

## PHYSICAL SCIENCE

Interlayer couplings, Moiré patterns, and 2D electronic superlattices in MoS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayersChendong Zhang,<sup>1</sup> Chih-Piao Chuu,<sup>2</sup> Xibiao Ren,<sup>3</sup> Ming-Yang Li,<sup>4,5</sup> Lain-Jong Li,<sup>4,5</sup> Chuanhong Jin,<sup>3</sup> Mei-Yin Chou,<sup>2,6,7</sup> Chih-Kang Shih<sup>1\*</sup>

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By using direct growth, we create a rotationally aligned MoS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer as a designer van der Waals hetero-structure. With rotational alignment, the lattice mismatch leads to a periodic variation of atomic registry between individual van der Waals layers, exhibiting a Moiré pattern with a well-defined periodicity. By combining scanning tunneling microscopy/spectroscopy, transmission electron microscopy, and first-principles calculations, we investigate interlayer coupling as a function of atomic registry. We quantitatively determine the influence of interlayer coupling on the electronic structure of the hetero-bilayer at different critical points. We show that the direct gap semiconductor concept is retained in the bilayer although the valence and conduction band edges are located at different layers. We further show that the local bandgap is periodically modulated in the X-Y direction with an amplitude of ~0.15 eV, leading to the formation of a two-dimensional electronic superlattice.

## INTRODUCTION

Stacking two-dimensional (2D) atomic crystals with different bandgaps into van der Waals (vdW) heterostructures has emerged as a very powerful method to create designer heterostructures (1). In designing these vdW heterostructures, the effect of interlayer coupling will play a critical role. As shown in graphene-hexagonal boron nitride (hBN) heterostructures, interlayer coupling can be tuned through spatial alignments between vdW layers, providing a designing parameter (without a counterpart in conventional heterostructures) to tailor the electronic structures of vdW heterostructures (2–8). The emergence of transition metal dichalcogenide (TMD)-based heterostructures brought again the role of interlayer coupling into the spotlight (9–12). The issue of interlayer coupling in TMD heterostructures is inherently complex. It is already known that for bilayer TMDs (referred to as homo-bilayers), interlayer coupling splits the degeneracy at the  $\Gamma$  point and transforms the direct gap in the monolayer (ML) into an indirect gap semiconductor (13, 14). This splitting is shown to be quite large (~0.7 eV) (14–16). It has also been seen that the rotational alignment can influence the interlayer coupling in these homo-bilayers although all exhibit an indirect bandgap (17–20). For heterostructures composed of two different ML-TMD materials (referred to as hetero-bilayers), the role of interlayer coupling remains an open issue (9–12, 21–25). Two questions stand out prominently: (i) Does interlayer coupling lead to an indirect gap in the hetero-bilayer, or is the direct gap retained? (ii) Can interlayer coupling be used as a design parameter for vdW TMD heterostructures?

Here, we examine these critical issues by using a rotationally aligned, lattice-mismatched MoS<sub>2</sub>/WSe<sub>2</sub> heterostructure. Even with rotational alignment, the lattice mismatch between the two atomic layers produces a periodic variation in the lateral atomic registry, facilitating a natural platform for the investigation of how lateral registry affects interlayer coupling. The structural information is directly probed using scanning

tunneling microscopy (STM) and transmission electron microscopy (TEM). Direct correlation of the lateral registry between the two atomic layers and the local electronic structures is revealed using comprehensive scanning tunneling spectroscopy (STS). Experimental observations are corroborated with first-principles calculations. We quantitatively show how interlayer coupling affects the electronic structure at different critical points. We find that the direct gap is retained with the valence and conduction band edges located at the same  $K$  point but in different layers. The local bandgap is modulated periodically in the X-Y direction with an amplitude of ~0.15 eV, creating an electronic superlattice.

## RESULTS AND DISCUSSION

Chemical vapor deposition (CVD) is used to achieve direct growth of vertically stacked ML-MoS<sub>2</sub> on ML-WSe<sub>2</sub> on graphite substrates (described in Materials and Methods) (26). Figure 1A is an STM image of this hetero-bilayer on a graphite substrate. The Moiré pattern with a lattice constant of  $8.7 \pm 0.2$  nm can be clearly observed on the top MoS<sub>2</sub> layer (zoom-in view shown in Fig. 1B). This superlattice periodicity should appear in a rotationally aligned MoS<sub>2</sub>/WSe<sub>2</sub> bilayer; namely, the rotational angle between two atomic lattices is either 0° (R) or 180° (H) (27, 28). A simulated Moiré supercell for 0° rotational angle is displayed in Fig. 1C, resembling the STM observation well. However, the STM is unable to resolve the R or H stacking because the chalcogen sublattice on the surface will look identical. We then use annular dark-field scanning transmission electron microscopy (ADF-STEM) to unravel the atomic structure that is consistent with an R stacking.

