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Moiré-related in-gap states in a twisted MoS₂/graphite heterojunctionChun-I Lu^{1,2}, Christopher J. Butler¹, Jing-Kai Huang³, Yu-Hsun Chu¹, Hung-Hsiang Yang¹, Ching-Ming Wei³, Lain-Jong Li^{3,4} and Minn-Tsong Lin^{1,3}

This report presents a series of low-temperature (4.5 K) scanning tunneling microscopy and spectroscopy experimental results on monolayer MoS₂ deposited on highly oriented pyrolytic graphite using chemical vapor deposition. To reveal the detailed connection between atomic morphology and conductivity in twisted MoS₂/graphite heterojunctions, we employ high-sensitivity tunneling spectroscopy measurements by choosing a reduced tip-sample distance. We discern previously unobserved conductance peaks within the band gap range of MoS₂, and by comparing the tunneling spectra from MoS₂ grains of varying rotation with respect to the substrate, show that these features have small but non-negligible dependence on the moiré superstructure. Furthermore, within a single moiré supercell, atomically resolved tunneling spectroscopy measurements show that the spectra between the moiré high and low areas are also distinct. These in-gap states are shown to have an energy shift attributed to their local lattice strain, matching corresponding behavior of the conduction band edge, and we therefore infer that these features are intrinsic to the density of states, rather than experimental artifacts, and attribute them to the twisted stacking and local strain energy of the MoS₂/graphite heterointerface.

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INTRODUCTION

MoS₂ is a semiconducting member of transition metal dichalcogenide family of layered van der Waals materials.^{1–4} Monolayer MoS₂ has been shown to be obtainable from the bulk material by micro-exfoliation, similar to the derivation of graphene from the graphite bulk.⁵ Such van der Waals 2D materials can be stacked with each other to form vertical heterojunction devices or composite nanomaterials, under the rationale that each layer can be chosen for its distinct electronic properties, which will be retained in the heterostructure.⁶

It is therefore worthwhile to examine the interlayer interactions and their effects on the electronic structure of such 2D interfaces in order to better understand and design advanced heterojunctions. Regarding the basics of interlayer stacking, when two 2D lattices are overlaid, a lattice mismatch and/or an interlayer rotation leads to an additional periodic corrugation called a moiré pattern.⁷ The moiré corrugation can behave like a periodic electron localization,^{8, 9} giving rise to minibands, quantum well confinement,^{10–13} or other phenomena. For example, twisted bilayer graphene can exhibit an overlapping of Dirac cones, forming saddle points and resulting in a van Hove singularity that mediates enhancement of electronic phenomena such as the van der Waals interaction.^{14–18} Scanning tunneling microscopy and spectroscopy (STM/STS) are ideal tools for investigating such effects as they can be used to resolve the interaction between morphology and electronic structure at the atomic scale, as has been demonstrated for twisted bilayer graphene.^{12, 13, 19–21}

The heterojunction of twisted MoS₂ deposited on graphene or graphite is also noteworthy. The band profile and morphology

have been revealed in previous STM/STS investigations,^{22–26} and the opening of a band gap in graphene by overlaying a MoS₂ monolayer has been observed using angle-resolved photoemission spectroscopy.^{27, 28} However, the detailed connection between the atomic structure of the twisted heterojunction and the corresponding electronic structure is still lacking. Huang et al. have visualized the moiré patterns clearly, and also shown using STS that the MoS₂ band gap is tunable by the local strain field.²³ But the tunneling spectra from adjacent MoS₂ grains with a relative difference in twisting angle of 18°, and a corresponding difference in moiré patterns, show no significant difference. This is not as expected according to first-principles calculations, which predict that the band structure varies with the rotational angle of the twisted bilayer.^{29, 30} We suggest that typical STM set-point parameters as used by Huang et al., such as a current feedback set-point on the order of tens of pico-Amperes and a bias set-point far into the conduction band, chosen to reduce the influence of the tip's electric field,^{23, 31} may actually render the measurement insufficiently sensitive to potential moiré related interfacial phenomena. For a further discussion of the effects of different tip-sample distance, we present a series of tunneling spectra by using different set-points in the [Supplementary Information](#). (Please check the [Supplementary Information](#) online for further discussion of the influence of tip-sample distance on the observation of in-gap states).

