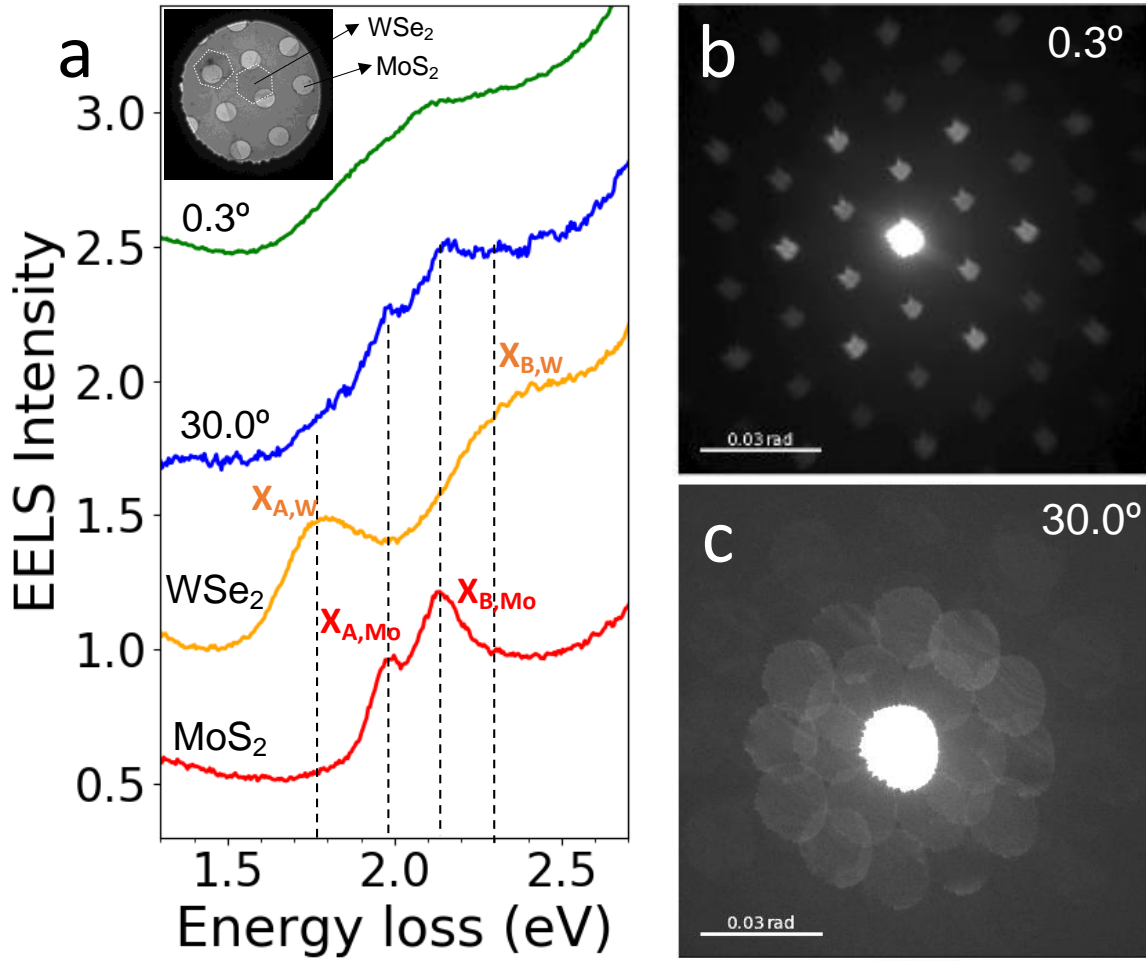


Figure 1. EELS spectroscopy of MoS₂/WSe₂ heterostructures. a) Average EELS spectrum of MoS₂, WSe₂ and MoS₂/WSe₂ heterostructures at anti-aligned (30°) and aligned (0.3°), respectively. Nanodiffraction of b) 0.3° and c) 30° twisted heterostructures. The zero-background of the peak is indicated by dashed horizontal black lines. The onset, indicated at the black solid vertical line, is at the point where the spectrum is just above the background. (presented by a horizontal line).