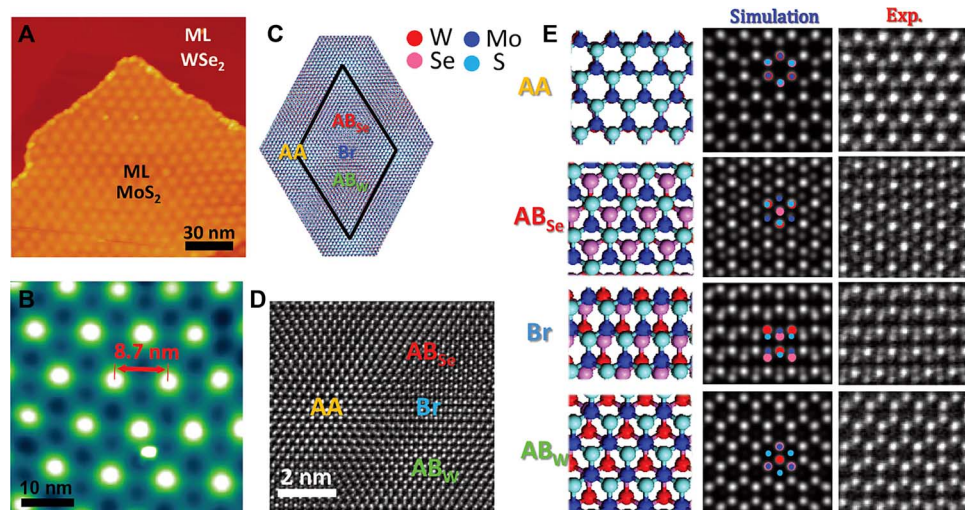
STEM samples are prepared by exfoliating the on-top TMD layers together with a very thin graphite layer. The ADF image intensity increases with the atomic number and the number of atomic layers. This makes the signal from ultrathin graphite much weaker than the signals from bilayer TMDs, which could be simply treated as background signals. The ADF-STEM image of the heterostructure stack is shown in Fig. 1D. Although MoS<sub>2</sub> and WSe<sub>2</sub> are rotationally aligned, their difference in lattice constants leads to locally different lateral registries, resulting in a periodic variation of these local alignments (that is, the Moiré pattern). In Fig. 1E, we show the ADF-STEM images at different local alignments [designated as AA, AB<sub>Se</sub>, Bridge (Br), and AB<sub>W</sub>] along with the simulated ADF-STEM images, which fit well with the experimental ones, and the corresponding models on the left. The symbol of

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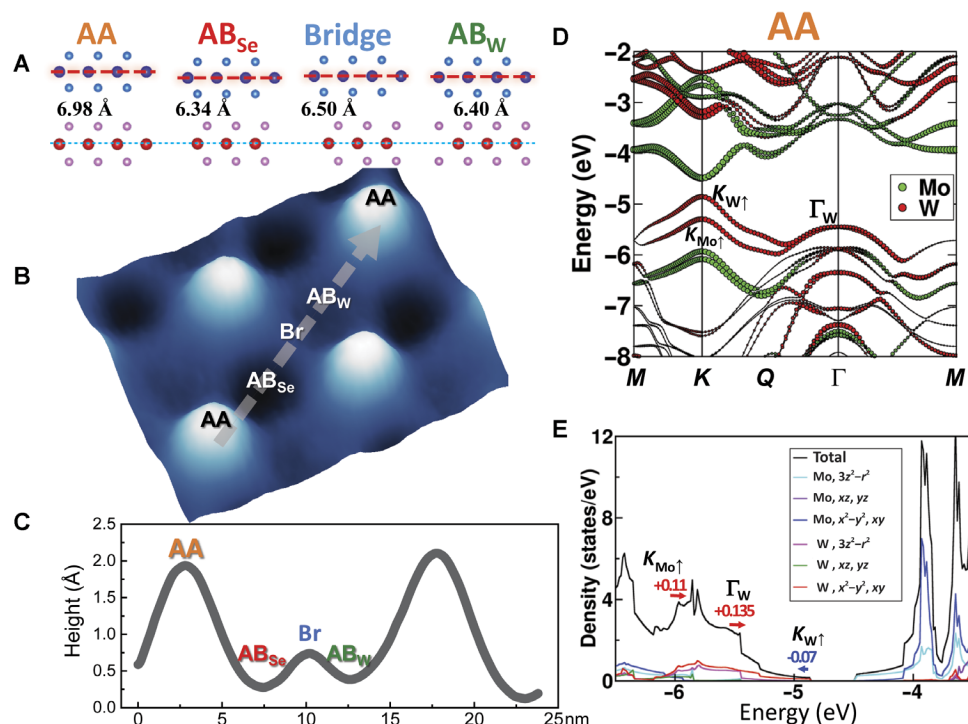
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**Fig. 1. Atomic structure of as-grown  $\text{MoS}_2/\text{WSe}_2$  vdW heterostructures revealed by STM and STEM.** (A) STM image for a  $\text{MoS}_2/\text{WSe}_2$  vdW heterostructure on the highly oriented pyrolytic-graphite (HOPG) substrate. (B) Close-up STM image showing the hexagonal Moiré pattern with a periodicity of 8.7 nm. (C) Schematic model of the Moiré pattern on an R-stacked  $\text{MoS}_2/\text{WSe}_2$  hetero-bilayer. By using the lattice constants of 3.16 Å for  $\text{MoS}_2$  and 3.28 Å for  $\text{WSe}_2$ , the simulated supercell marked by black solid lines shows a periodicity of 8.64 nm. (D) Atomically resolved STEM image. Typical regions in an R-stacked heterostructure—AA,  $\text{AB}_{\text{Se}}$ , Br, and  $\text{AB}_{\text{W}}$ —are labeled in both (C) and (D). The close-up STEM images for each region are shown in the right column of (E). The simulated images (based on an R-type stacking) and their corresponding atomic models are displayed in the middle and left columns of (E), respectively. (A and B)  $-3.0$  V,  $10$  pA. Exp., experimental.