In this work, we examine the effects of interlayer rotation on the MoS₂/graphite heterointerface, using STS measurements with increased sensitivity as compared to previous works, and focus on moiré dependent phenomena in the local density of states. In

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order to enhance the sensitivity of the dI/dV conductance signal, measurements were performed at 4.5 K and with feedback set-points corresponding to a relatively short tip-sample distance. We find small conductance peaks appearing within the original band gap range of MoS₂, and observe a variation of these peaks' intensity in two adjacent MoS₂ grains with differing moiré patterns. Furthermore, we observe that the peaks shift toward the Fermi level as the measurement position approaches a grain boundary, matching the previously reported shift of the conduction band, which was attributed to a local modification of the strain field. The peak intensities are shown to be distinct between the highs and lows within a moiré supercell, except in the case of large rotation angle, where the peaks have no location dependence, but shift slightly toward the Fermi level. In conclusion, we attribute behavior of these peaks to modification of the heterointerface's electronic structure by variations in the geometric stacking.

RESULTS

Figure 1a displays the boundary region where two adjacent monolayer MoS₂ grains of different orientations impinge on each other during growth. Figure 1b shows that each of the two grains exhibits a distinct moiré pattern. The image was calibrated by measuring the nearby bare HOPG surface, and moiré period was derived using a 2D fast Fourier transform (FFT). The moiré lattice constant is 1.11 ± 0.05 nm on the left side and 0.80 ± 0.05 nm on the right. The error bar is estimated according to the 2D FFT wavenumber resolution based on the scanning region of 40×40 nm² with pixel number 800×800 . The relative rotational angles between the top layer MoS₂ and the HOPG substrate are 1° and 14° for the left and right grains respectively, derived by measuring the lattice orientation of nearby bare substrate. The schematic diagram of the two grains' twisted stacking are illustrated in Fig. 1c. The supercell periodicities are determined by selecting a point of commensurate stacking (for example, of the S atom above a graphite on-top site, as shown), then shifting a distance to the nearest commensurate point. The supercells are each labeled as a black rhombus in Fig. 1c and are noted as R(37/61) and R(19/31) for the left and right regions, respectively. The notation R(37/61)

denotes that the top MoS₂ unit cell length of 0.315 nm multiplied by $\sqrt{37}$, and the bottom graphite unit cell length of 0.246 nm multiplied by $\sqrt{61}$, both exactly fulfill the supercell periodicity. The values 37 and 61 are the vector lengths composed by the vectors (4,3) and (5,4) in the hexagonal basis sets of the MoS₂ and graphite lattices.^{29, 32} Note that the actual supercell period is not necessarily equal to the apparent moiré pattern's period. Generally, adjacent apparent moiré peaks are seen to have a small difference upon close inspection, and a larger periodicity is necessary for finding another point of exactly commensurate stacking.²⁴

We performed a series of STS measurements in the vicinity of this intersection, using a measurement frame of size 40×8 nm² spanning the boundary. The frame consists of 200×40 pixels, each with one tunneling spectrum. Curves acquired on either side of the boundary shared the same physical condition of the tip apex, and the same set-point parameters. Figure 1d presents averaged tunneling spectra obtained in a 85 nm² region on each side, each separated by 2 nm from the boundary to avoid edge effects.²² We observe that the conduction band minimum (CBM) resides at 0.37 V for R(37/61) and at 0.34 V for R(19/31). This supports the experimental results in ref. 22: The formation of a vertical heterojunction between MoS₂ and the graphite represents an extrinsic modification of the MoS₂ CBM value.

In the negative bias range, peaks appear at -0.27 , -0.78 , and -1.48 V in the region to the left, and at -0.29 , -0.78 , and -1.44 V in the region to the right. The valence band maximum (VBM) of MoS₂ has been reported at around -1.8 V,^{22, 33} and a substantially shorter tip-sample distance is thought to lead to the apparent difference in the measurements presented here.³¹ Qualitatively, we can observe that the peaks appear inside the range normally considered to represent the band gap. The two regions represent identical MoS₂ overlayers covering an identical substrate but with different orientations, and the STS results show the small but not negligible difference in the electronic structure.