With the knowledge on intrinsic intralayer excitons in MoS₂ and WSe₂, we now understand the exciton absorption in MoS₂/WSe₂ heterostructures. In anti-aligned heterostructures (30° twist), there are three distinct peaks (1.74 eV, 1.93 eV and 2.08 eV) observed at similar energies to

$X_{A,W}$, $X_{A,M0}$ and $X_{B,M0}$ respectively. The three excitonic lines observed at similar energies to those in the intrinsic monolayers suggest a weak interaction between the layers for this configuration. However, the peak at the WSe₂-related $X_{A,W}$ is weaker than the other two, indicating that the optical response is influenced by the heterostructure.

In sharp contrast, EELS spectra of the aligned heterostructure (0.3° twist), is broader with a lower energy onset (~1.6 eV) than the $X_{A,W}$ peak in the anti-aligned heterostructure configuration indicating a significant modification of the optical response due to the moiré pattern. Since, the spectrum here is averaged out over a large (50 nm) region, a distinct moiré exciton peak is not observed unlike in previous optical spectroscopy studies.^{3,4,11} It is to be noted that the width of the all the EELS peaks are broader than the ones measured by confocal optical spectroscopy techniques. This is probably due to presence of native defects in the CVD grown intrinsic MoS₂ and WSe₂ monolayers used to produce the heterostructures. Furthermore, as-transferred samples used in the this experiment have not been encapsulated within h-BN layers, a technique which has been demonstrated to be very effective in preserving the optical response of 2D materials by strongly limiting their aging effect.^{11,32}

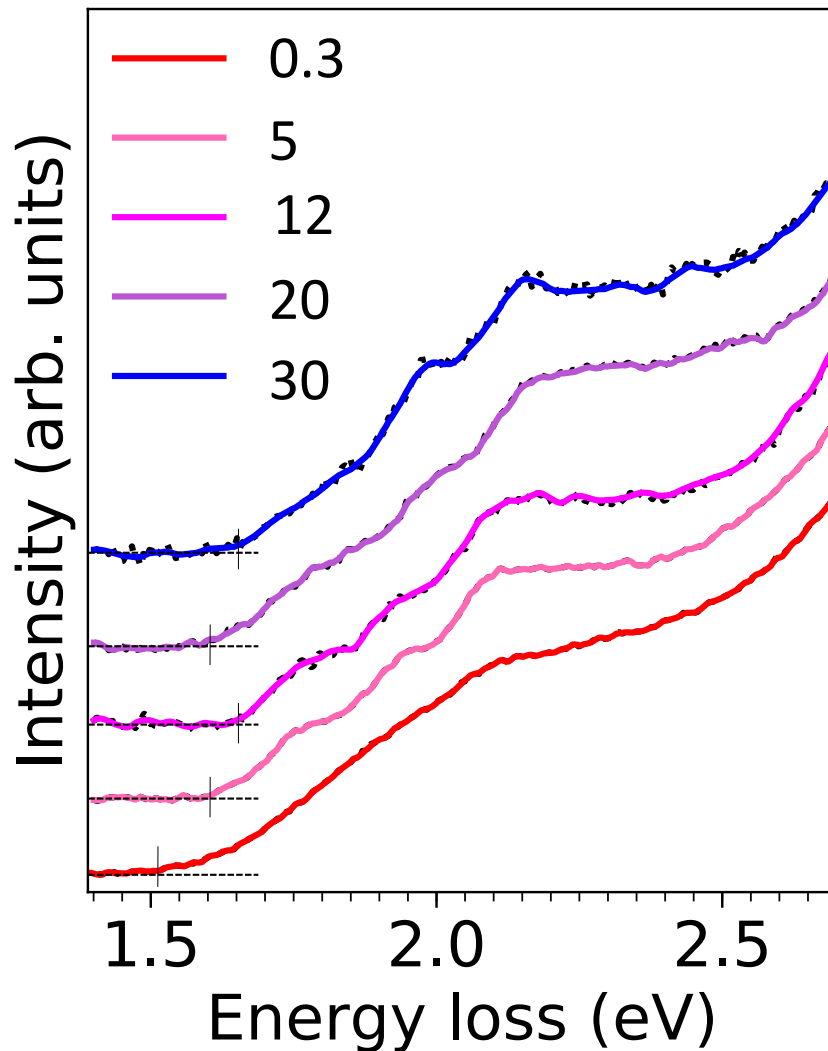


Figure 2. Average and smoothed EELS spectra of MoS₂/WSe₂ heterostructures with different twist angle. The zero-background of the peak is indicated by dashed horizontal black lines. The onset, indicated at the black solid vertical line, is at the point where the spectrum is just above the background.