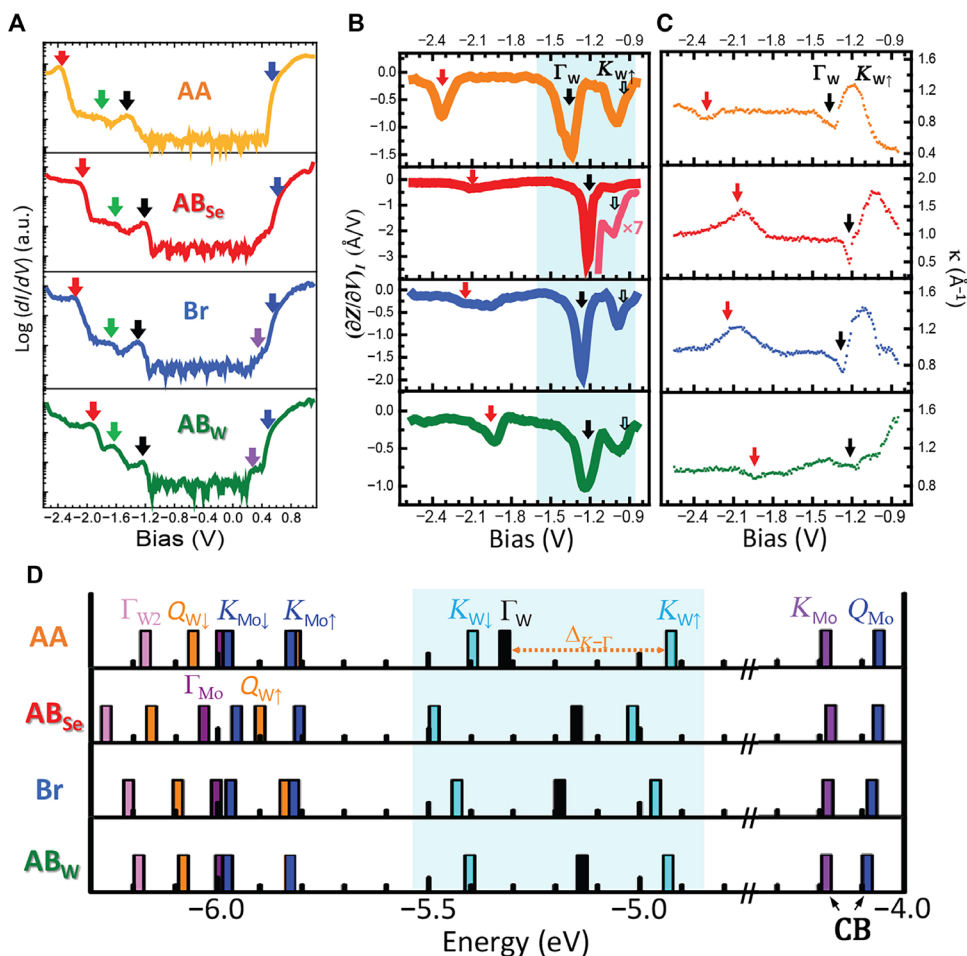
**Fig. 2. First-principles calculations for the interlayer separations and electronic structures of representative sites in an R-stacked  $\text{MoS}_2/\text{WSe}_2$  heterostructure.** (A) Side views of the atomic models for AA,  $\text{AB}_{\text{Se}}$ , Br, and  $\text{AB}_{\text{W}}$  regions with an average lattice constant (Supplementary Materials). The calculated interlayer separations for four atomic alignments are labeled in (A). (B) A perspective view of an STM image zoomed in on a unit cell of the Moiré pattern. A height profile along the diagonal line from AA to AA [gray dashed line in (B)] is shown in (C). Energy band structure of the AA registry is displayed in (D), whereas its corresponding density of states (DOS) diagrams are shown in (E). The size of the green (red) circles represents the projected weight on the  $d$  orbitals of Mo (W), and the states are labeled in the subscript based on this project. The corrections for the strain resulting from the average lattice constant used in the calculation are labeled for the typical critical points in the DOS diagram. Results for other sites can be found in the Supplementary Materials. (B)  $-3.0$  V,  $10$  pA.