Figure 2 presents how these peaks behave near the grain boundary. We analyze the same STS data set of Fig. 1, but arrange the local conductance curves according to their lateral position. Figure 2a displays the tunneling spectra averaged over small regions at selected positions (with centers marked by stars on the

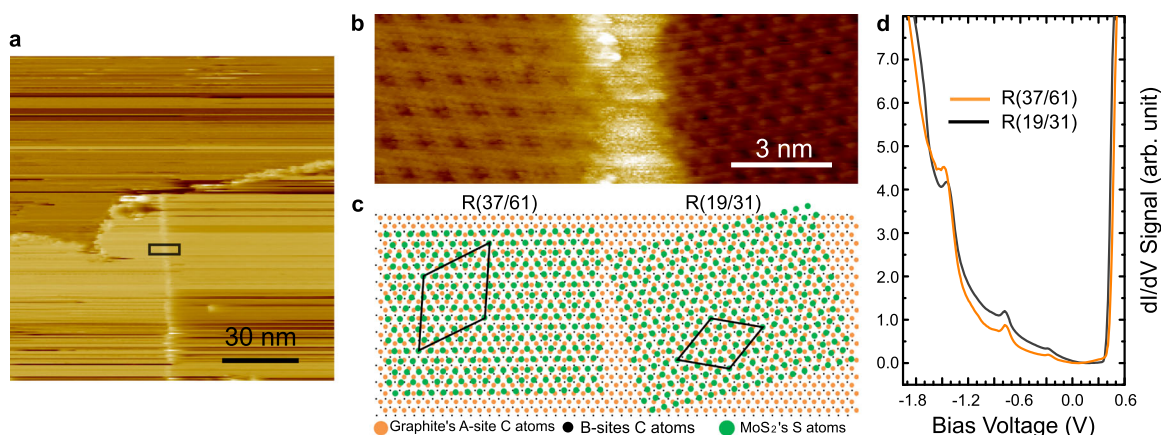


Fig. 1 Two moiré domains. **a** Large scale STM image ($V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 0.5$ nA) showing the position of the scanning range for **b**. **b** An atomically resolved STM image including two distinct moiré patterns on either side of a boundary ($V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 0.5$ nA). **c** Schematic representations of the two domains with rotational angles of 1° for the left side and 14° for the right side. For clarity, here we only draw the S atoms instead of the complete MoS₂ structure since only the lower S atoms are at the interface, and they occupy the same projected positions as the atomic peaks in the topography image. The superstructures determined for the left and right regions, each indicated by a black rhombus, are R(37/61) and R(19/31), respectively. **d** The averaged STS for the left and right regions. (Set point: $V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 0.5$ nA). The conductivity onset in the conduction band region is located at 0.37 V for R(37/61) and at 0.34 V for R(19/31). In the negative bias range, the peaks appear at -0.27 , -0.78 , and -1.48 V for R(37/61), and at -0.29 , -0.78 , and -1.44 V for R(19/31). The tunneling spectra reveal the difference in electronic structure between the R(37/61) and R(19/31) regions

accompanying topography image) along a path crossing the grain boundary, to visualize the position dependence. Each sampling area size is about 5 nm² and contains over 100 tunneling spectra. Here we focus on the evolution of the peaks in the negative bias

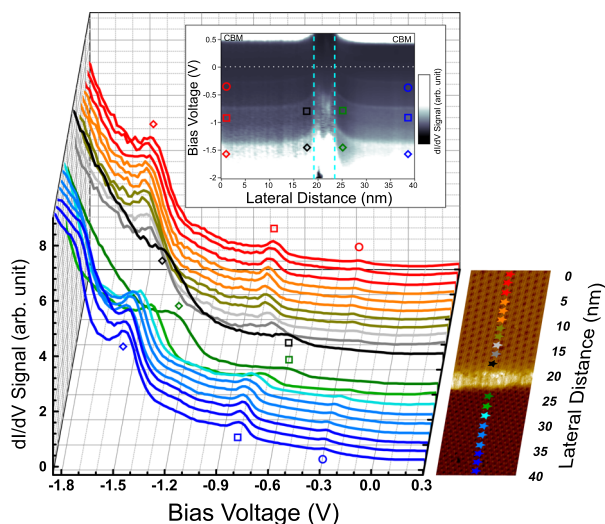


Fig. 2 Spatially resolved STS across the grain boundary. (Set point: $V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 0.5$ nA) The upper and lower parts are the R(37/61) and R(19/31) regions, respectively. The spectra show the energy shift of the peaks when the measurement point approaches the boundary. The inset displays the STS line profile. The aqua dashed line labels the boundary of contaminations and the white dashed line labels the Fermi level. The diamonds, squares, and circles represent the three peaks. We observe that the diamonds belonging to the R(19/31) region are shifted from -1.46 V (blue) to -1.28 V (green), and the squares are shifted from -0.78 V move to -0.62 V. For the circles, they shift from -0.29 to -0.22 V, but vanish very near the boundary (deep green curve). In the R(37/61) region, the diamonds are shifted from -1.49 V (red) to -1.34 V (black), and squares from -0.78 to -0.64 V. The circles shift from -0.29 to -0.22 V and also vanish near the boundary (black curve)

