Supplementary Materials for

Interlayer couplings, Moiré patterns, and 2D electronic superlattices in MoS$_2$/WSe$_2$ hetero-bilayers

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DOI: 10.1126/sciadv.1601459

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Determining the R stacking and local atomic registries by intensity profiles of STEM images

Figure S1A is the large scale ADF image showing monolayer MoS$_2$ (ML-MoS$_2$) stacked on top of ML-WSe$_2$ as labeled. The insert is a close-up image of ML-WSe$_2$ where the contrast between W and Se dimmer can be clearly seen. The corresponding fast Fourier transformed (FFT) image of fig. S1A shows that WSe$_2$ and MoS$_2$ are rotationally aligned with no twist angle (fig. S1B); the discriminable two sets of reciprocal lattices are marked in the zoomed-in inset. In Fig. 1C, simulated images are compared to the experimental observations. Three experimental intensity profiles are displayed in fig. S1D with their corresponding pathways labeled in the right column of Fig. 1C. All experimental line profiles reproduced the distinctive features shown in the corresponding simulation, albeit there exist minor variations in the intensity amplitude. The great consistency between experiment and simulation further confirms the R stacking in our sample.

Moreover, the intensity profile for the AA to AB$_W$ region is shown in a large length scale in fig. S2. Figure S2 (A to C) are the experimental image, simulated image and schematic model of the AA-to-AB$_W$ region, respectively. The intensity profiles shown in fig. S2D are along the pathways labeled in fig. S2, A and B. The minor peaks marked by red arrows in the profile are from S dimers labeled by arrows in the schematic model (fig. S2C), which can be barely seen in the images due to the limited contrast. The relatively weak contrast of the S atoms makes it difficult to determine the stacking mode. Here we present another unambiguous evidence which further supports the R stacking. As marked by arrows in the schematic model (fig. S2C), the relative positions of these S dimers vary along the profile direction. Furthermore, such a variation observed in the experimental intensity profile (red line in fig. S2A) is consistent with the simulation results (blue line in fig. S2C). Thus, the presence of this regular variation could help us safely rule out the uncertainties on determining the stacking consequence due to the experimental errors, e.g. tails of the probe, scanning noises, residual aberrations or background signal.
First-principles calculation of the site-dependent band structures

Here we further illustrate how the calculations are performed. An atomic model of the Moiré structure with R-type stacking is displayed in fig. S4A. For each typical site, as labeled in fig. S4A, we created a $1 \times 1$ WSe$_2$/MoS$_2$ unit cell with a lattice constant of 3.23 Å, which is the average of the WSe$_2$ and MoS$_2$ lattice constants. In other words, in the DFT calculations, at first the MoS$_2$ lattice is stretched while the WSe$_2$ lattice is compressed. The correction to such strain effect was then calculated separately by comparing the energy bands of a freestanding unstrained and strained monolayer of each material. This correction scheme is based on the expectation that the characteristics of the interlayer interaction are mainly determined by the atomic layer registry and is minimally affected by the strain in individual layers. We have verified the validity of this approach by comparing our results with direct calculations using manageable supercells. Table S1 summarizes the strain-corrections for the energy differences between key critical points near the band edges. The DFT calculation results of the band structures for AB$_{Se}$, AB$_{W}$ and Br sites are displayed in fig. S3, A to C.

As we discussed in the main text, new features surrounding AA were observed at -2.3 V (Fig. 5C). These new features correspond to another bridge site (Br$_2$) located in the middle of AA and AB$_W$ sites (see fig. S4A). The energy locations of key critical points on Br and Br$_2$ are displayed in fig. S4B. As one can see, the difference between Br$_2$ and Br is minor, the most distinguished difference lies in a shifting of $\Gamma_W$ by ~ 60 meV. This is indeed consistent with the STM observations that Br$_2$ and Br merge together once the scanning bias deviates a bit from -2.3V. Note that the lateral atomic registry is a continuous variable over a Moiré supercell. In this work, we have only focused on several high-symmetry sites (i.e. AA, AB$_{Se}$, AB$_W$ and Br), which ought to represent the most dramatic spatial modulations of the electronic structures in MoS$_2$/WSe$_2$ hetero-bilayers.
Additional discussions for STM and STS results

*Estimation of interlayer separations using the STM height profile.* The experimental height profile in Fig. 2C was taken with a bias of -3.0 V, far from the valence band edge where the most significant differences occur. A relatively large integral window (-3.0 V to Fermi level) leads to a finite weighting of the band edge states in the total tunneling current. In other words, the height profile shown in Fig. 2C should mainly represent the real Z topography while the spatial difference in the electronic structures can be ignored. This is indeed why the height contrast (*i.e.*, the image topography) remains almost unchanged when the bias varying from -2.5 to -3.5 V. Therefore, by comparing with the theoretical results of the interlayer separations (Fig. 2A), we can determine the local stacking types in a STM image as labeled in Fig. 2B and C. Note that, such assignments lead to a same spatial sequence with the theoretical predictions, *i.e.* the second highest site is located between the lowest and the second lowest sites. Moreover, the good agreement of the electronic structures for each site (as shown in Fig. 3) also validate this assignment.