$AB_{Se}$  ( $AB_W$ ) means that the hexagonal lattices of the metal atoms in the two MLs are stacked in an AB manner (analogous to bilayer graphene), with the Se(W) atoms in the bottom ML not covered by any atoms in the upper ML. A more detailed ADF-STEM analysis, including intensity line profile analysis in different regions, can be found in figs. S1 and S2.

The rotationally aligned  $MoS_2/WSe_2$  stack has a lattice constant of 8.7 nm, and a unit cell contains about 4000 atoms. Theoretically, it is very challenging to use a very large unit cell for electronic structure calculations with density functional theory (DFT). To circumvent this difficulty, we first examine the effect of different local interlayer atomic registries on the electronic structure using the average lattice constant for both  $MoS_2$  and  $WSe_2$  (see the Supplementary Materials for details). It is expected that the results reflect the corresponding changes caused by the local registry in the large unit cell. The calculated band diagram for the AA site is shown in Fig. 2D (other sites are shown in fig. S3). The interlayer separations at different sites (labeled in Fig. 2A), which show an order of  $AA > Br > AB_W > AB_{Se}$ , are also calculated. These differences in height can be used to distinguish the high-symmetry sites in STM observations (detailed discussion in the Supplementary Materials). As shown in Fig. 2 (B and C), AA,  $AB_{Se}$ , Br, and  $AB_W$  are

labeled along the diagonal line of one supercell, following the same sequence predicted by calculations despite a smaller amplitude in their differences.

The second step of the theoretical calculation entails a posterior strain correction to gain a more accurate description for the electronic structure of individual “unstrained” MLs. This is justifiable because little mixing exists between electronic states coming from different layers in the bilayer system. These strain corrections lead to systematic shifts in critical point energy locations, as labeled by the arrows shown in Fig. 2E. It is found that significant differences exist in electronic structures between AA and  $AB_{Se}$  sites, especially for electronic states at the  $\Gamma$  point in the valence band. This is due to the fact that the interlayer coupling at the  $\Gamma$  point is mediated through the chalcogen  $p_z$  orbitals. The difference in the local atomic registry (for example, AA versus  $AB_{Se}$ ) is primarily in the lateral alignment of the chalcogen atoms, that is, Se in the top  $WSe_2$  layer and S in the bottom  $MoS_2$  layer, as shown in Fig. 2A. Consequently, interlayer coupling would be significantly influenced. Theoretical calculations for energy locations (after strain correction) of key critical points for these four different local atomic registries are shown in Fig. 3D. Not all of them are resolved experimentally. Up arrow



**Fig. 3. Scanning tunneling spectra of AA,  $AB_{Se}$ , Br, and  $AB_W$  regions.** (A)  $dI/dV$  spectra. (B and C)  $(\partial^2 Z / \partial V^2)_I$  and decay constant  $\kappa$  spectra of valence bands, respectively. (D) Calculated energy values at key critical points for AA,  $AB_{Se}$ , Br, and  $AB_W$  sites, respectively. The energies are with respect to the vacuum level. The shaded regions in (B) and (D) represent the valence band edges and show consistent movements of the energy locations of  $\Gamma_W$  (black) and  $K_W$  (cyan). In a deeper lying energy range, the spectral features marked by red and green arrows in (A) to (C) correspond to the energy window where the  $Q_{W\downarrow}$ ,  $K_{Mo\downarrow}$ , and  $\Gamma_{Mo}$  states and a lower  $\Gamma_W$  (labeled as  $\Gamma_{W2}$ ) state are located. The complicated movements in their relative energy locations result in a complex behavior in  $\kappa$  spectra [red arrows in (C)], making the direct identification of individual states nontrivial.



and down arrow subscripts are used to represent the higher and lower energy levels in spin-orbit split  $K$  ( $Q$ ) states, respectively.

STM and STS reveal detailed information on how interlayer atomic registry affects the local electronic structures of the  $\text{MoS}_2/\text{WSe}_2$  heterobilayer. In Fig. 3, three different STS modes are displayed: the conventional  $dI/dV$  acquired at constant  $Z$  (Fig. 3A), the  $\partial Z/\partial V$  at constant current (Fig. 3B), and the tunneling decay constant defined as  $\kappa = -1/2 (d\ln I/dZ)$  (Fig. 3C). As discussed recently, the  $(\partial Z/\partial V)_I$  spectrum provides the signature for the onset of different thresholds in the tunneling process, whereas the  $\kappa$  spectrum helps us to identify the origin of these thresholds in the Brillouin zones (29).