range. The inset is the STS line profile which shows the peaks' energy positions move toward the Fermi level and CBM move farther the Fermi level as the position approaches the boundary. According to previous reports, a similar behavior is observed for the CBM and VBM of MoS₂, and is attributed to the local strain field which can be altered by the grain boundary.^{23, 29} In our case, the same tendency can also be inferred for the in-gap peaks. The amount of the shifting reaches 0.16 and 0.21 V for the two lower energy peaks of R(19/31), 0.13 and 0.14 V for R(37/61). Note that the boundary's tunneling spectra are not shown here as such boundaries are covered by contaminations and the spectra are very different from those of the pristine MoS₂ regions. The contaminations are supposed to bond with MoS₂ tightly since MoS₂ has chemically active edges.^{34, 35} The adsorbates may shift the absorbents' electronic states due to the charge transfer between each other and that could be detected by STS.³⁶ However, this kind of influence should be in a short range. For example, the nitrogen-doped epitaxial graphene case shows that the nitrogen influences only the surrounding atoms.³⁷ In this work, all spectra in this manuscript, were obtained at least 2 nm from the edge in order to avoid the mixed the effects of the contaminations and the lattice strain.

We are also interested in how the electronic structure varies within a single moiré superstructure cell. Figure 3a shows a zoom-in STM topography image of the R(37/61) superstructure region, which is shown at the left side of Fig. 1. The black and red circles label the moiré pattern's higher (H) and lower (L) areas. The line profile in Fig. 3b shows that the apparent height corrugation was measured to be approximately 12 pm. Furthermore, we extracted the tunneling spectra of the R(37/61) area from the STS measurement of Fig. 1, and classified them into two groups: Those from moiré H areas and L areas. In Fig. 3c, each curve is averaged over about 60 spectra from H or L areas. We observe that the shapes of the black and red curves are almost identical except at the two bias voltages -1.48 and -0.78 V, where the peaks of the L areas have a larger signal than those of the H areas. This phenomenon implies that the two states are intimately related to the details of stacking and strain in the moiré structure.