To have a better understanding of how these interlayer excitations depend on the twist angle, EELS was repeated in multiple areas with different twist angle (Figure 2). Spectra have been smoothed using the Savitzky-Golay algorithm (implemented in the Scipy library of Python).³³ Energy positions (Table 1) of the peaks have been extracted from fits to the second derivative of the smoothed spectra extracted using the same algorithm (Figure S4).

Moiré angle	$X_{A,W}$ (eV)	$X_{A,Mo}$ (eV)	$X_{B,Mo}$ (eV)
0.3 degree		1.87	2.10
5 degree	1.75	1.93	2.10
12 degrees	1.76	1.93	2.11
21 degrees	1.77	1.97	2.19
30 degrees	1.75	1.96	2.16
MoS ₂		1.96	2.15
WSe ₂	1.75		

Table 1. EELS peaks position derived gaussian fits from their respective second derivative spectra. The typical standard deviation of the peak center fitting coefficient was between 1-4 meV. These uncertainties are added to possible variations due to sample heterogeneity, as discussed in the main text.

From Figure 2 and Table 1 two key observations can be extracted. First, the intralayer excitons peaks associated to $X_{A,W}$, $X_{A,Mo}$ and $X_{B,Mo}$ remain invariant at higher twist angles ($5 < \theta < 30$) at 1.76 ± 0.01 eV, 1.94 ± 0.02 eV and 2.14 ± 0.02 eV respectively. The few tens of meV variation in exciton absorption is likely due to variation in strain and defect density.³¹ The intralayer exciton energies for heterostructures are similar to intrinsic intralayer excitons for monolayer MoS₂ and WSe₂ respectively implying less/no coupling at higher twist angles. Second, there is an early onset for the EELS absorption at the nearly aligned heterostructure. We also observe a significant broadening of the spectra. We suspect that this early onset is due to the stronger interaction between MoS₂ and WSe₂ for nearly aligned configuration. Since the overall EELS spectra for lower angles is broader than those with higher angles, we are unable to draw conclusions about specific exciton peak shift. However, our observation of an early EELS onset agrees with the previous reports on the rotation dependence of both the interlayer and intralayer

exciton peaks by photoluminescence, optical reflectance and low-magnification EELS in several TMD heterostructures e.g. MoSe₂/WS₂, MoS₂/WSe₂ heterostructures.^{3,11,25}

Contrary to widely used optical techniques, EELS can measure the spectroscopic response at a very high spatial resolution, below the optical diffraction limit but this capability has not yet been employed in the case of TMD moiré heterostructures on which notable spatial variations might exist. The perturbation theory Wu et. al. has proposed that the periodic moiré potential produces changes in the local registry of atoms which ultimately influence the interlayer exciton dynamics.³⁴ The periodic potential splits the interlayer excitons into independent eigen states which tend to be confined at the proximity of potential minima at high symmetry points of the moiré lattice.^{3,4,6,12,13,34} Low angle moiré patterns between MoS₂ and WSe₂ correspond to supercells having a period larger than the typical exciton radius for TMDs (~1nm) which might lead to spatially varying exciton spectra. In order to understand the spatial variation in the excitons strong-coupling regime or nearly aligned configuration, it is important to first understand the local configuration within one moiré supercell in the MoS₂/WSe₂ heterostructures. Several quasi high symmetry local stacking orders can occur within the moiré lattice. In two configurations the hexagons overlap: (i) AA, Mo on top of W and S on top of Se, and (ii) AA', Mo on top of Se and W on top of S. Four configurations present a Bernal type stacking which can be notated as (iii) AB_{Se}^{Mo} , (iv) AB_W^S , (v) AB_W^{Mo} , (vi) AB_{Se}^S where the atomic species at the top layer and bottom layer overlap at the β sites (where two atoms stack vertically) which do not explicitly occur at the center of the hexagon of the adjacent layer. In low twist angle moiré structures, it is possible to find the spatially separated AA, AB_W^S , AB_{Se}^{Mo} configurations by a simple plane glide. However, in moiré structures with twist angles close to 30° the AA', AB_W^{Mo} , and AB_{Se}^S structures can be overlapped. In between these high symmetry

configurations, there are regions where the atoms of one layer lie in a bridge position with respect to the atoms of the adjacent layer (a general seventh configuration here identified as Br).