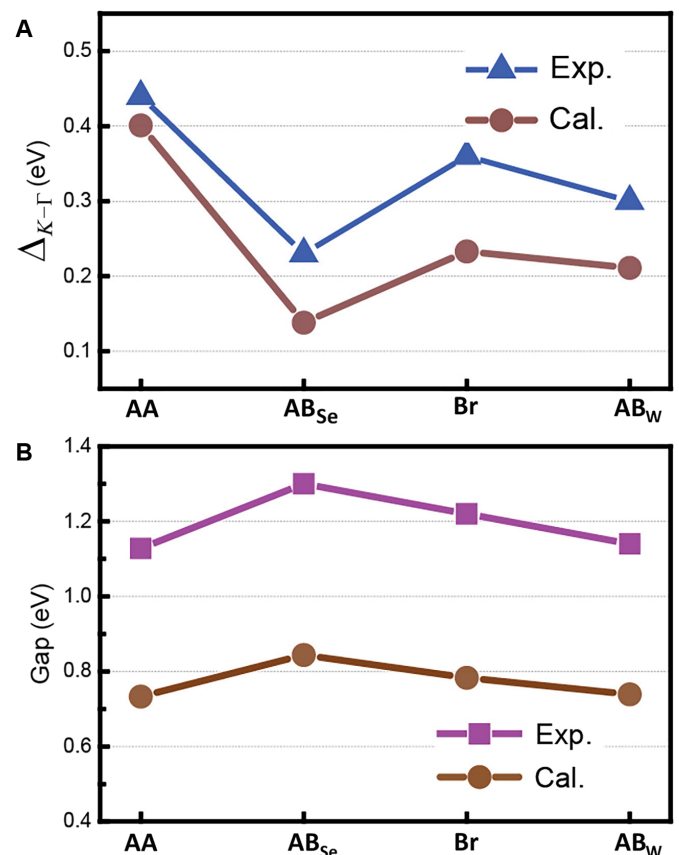
In the conventional  $dI/dV$  spectrum (displayed in the logarithmic scale), several spectral features are identified (labeled with arrows in different colors). The states marked by the black arrows are the  $\Gamma_W$  states that reside primarily in the  $\text{WSe}_2$  layer (Fig. 2D). This assignment is corroborated by both the  $(\partial Z/\partial V)_I$  and the  $\kappa$  measurements shown in Fig. 3 (B and C). At a constant current, when the sample bias ( $V_S$ ) is scanned from below to above  $\Gamma_W$ , the loss of  $\Gamma_W$  states forces the tip to move inward to compensate for this loss, resulting in a dip in the  $(\partial Z/\partial V)_I$  (that is, a sudden drop in  $Z$ ). This allows us to probe a critical point in the band structure. Moreover, because the parallel momentum  $k_{\parallel} = 0$  at the  $\Gamma$  point, one anticipates to observe a sharp minimum in  $\kappa$ , as  $\kappa = \sqrt{\frac{2m\phi_o}{\hbar^2} + k_{\parallel}^2}$ , where  $\phi_o$  is the barrier height. This is observed in Fig. 3C (marked by black arrows).

In the  $dI/dV$  spectra acquired with  $Z$  stabilized at  $V_S = -2.6$  V, the  $Z$  value is not small enough to detect the states above  $\Gamma_W$  (particularly states near  $K_{W\uparrow}$ ) because of their high decay constant. In the constant current spectrum, this sensitivity issue is removed. The threshold at  $K_{W\uparrow}$  appears as another dip in  $(\partial Z/\partial V)_I$ . This occurs when the sample bias is moved above the energy location of  $K_W$ , and the tip needs to move closer to the sample to achieve tunneling to the underlying graphite states. The large decay constant  $\kappa$  measured near  $K_{W\uparrow}$  also reflects the high  $k_{\parallel}$  value. It should be noted that because of the mixing of underlying graphite states in tunneling, simulation becomes necessary for an accurate determination of  $K_W$ , which suggests that the location of  $K_W$  is slightly above the dip location of  $(\partial Z/\partial V)_I$  by about 0.05 eV (29).