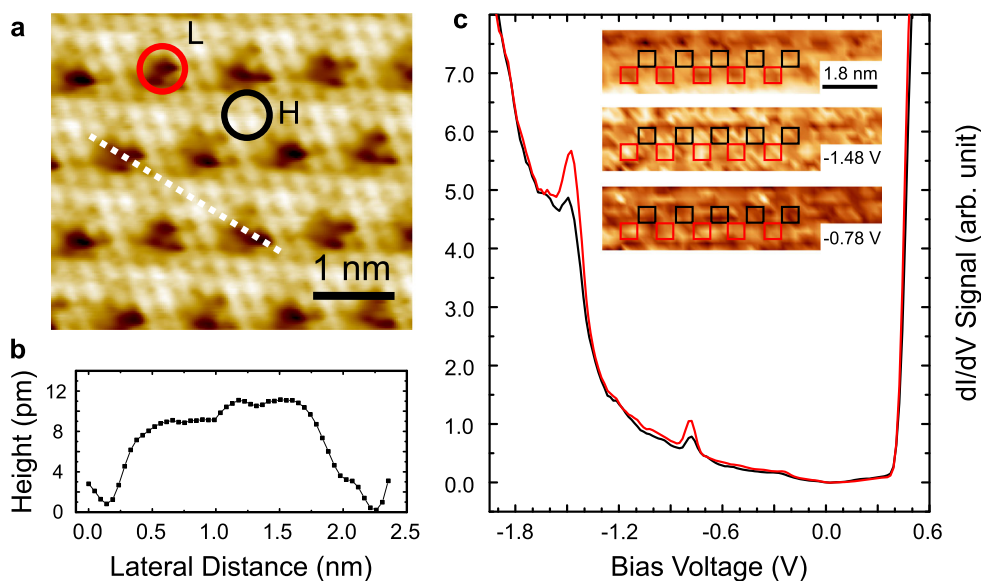


Fig. 3 Moiré high and moiré low regions. **a** An STM image of the R(37/61) region shown on the left side of Fig. 1 ($V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 0.5$ nA). The black and red circles are label examples of high (H) and low (L) points of the moiré pattern. The dashed white line shows an apparent height corrugation of 12 pm over one period of the moiré pattern. **b** The height profile following the dashed white line. **c** The STS curves averaged over H and L areas are distinct. The red and black curves were averaged from the corresponding rectangular areas shown in the first inset and each rectangle includes around ten spectra. The second and third insets present the dI/dV conductance mapping at each in-gap peak's energy, -1.48 and -0.78 V. (The spectra are zoom-in of Fig. 2.)

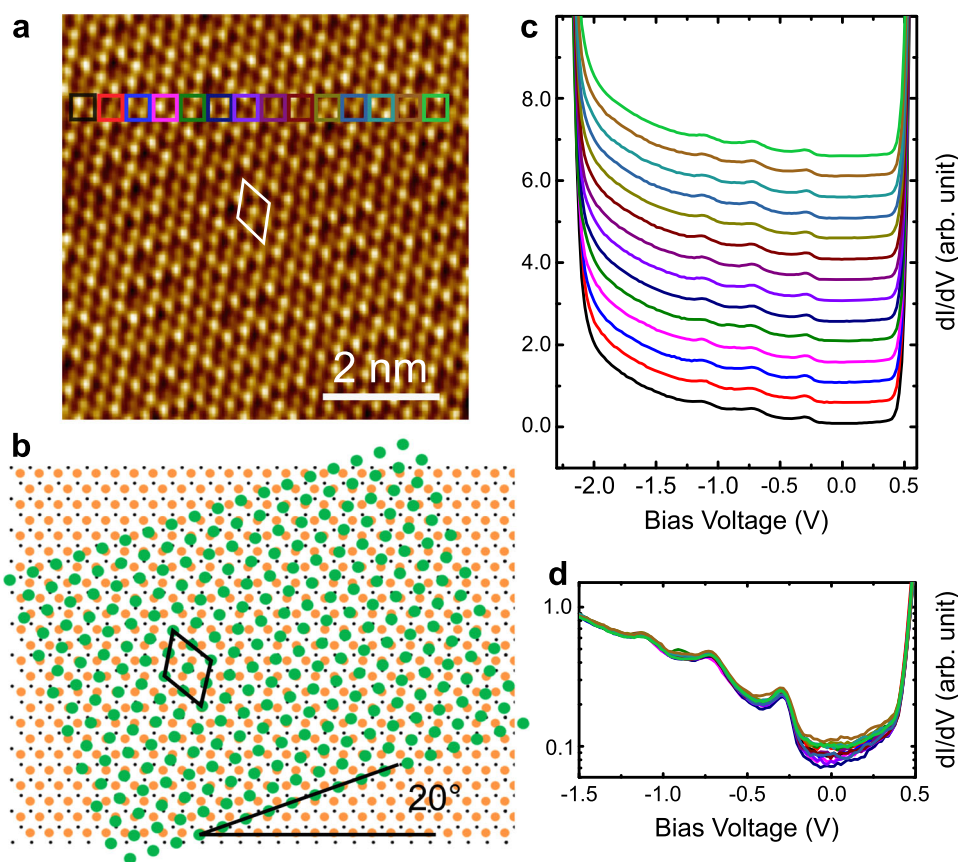


Fig. 4 Large-angle overlaps. **a** The STM topography of monolayer MoS₂ with a 20° rotation angle with respect to the HOPG substrate (Set point: $V_{\text{bias}} = -1$ V, $I_{\text{set}} = 1$ nA). **b** Ball model illustrating the 20° rotated case. The black rhombus labels the moiré superstructure period of the R(4/7) superlattice. **c** The STS curves of the corresponding colored area. The curves are vertically offset for presentation. The set point was: $V_{\text{bias}} = -1$ V, $I_{\text{set}} = 1$ nA, and the lock-in modulation was $V_{\text{mod}} = 30$ mV. **d** The Zoom-in view of the spectra in **c**, with the dI/dV signal displayed on a logarithmic scale. The peak positions are -0.29 , -0.71 , and -1.11 V, and the CBM is at 0.46 V