From a rigorous crystallographic point of view, a moiré super period occurs only when the two layers have commensurable lattices. However, even when this strict condition is not satisfied, quasi-high symmetry stacking regions are regularly distributed across the heterostructure and a moiré-like structure arises. This effect has been extensively discussed to explain the triangular patterns observed in STM images^{35,36} and analogous considerations can be applied to the case of STEM images. Furthermore, moiré superstructures with slightly different twist angles could present very different periods but the distance between high symmetry stacking regions and the associated apparent period do not drastically change.³⁵

Figure 3a shows a high angle annular dark field (HAADF) image of a MoS₂/WSe₂ heterostructure where equivalent brighter regions are about 14 nm apart. Figure 3b shows the associated nano-diffraction pattern from which a twist angle of $0.3 \pm 0.1^\circ$ and a lattice mismatch of $2.3 \pm 0.9\%$ can be derived. Bulk lattice parameters differ by about 4%, but this discrepancy can be lowered by deformations induced by interlayer coupling. The strain caused by the lattice mismatch will induce energy shifts of the excitonic lines of both materials, with compressive /tensile strain leading to blue/red shifts, respectively. Both uniaxial³⁷⁻³⁹ and biaxial⁴⁰ strain lead to similar behavior in TMD monolayers, with different amplitudes of energy shift for a given strain percentage. These values are in accordance with the pattern observed in HAADF images. Indeed, the very low twist angle imposes that the apparent period would be very close to those obtained for aligned layers. The measured lattice mismatch defines a superperiod corresponding to $n+1$ MoS₂ unit cells over n WSe₂ unit cells with n approximately equal to 40. Using the

experimentally observed lattice mismatch (δ), moiré angle (θ) and bulk lattice parameters of MoS₂ (a), the expected moiré period (L) was determined from the following equation.⁴¹

$$L = \frac{(1 + \delta)a}{\sqrt{\delta^2 + 2(1 + \delta)(1 - \cos \theta)}}$$

The expected moiré periodicity, 13.5 nm, is in good agreement with the HAADF images. The measured lattice mismatch, 2.3 %, is crucial to match the correct structure, as the bulk mismatch of 4% leads to a smaller moiré period (8.6 nm). (Figure S6)

An atomic model of an heterostructure formed by aligning and overlapping (41×41) MoS₂ and (40×40) WSe₂ supercells is given in Figure 3c, where the location of high symmetry configurations has been highlighted. These local structures can be clearly identified in the Figure 3a. Regions indicated by the correspondingly-colored rectangles have been magnified in Figure 3d-g. In HAADF images, each illuminated atom provides a signal which depends on its atomic number ($\propto Z^{1.6}$) and therefore the technique allows us to easily discriminate heavy and light atomic species. The three high symmetry configurations expected for a low angle twist can then be identified in the Figure 3c. For the *AA* configuration, the bright and dark atomic columns correspond to the superposition of the metal and chalcogen atoms respectively (Figure 3d). In the *AB_{Se}^{Mo}* configuration, the intensity derived from the overlapping of a Mo and two Se atoms is very close to those of the W atom while the much lighter sulfur atoms make minimal contribution to the image intensity (Figure 3e). In the *AB_W^S*, the brighter triangular lattice is formed by the overlap of W and S atoms while the intensity of Mo and the two Se sites is very similar (Figure 3f). The intermediate bridge positions can also be imaged (Figure 3g). This allows a direct connection between the observed intensity patterns observed at low magnification

with the local atomic stacking: bright, medium, and dark intensity spots correspond to AB_{Se}^{Mo} , AA, and AB_W^S configuration, respectively.