The behavior of the electronic states near the valence band maximum (VBM) corroborated very well with the theoretical calculations shown in Fig. 3D, particularly for states near the VBM (shaded region in Fig. 3, B and D). These states ( $\Gamma_W$  and  $K_W$ ) have spectral weights located at the  $\text{WSe}_2$  layer. The theoretical results are in excellent agreement with the experimental result in energy locations of the  $\Gamma_W$  (showing an order of  $AA < Br < AB_{Se} < AB_W$ ) and the energy separations between  $\Gamma_W$  and  $K_{W\uparrow}$  (labeled as  $\Delta_{K-\Gamma}$  and shown in Fig. 4A). The  $K_{W\uparrow}$  state is located above  $\Gamma_W$ , and its signature can be identified much more clearly because it occurs in the bias range where  $\Gamma_W$  no longer contributes to the tunneling current. On the other hand, the state  $K_{W\downarrow}$  is located below  $\Gamma_W$ , making its signature difficult to be detected because the tunneling current would be dominated by the states that originated near  $\Gamma_W$ . In a deeper lying energy range (marked by the red and green arrows in Fig. 3A), theory shows that these states correspond to the energy window where the  $Q_W$ ,  $K_{Mo}$ , and  $\Gamma_{Mo}$  states and a lower  $\Gamma_W$  (labeled as  $\Gamma_{W2}$  in Fig. 3D) state are intertwined. The complicated movements in their relative energy locations make the direct identification of individual states nontrivial. Nevertheless, on the basis of the comparison with theoretical calculations (Fig. 3D), the features marked by the green arrows in Fig. 3A can be tentatively attributed to be  $K_{Mo\uparrow}$  states.

In the conduction band, near the band edge, two clear thresholds (labeled with blue and purple arrows in Fig. 3A) are observed at the  $AB_{Se}$ , Br, and  $AB_W$  sites, similar to those observed in isolated ML- $\text{MoS}_2$  (29, 30). These two thresholds have been previously identified as thresholds at two different critical points,  $Q$  and  $K$ , with the conduction band minimum (CBM) located at the  $K$  point. At the AA site, the lower threshold is not present because of a large tip-to-sample distance at the AA site for the stabilization voltage ( $-2.6$  V) used in constant  $Z$  spectroscopy. The energy separation between these two thresholds remains relatively unchanged ( $\sim 0.20$  eV), but their absolute energy locations are site-dependent. The positions of the conduction band  $Q$  point follow the order of  $AA \sim AB_{Se} > Br > AB_W$ . The total change for the  $Q$  point position from  $AB_{Se}$  to  $AB_W$  is  $\sim 0.1$  eV (similarly for the  $K$  point). Theoretical calculations show a similar order in the energy location (Fig. 3D), although the variation is smaller (only  $\sim 0.03$  eV).

A very important consequence of interlayer coupling is that the local bandgap  $E_g$  is site-dependent. For example, at the  $AB_{Se}$  site,  $E_g = 1.30$  eV with the VBM located at  $-0.98$  eV and the CBM located at  $+0.32$  eV. On the other hand, at the  $AB_W$  site,  $E_g = 1.14$  eV with the VBM located at  $-0.93$  eV and the CBM located at  $+0.21$  eV. Experimental results for  $E_g$  at four different sites are shown in Fig. 4B, with the calculated  $E_g$  shown as brown circles. It is understood that DFT calculations significantly underestimate the bandgap values (31, 32),



**Fig. 4. Summary of the site-dependent electronic structures in  $\text{MoS}_2/\text{WSe}_2$  heterobilayers.** (A) Energy differences between  $K_W$  and  $\Gamma_W$  ( $\Delta_{K-\Gamma}$ ) for the four different local lateral alignments. The experimental values are labeled as blue triangles, whereas the calculated DFT results are presented as brown circles. (B) Local bandgap  $E_g$  formed between the CBM of  $\text{MoS}_2$  and the VBM of  $\text{WSe}_2$ . Experimental and calculated DFT results are displayed in purple and brown, respectively.

but the current results excellently replicate the overall trend in band-gap variations observed experimentally.

The periodic variation of local electronic structures as a consequence of the variation of the interlayer coupling due to the difference in local interlayer atomic registry of the MoS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer also indicates the formation of an electronic superlattice. This is similar to the case of the graphene-hBN hetero-bilayer, except that the amplitude of bandgap variations is much larger in the current case. The formation of this electron superlattice is also visualized in the sequence of bias-dependent images shown in Fig. 5.

At a high negative bias, that is, from  $-3.0$  to  $-2.4$  V, a similar STM contrast is observed (Fig. 5, A and B). However, at  $-2.3$  V, where the spectral feature of the AA site at  $-2.4$  V (marked by the red arrow in Fig. 3A) is out of the tunneling range, a lowering of the topographic height at the AA site occurs. Accompanying this lowering is the appearance of three new features surrounding AA. These new features correspond to the locations of other bridge sites (labeled as Br<sub>2</sub> and discussed in more detail in the Supplementary Materials). Theory indicates that the electronic structures of Br<sub>2</sub> and Br are nearly the same. Indeed, at above  $-2.1$  V, Br<sub>2</sub> and Br features merge, forming a circular ring feature. At  $-1.6$  V,  $\Gamma_W$  states at all four sites are still in the tunneling window, and the AA site remains to have the highest topographic height. The most marked change is the turning of the bright feature at the AA site into a deep hole at  $-1.4$  V. This is due to the fact that the  $\Gamma_W$  state at the AA site moves out of the tunneling window, whereas that of the other sites continues to contribute. The evolution continues as states at different sites move out of the tunneling window at a slightly different bias (discussed further in the Supplementary Materials). In the positive bias range, when the bias is above  $0.85$  V,