*Image morphologies near the valence band edge.* In the main text, the evolution of STM image morphology in Fig. 5 has been discussed. Here, we’d like to expand it more. As seen in Fig. 5G, the contrast at -1.3 V is still consistent with the fact that \( \Gamma_W \) state at the \( \text{AB}_W \) site is located at a higher energy location. However, at -1.0 V (very close to the band edge), the \( \text{AA} \) site remains dark despite that the \( \kappa_W \) state at the \( \text{AA} \) site is about the same as that at the \( \text{AB}_W \) site. Thus the earlier line of argument cannot explain the contrast being observed. Note that very near the band edge, the states all originate from W orbitals in the WSe\(_2\) layer and the top MoS\(_2\) layer would acts as part of the tunneling barrier. A likely scenario is that the W atom at the bottom layer is more exposed at the \( \text{AB}_W \) site and the effective barrier there might be slightly smaller. This is only a tentative interpretation and more thorough investigations in the future will be needed.

*Valence band edge of MoS\(_2\).* As discussed in previous publication (ref. 29), our STS method is only effective to reveal critical points when the key critical points are well isolated. In the heterobilayer system, the valence band edge of MoS\(_2\) is intertwined with the deeper lying states of WSe\(_2\) layer (*e.g.* \( Q_W \) and \( \Gamma_{W2} \)). Therefore, the direct identification of the VB edge of MoS\(_2\) is
non-trivial. However, if tentatively assigning the peaks labeled by the green arrows in Fig. 3A as the $K_{Mo\uparrow}$, together with the positions of $K_{W\uparrow}$, one can deduce the “valence band offset” values at these four different sites. They are 0.87 eV, 0.63 eV, 0.72 eV, and 0.71 eV for the AA, AB$_{Se}$, Br and AB$_{W}$ sites with error bars of ± 0.1 eV. The tendency agrees quite well with the theoretical results shown in table S1.

**Statistical analyses of spectroscopic measurements.** In fig. S5, we show statistical distributions of the $\Gamma_{W}$ energy locations based on multiple $dI/dV$ measurements. Only the results of the AA and AB$_{Se}$ sites, which show the most significant difference, are displayed. The experimental errors of the energy locations of critical points can be determined as ± 0.03 eV. This is consistent with our previous studies on single layer TMDs [ref. 29, 30]. If assuming $\Delta_{total} = \sqrt{\Delta_{1}^2 + \Delta_{2}^2}$, we can tentatively estimate the error bars for the energy differences and band gaps shown in Fig. 4 as ~ 0.05 eV.
fig. S1. ADF-STEM results of the MoS$_2$/WSe$_2$ heterostructures. (A) Large scale STEM image. The inset is a close-up image of the bare WSe$_2$ region with atomic resolution (the position is marked by green square in (A)). (B) FFT pattern from the whole image of (A) showing a rotational alignment of the MoS$_2$ and WSe$_2$ lattices. The inset is a close-up image of the orange square in (B) illustrating the discriminable reciprocal lattices of MoS$_2$ and WSe$_2$, respectively. (C) Simulated and experimental images for the AA, AB$_{Se}$, Br, and AB$_{W}$ regions (from top to bottom). (D) Intensity profiles extracted from both simulation and experimental images. The black lines are simulation results along the white pathways in the left column of (C). Three experimental lines are displayed in difference colors with their pathways labeled correspondingly in the right column of (C).
**fig. S2. Intensity profile along AA-to-ABw in STEM images.** (A) and (B) are the experimental and simulated STEM images zoomed in on the AA-to-ABw region. (C) The corresponding schematic model of the atomic structure. (D) Intensity profiles along the pathways in (A) and (B). The blue and Red lines correspond to simulation and experiment, respectively.
fig. S3. First-principles calculations of the electronic structures of AB_{Se}, Br, and AB_{W}. (A to C) are results for AB_{Se}, Br and AB_{W} sites, respectively. Energy band structures are displayed in the left columns, while their corresponding density of states diagrams are shown in the right columns.
**fig. S4. Atomic model and the electronic structures of the Br$_2$ site.** (A) Atomic model of the Moiré supercell with R stacking. The typical sites are labeled as shown. The side views of Br and Br$_2$ are displayed in the corresponding insets. (B) Calculation results of the energy locations of key critical points for Br and Br$_2$. The energies are with respect to the vacuum level.
fig. S5. Statistical distributions of the $\Gamma^\text{W}$ energy locations. The analyses are based on multiple $dI/dV$ measurements on different heterobilayers flakes. The solid curves are normal distribution fittings.
### Table S1. Calculation results of the energy differences between key critical points.

Red columns represent the DFT results using the average lattice constant. Blue columns are the values after the strain corrections are included. The minor spin-orbit splitting in the conduction band is ignored here.

<table>
<thead>
<tr>
<th>Energy difference ΔE (eV)</th>
<th>AA</th>
<th>AB$_{Se}$</th>
<th>Br</th>
<th>AB$_{W}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{W\uparrow} - K_{W\downarrow}$</td>
<td>0.44</td>
<td>0.47</td>
<td>0.44</td>
<td>0.47</td>
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<tr>
<td>$K_{W\uparrow} - \Gamma_W$</td>
<td>0.59</td>
<td>0.39</td>
<td>0.33</td>
<td>0.13</td>
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<tr>
<td>$\Gamma_W - \Gamma_{Mo}$</td>
<td>0.41</td>
<td>0.67</td>
<td>0.62</td>
<td>0.88</td>
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<tr>
<td>$K_{W\uparrow} - K_{Mo\uparrow}$</td>
<td>1.08</td>
<td>0.901</td>
<td>0.96</td>
<td>0.79</td>
</tr>
<tr>
<td>CB: $Q_{Mo} - K_{Mo}$</td>
<td>0.41</td>
<td>0.13</td>
<td>0.40</td>
<td>0.11</td>
</tr>
</tbody>
</table>

[Uncorrected](#) [Corrected](#)