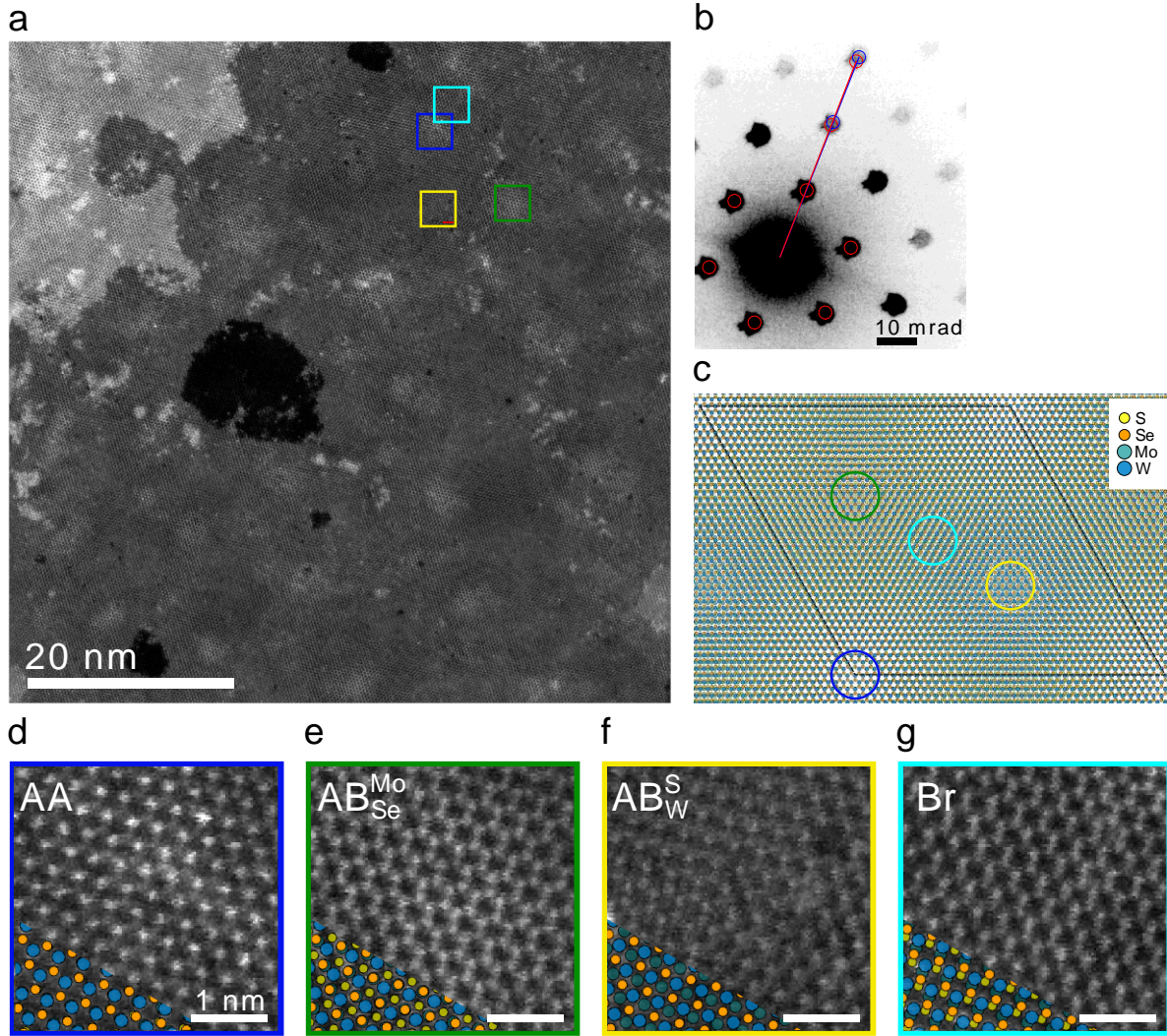


Figure 3. Identification of atomic configuration within one moiré supercell. a) Large field of view HAADF image of a low angle moiré structure with period 14 nm. b) Diffraction pattern of the region, showing the two diffraction patterns of the two monolayers almost perfectly superposed. Differences can only be seen for higher order reflections. c) Schematics of the moiré pattern formed when MoS₂ and WSe₂ are aligned with 0.3° rotation. The difference in the lattice parameter between the two materials result in 14 nm moiré period. Within the moiré supercell, there are four configurations whose zoomed-in images are displaced in d-g.