all images have a “normal” contrast. At  $0.5$  V, the  $Q_{Mo}$  states at AA and AB<sub>Se</sub> start to move out of the tunneling window, and the topographic height drops (note that the AB<sub>Se</sub> site is the lowest in the first place and the drop does not lead to a contrast change as marked as that at the AA site). Because the AB<sub>W</sub> site has the lowest CBM location (see Fig. 3A marked by the purple arrow), the AB<sub>W</sub> site becomes the highest topographic feature as the bias continues to decrease to  $0.2$  V.

These rich features in the evolution of the bias-dependent STM images are just another manifestation of the lateral modulation of the electronic structures due to the local variation of interlayer atomic registry in the hetero-bilayer. The states that are affected the most are the valence states at the  $\Gamma$  point. However, the VBM of the overall double-layer stack remains at the  $K$  position, whose spectral weight is completely at the WSe<sub>2</sub> layer, whereas the CBM is also at the  $K$  position, but the spectral weight is completely at the MoS<sub>2</sub> layer. Thus, the notion of an interfacial exciton is unperturbed despite the fact that there is a strong enough interlayer coupling that changes other parts of the electronic structure significantly, but most importantly, the local bandgap of the double-layer stacks is modulated periodically with an amplitude of  $\sim 0.15$  eV, forming a 2D electronic superlattice defined by the Moiré pattern. This would also mean that the interfacial exciton will experience a periodic potential modulation as large as  $0.15$  eV.

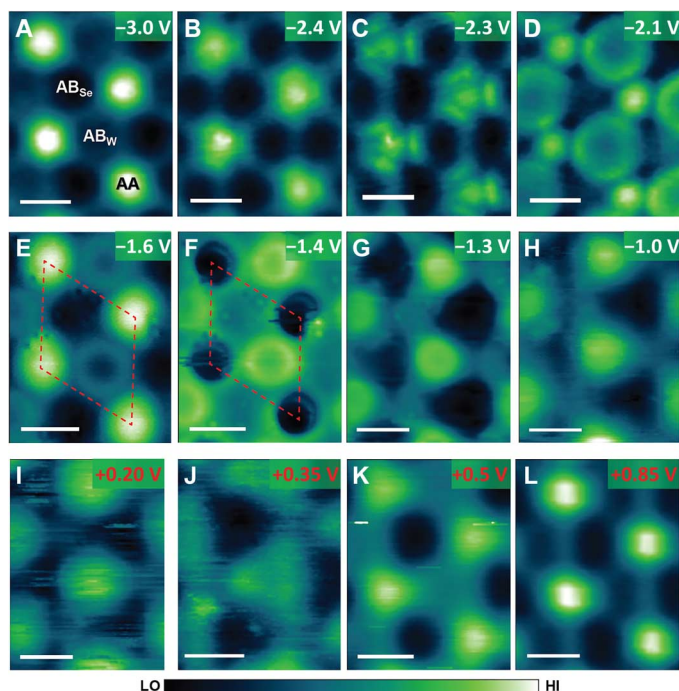
## CONCLUSION

Our study clearly shows that the atomic registry between vdW layers dictates the behavior of interlayer electronic coupling, which can be used as a designing parameter for novel 2D electronic systems based on vdW heterostructures. The same principle should be commonly applicable to twisted vdW hetero-bilayers as well. The large amplitude of bandgap modulation raises the prospects for device applications at room temperature for these 2D electronic superlattices. Our findings will stimulate research interests in similar superstructures extensively formed in the flourishing family of 2D materials (33–37).

## MATERIALS AND METHODS

### Growth of MoS<sub>2</sub>/WSe<sub>2</sub> vdW heterostructure samples

The WSe<sub>2</sub>/MoS<sub>2</sub> vdW heterostructures were grown using the developed two-step CVD method (26, 38). First, an ML WSe<sub>2</sub> single crystal was grown on the HOPG substrate. The WO<sub>3</sub> powder (0.6 g) was placed in a quartz boat located in the heating zone center, and the HOPG substrate was put at the downstream side. The Se powder was placed in a separate quartz boat at the upper stream side of the quartz tube. The Se powder was heated to  $260^\circ\text{C}$  and brought to the downstream side by an Ar/H<sub>2</sub> flow [Ar = 90 standard cubic centimeters per minute (sccm) and H<sub>2</sub> = 6 sccm], and the chamber pressure was controlled at 20 torr. The WO<sub>3</sub> powder was heated to  $935^\circ\text{C}$  for growth. After reaching the desired growth temperature, it was kept for 15 min, and the furnace was then naturally cooled down to room temperature. The as-grown WSe<sub>2</sub> sample was then put into a separate furnace for the second step of MoS<sub>2</sub> growth. The setup for MoS<sub>2</sub> synthesis is similar to that for WSe<sub>2</sub>, and the reactants were changed to MoO<sub>3</sub> (0.6 g) and S. The Ar gas flow was set at 70 sccm, and the pressure was controlled at 40 torr. The MoO<sub>3</sub> and S sources were heated to  $755^\circ$  and  $190^\circ\text{C}$ , held for 15 min for synthesis, and then naturally cooled down to room temperature.