Figure 4 presents another case, exhibiting a larger interlayer rotational angle of about 20°, with respect to the lattice of the nearby bare HOPG surface. This case is rare since the rotational angles of CVD grown MoS₂ on HOPG, tend to be small.^{23–26} The corresponding ball model is drawn in Fig. 4b. The black rhombus labels the supercell, which is determined in the same way as that shown in Fig. 1c. The supercell period can be composited by an upper sulfur basis with hexagonal vectors (2,0) and (1,2) in the basis of the underlying carbon array. Hence, this case can be labeled as R(4/7). The average over 100 STS curves for each corresponding local area are shown in Fig. 4c. Figure 4d is a further zoom-in view of the band gap region. The peaks appear at -0.29 , -0.71 , and -1.11 V, and the CBM is at 0.46 V. The theoretical band structure of the R(4/7) case has also been investigated by Wang et al. (in which it is denoted as $\sqrt{7}:4$). By comparing the distance between the CBM and the peaks in Fig. 4d and the calculated total density of states in ref. 29, the magnitudes of 1.17 V (0.46 to -0.71 V) and 1.57 V (0.46 to -1.11 V), agree with the values of 1.28 V (CBM to Γ point) and 1.53 V (CBM to K point) in the reference. Also, the small feature in the DFT result, which is in the middle of band gap (below 0.7 V of the CBM), matches our data's first peak which is also below 0.75 V of the CBM (0.46 to -0.29 V) reasonably well. On the other hand, we do not see any position dependence of the tunneling spectra, even in the range of bias near 0 V in Fig. 4d. We suggest this could be explained by the possible decoupling of the top layer from the bottom layer due to the large rotational angle, a phenomenon which is well known in the twisted bilayer graphene system.¹²

DISCUSSION AND CONCLUSION

As compared to previous STM investigations on the MoS₂/HOPG system, we use a shorter tip-sample distance to yield increased sensitivity to anticipated moiré dependent phenomena. Such a reduced tip-sample distance could in principle lead to a tip-induced electric field, which plays a critical role in STM measurements on semiconductor surfaces. Dombrowski et al. demonstrated that the tip-induced band bending (TIBB) effect can induce a quantum dot and create new states within the band gap of semiconductors such as InAs during STS measurements.³⁸ These quantum states were shown to reside within -0.1 V to several tens of mV of the conduction band edge, from which they effectively split off while the tip bias voltage is negative. The states appearing in our measurements are removed from the conduction band edge by a considerably larger margin. Furthermore, although MoS₂ is a semiconductor, the TIBB effect is probably suppressed in the MoS₂/HOPG system as compared to typical bulk semiconductor materials, due to strong screening from the metallic substrate.³⁹ Therefore the TIBB effect can not adequately explain our result. The peaks we observe might be attributable to an intrinsic property of the system, rather than an artificial effect of the tip.

The mechanism of observing moiré patterns by using STM does not only involve the top layer, but the process of three-dimensional tunneling, including from buried layers.⁴⁰ In our experience, the underlying HOPG substrate can be imaged directly, by using an atypically large set-point current of 50 nA.²⁴ Thus, not only the surface's information, but also that of the underlying layer can be detected using STM.³¹ On the other hand,

first-principles investigations have revealed that there may be a weak but clear charge redistribution in the space between MoS₂ and graphene.^{29, 30} In view of the above, we suppose that the newly found peaks are the emergent electronic states associated with the charge distribution in the interlayer space, which can be probed through tunneling channels made accessible by using the shorter tip-sample distance. However, this suggestion can still benefit from further investigation, and to the best of our knowledge, there are, as of yet, no reports focusing on the interlayer charge distribution.