After identifying all the configurations, STEM-EELS mapping at cryogenic temperature (120 K) was carried out to map the optical response of different moiré structures. Mapping was

performed in raster mode wherein each pixel of the image corresponds to an EELS spectrum as a hyperspectral image. Figure 4a shows a medium angle annular dark field (MAADF) image of the heterostructure, with the white rectangle marking the region where the hyperspectral image was acquired. The image displays three intensity levels of bright, medium, and dark. From the relation between structure and intensity in images shown in Figure 3, we attribute bright, medium, and dark regions to AB_{Se}^{Mo} , AA , and AB_W^S configurations, respectively

Here we will focus on the low energy part of the spectra, where an interlayer exciton has been observed in previous works.^{16,18} STS experiments have observed a decrease of the band gap and the appearance of lower energy states with respect to the conduction band, confined to specific positions of a moiré superlattice.^{16,18} Figure 4d shows the representative EELS spectra collected from regions of three different levels of intensity (bright, medium and dark) from a different location to Figure 3. Spectra (marked red, green and blue) were extracted from the equivalent sites (16x16 pixels each) marked in Figure 4b, where the moiré pattern is periodic. Ten equivalent sites from the bright, medium and dark intensity were summed up for EELS spectra. (EELS spectra summed up=10x16x16 pixels) For the medium intensity region or AA configuration (green square in Figure 4b), we observe a slight decrease of the absorption onset and the appearance of a minor absorption peak; attributed to additional electronic levels. Magnified spectra from 1.4-1.8 eV range is described in inset. Details of the background subtraction are presented in supplementary information (Figure S7). According to the previous optical reflectance and PL studies, the onset of absorption on semiconducting transition metal dichalcogenides is given by an excitonic transition.^{3,4,6,10,11} The additional electronic levels at zero degree moiré closely matches with momentum space indirect exciton reported by Kunstmann et. al. (PL and DFT calculations).¹⁰ Further, from the filtered maps (1.4-1.6 eV

energy range) in Figure 4e, it can be observed that the broad minor absorption peak is mostly confined to medium spots or *AA* configuration. We also do observe a weak signal from the dark spots. The small peak occurring at the medium intensity locations disappears in a disordered arrangement of bright, medium or dark intensity.