**Fig. 5. Bias-dependent STM images of the Moiré pattern.** The corresponding sample bias voltage is labeled for each image as shown. A dashed red rhombus in (E) and (F) represents a unit cell of the superlattice. A color bar is shown at the bottom to represent the relative height differences (that is, low and high) in (A) to (L). Scale bars, 5 nm in all images.

## STM and STS

STM and STS investigations were acquired at 77 K in ultrahigh vacuum (base pressure,  $<6 \times 10^{-11}$  torr). Electrochemically etched W-tips were cleaned in situ with electron beam bombardment. The tunneling bias was applied to the sample. The  $dI/dV$  spectroscopy at constant  $Z$  was taken by using a lock-in amplifier with a modulation voltage of 10 mV at a frequency of 914 Hz. The  $(\partial Z/\partial V)_I$  spectra were acquired by sweeping the sample bias while feedback loop was on (constant tunneling current). The tunneling decay constant  $\kappa$  is equal to  $-\ln I/2dZ \equiv -(dI/dZ)/2I_0$ .  $dI/dZ$  can be acquired by using the lock-in amplifier with a  $Z$ -modulation amplitude of 0.01 nm and a modulation frequency of 914 Hz, which is faster than the feedback time constant. This results in a small current modulation superimposed on the feedback set current  $I_0$ . If the sample bias is swept slowly, the  $\kappa$  and  $(\partial Z/\partial V)_I$  can be acquired at the same time.

## ADF-STEM characterization and image simulation

The sample was transferred onto a TEM grid following a previous report with minor modifications (39). ADF-STEM images were recorded with a probe-corrected Titan ChemiSTEM (FEI), which was operated at an acceleration voltage of 200 kV. The probe current was set at 47 pA with a convergent angle of 22 mrad for illumination. The inner collection angle was adjusted to 44 mrad to enhance the contrast of sulfur atoms. The experimental ADF-STEM images shown in the main text were superimposed by 10 frames after drift compensation and then processed with an improved Wiener filtering method to increase the signal-to-noise ratio for a better display. ADF-STEM image simulations were performed using QSTEM software (40), with the input parameters being the same as the experimental settings.

## First-principles calculations

First-principles calculations were carried out using DFT as implemented in the Vienna Ab initio Simulation Package (41). The interaction between electrons and ionic cores was approximated by the projector augmented wave method (42), and the exchange-correlation potential was described by the Perdew-Burke-Ernzerhof generalized gradient approximation (43), with the vdW correction incorporated by the vdW-DF (optB86) functionals (44). A supercell size of 25 Å along the  $z$  direction was used with a vacuum thickness larger than 18 Å to eliminate the spurious interaction in the slab calculation, and the energy cutoff of plane waves was 600 eV. The structure was fully relaxed until the change of the energy and the force reached  $10^{-6}$  eV per  $1 \times 1$  cell and  $10^{-3}$  eV/Å, respectively. A  $12 \times 12 \times 1$  k-grid was used for  $1 \times 1$  unit cell of  $\text{MoS}_2/\text{WSe}_2$ , and a finer k-grid of  $81 \times 81 \times 1$  was used for the DOS calculation with the spin-orbit coupling effect included for both the DOS and electronic band structure calculations. To perform calculations for the local atomic alignments, we used an average lattice constant of 3.23 Å for both  $\text{MoS}_2$  and  $\text{WSe}_2$  to create the  $1 \times 1$  unit cell. The strain effects resulting from the usage of the averaged lattice parameter were estimated by comparing the band structures of unstrained and strained (3.23 Å) freestanding MLs (details in the Supplementary Materials). These strain effects were corrected in Figs. 3D and 4.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/1/e1601459/DC1>

Determining the R stacking and local atomic registries by intensity profiles of STEM images  
First-principles calculation of the site-dependent band structures

Additional discussions for STM and STS results

fig. S1. ADF-STEM results of the  $\text{MoS}_2/\text{WSe}_2$  heterostructures.

fig. S2. Intensity profile along AA-to-AB<sub>W</sub> in STEM images.

fig. S3. First-principles calculations of the electronic structures of AB<sub>Se</sub>, Br, and AB<sub>W</sub>.

fig. S4. Atomic model and the electronic structures of the Br<sub>2</sub> site.

fig. S5. Statistical distributions of the  $\Gamma_W$  energy locations.

table S1. Calculation results of the energy differences between key critical points.

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