Examining these peaks' bias position, we observe that the three peaks for R(4/7) are shifted toward the Fermi level relative to those discussed above. This implies a relation between the coupling strength between the MoS₂ over-layer and substrate, and the associated lattice strain field, also related to the lattice mismatch. The lattice mismatch between MoS₂ and HOPG can be defined using the simple formula $f = \frac{a_s - a_e}{a_e}$, where a_s and a_e are the lattice constant of the substrate and the over-layer, respectively.⁴¹ In the MoS₂/HOPG case, the mismatch is quite large: $(0.246 - 0.315 \text{ nm}) / 0.315 \text{ nm} = 22\%$. However, the strain energy could be reduced by skewed stacking the MoS₂ and HOPG. For the 1° rotation case, resulting in a R(37/61) superlattice, the mismatch $f = (\sqrt{61} \times 0.246 - \sqrt{37} \times 0.315) / \sqrt{37} \times 0.315 = 0.26\%$. Similarly, for R(19/31), $f = -0.22\%$ and for R(4/7) $f = 3.3\%$.⁴² Regarding the conclusion made by Huang et al., the lattice strain energy shifts the VBM toward the Fermi level and the CBM further upwards.²³ In this sense, this could explain why the peak positions of the R(37/61) and R(19/31) cases are similar to each other, but different from the R(4/7) case, due to the strain associated with lattice mismatch.

In conclusion, we discover small previously unobserved in-gap states emerging at the twisted MoS₂/HOPG heterointerface. These peaks exhibit an energy shift where the lattice strain field changes approaching a grain boundary. Moreover, within a single moiré supercell, the spectra change between moiré high- and low-points. These in-gap states we found are intrinsic, reproducible, and comparable with DFT calculations. With reference to previous theoretical investigations of the MoS₂/graphene heterojunction, we suggest that these emergent states are intrinsic to the MoS₂/graphene interface, and may derive from interlayer charges. This finding provides insights for the design of 2D material heterojunctions, highlighting stacking and strain engineering as methods for electronic structure modification.

METHODS

Sample preparation

Monolayer MoS₂ islands were prepared on highly oriented pyrolytic graphite (HOPG) using the chemical vapor deposition (CVD) method described previously by Lee et al.⁴³ The HOPG crystal was purchased from SPI Supplies, 10 × 10 × 2 mm, SPI Grade 1. MoO₃ (99%, Aldrich) and S powder (99.5%, Alfa Aesar) reactants were placed in a nitrogen environment. The MoO₃ powder was reduced to a volatile suboxide MoO_{3-x} by the sulfur vapor. The CVD chamber was heated to 650 °C, such that the MoO_{3-x} molecules diffused on to the HOPG surface, acquired sulfur atoms from the vapor, and were then deposited on the surface. After deposition in the CVD chamber, the samples were quickly transferred in atmosphere to an ultrahigh-vacuum system for STM measurements. To maintain the thin film's orientation, the sample was directly transferred to the low-temperature STM stage without any heat treatment.

STM measurements

STM measurements were performed at a temperature of 4.5 K, using an electrochemically etched tungsten tip within commercial LT STM from Scienta Omicron. Atomic lattice unit cells and moiré supercells were determined from atomically resolved STM images as follows: The STM images were calibrated using the ideal HOPG lattice as a reference. The dI/dV spectroscopy signal was derived using the lock-in technique by applying a modulation voltage, $V_{mod} = 15 \text{ meV}$, whose

frequency was chosen to be higher than 1 kHz to avoid triggering the feedback loop. The tip was stabilized using a set-point parameters corresponding to a tunnel resistance of 1 GΩ, after which the dI/dV intensity was recorded as a function of bias voltage with the feedback loop open. The energy resolution of dI/dV measurements, determined as the modulation voltage used in the lock-in technique, was 15 mV unless specifically noted otherwise. STM images were processed using the Scanning Probe Image Processor Ver. 4.6.5 and WSxM Ver. 4.0 Beta software packages.⁴⁴

Data availability

All relevant data are available from the authors. Requests for data and materials should be addressed to M.-T. Lin.

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AUTHOR CONTRIBUTIONS

C.-I.L. performed STM and STS with assistance from C.J.B., Y.-H.C. and H.-H.Y. The data analysis was performed by C.-I.L. and discussed in depth with C.J.B., Y.-H.C. and M.-T.L. The monolayer MoS₂ was grown by J.-K.H. under supervision of L.-J.L. The theoretical support was provided by C.-M.W. The manuscript was prepared by C.-I.L. and M.-T.L. with assistance from C.J.B. and Y.-H.C. This project was conceived and led by M.-T.L.

ADDITIONAL INFORMATION

Supplementary Information accompanies the paper on the *npj 2D Materials and Applications* website (doi:10.1038/s41699-017-0030-6).

Competing Interests: The authors declare no competing financial interests.

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