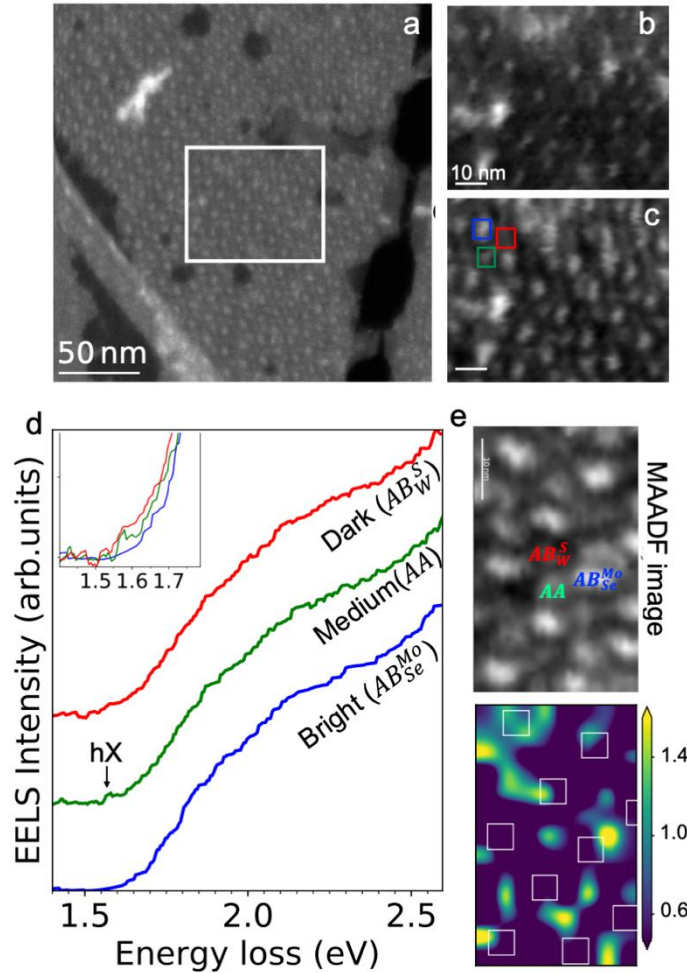


Figure 4. High resolution EELS maps of nearly aligned (0.3 degree) MoS₂/WSe₂ heterostructure. a) low magnification MAADF image of the moiré pattern. The white rectangle marks the region where the hyperspectral image was acquired. b-c) ADF and MAADF images, respectively, acquired with a hyperspectral image on the moiré structure. d) EELS spectra averaged over multiple equivalent sites of the bright or AB_{Se}^{Mo} (blue square), medium or *AA* (green square) and dark or AB_W^S (red square) intensity regions in the MAADF image. The EELS comparison plot shown on the below is sum of EELS spectra extracted from ordered arrangement of bright (AB_{Se}^{Mo}), medium (*AA*) and dark (AB_W^S) intensity regions. Inset shows the zoomed in spectrum from 1.4-1.8 eV. e) MAADF image and the corresponding energy filtered map from the 1.4-1.6 eV energy window. The bright spots from MAADF image are marked as

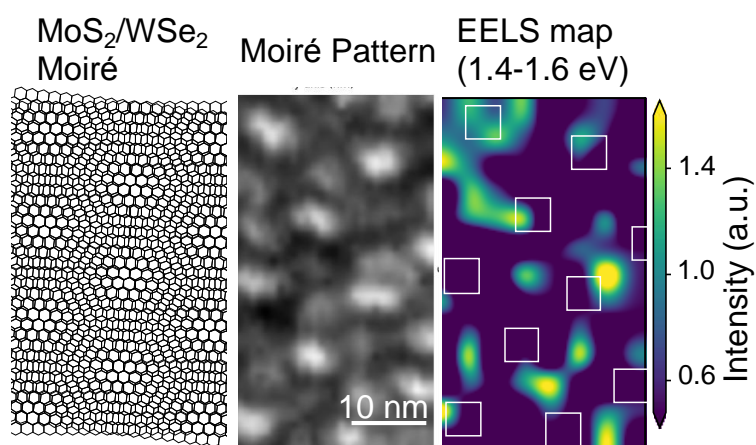
white squares in the filtered maps. The additional electronic levels are observed prominently in the medium regions of the MAADF image. The map was normalized by the total intensity in the EEL spectrum to avoid diffraction effects in the filtered maps presented.

Conclusions:

In conclusion, we have observed that in moiré structures formed by MoS₂ and a WSe₂ monolayers the onset of the EELS spectral response can be modified by the twist angle between the two layers. The low angle structures (0.3°) are strongly coupled, while the higher angle ones (30°) behave almost as independent layers. Furthermore, for a nearly aligned configuration (0.3° twist angle) an additional shallow peak appears near the adsorption edge. This spectral feature is mostly localized to AA regions of the moiré MAADF images and can be tentatively assigned to an interlayer moiré exciton

ASSOCIATED CONTENT

TOC Figure:



Supporting Information.

The following files are available free of charge.

experimental methods and supporting figures (Supplementary information.pdf)

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Author Contributions

S.S prepared the microscopy samples, performed HAADF imaging, analyzed most HAADF and EELS data and participated in EELS experiments. L.S. grew the CVD samples and made the MoS₂/WSe₂ heterostructure assembly. A.Z. analyzed the moiré structure of MoS₂/WSe₂ and was involved extensively in STEM-EELS technical discussion. S.Y.W helped in the technical discussion and EELS experiments. L.H.G.T. performed the EELS experiments and helped in EELS data analysis. L.H.G, O.S and P.MA conceived the idea and supervised the overall project. SS, L.S, LH.G.T and A.Z co-wrote the manuscript. All authors have given approval to the final version of the manuscript.

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