Moiré induced electronic structure in monolayer V$_2$S$_3$ on Au(111)

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There is immense interest in how the local environment influences the electronic structure of materials at the single layer limit. We characterize moiré induced spatial variations in the electronic structure of in-situ grown monolayer V$_2$S$_3$ on Au(111) by means of low temperature scanning tunneling microscopy and spectroscopy. We observe a long-range modulation of the integrated local density of states (LDOS), and quantify this modulation with respect to the moiré superstructure for multiple orientations of the monolayer with respect to the substrate. Scanning tunneling spectroscopy reveals a prominent peak in the LDOS, which is shifted in energy at different points of the moiré superstructure. Comparing ab initio calculations with angle-resolved photoemission, we are able to attribute this peak to bands that exhibit out-of-plane $d$-orbital character. We further identify an instability wave vector in the calculated electronic susceptibility of the free-standing layer, that coincides with a higher-order Fourier component of the moiré superstructure, suggesting the possibility of a complex interplay between the moiré superstructure, electronic structure and electronic instabilities in this material system.
Moiré superstructures, constructed from van der Waals (vdW) monolayers like graphene, have emerged as a tunable platform to artificially create novel quantum states of matter [1-5]. As demonstrated in monolayer graphene, moiré interference can lead to long-range structural and electronic modulations, which can be imaged with scanning tunneling microscopy/spectroscopy (STM/STS) and low energy electron diffraction (LEED) [6,7]. Such moiré superstructures for monolayer graphene lead to various modifications of the band structure [8], such as the minigap and replica band features observed in angle-resolved photoemission spectroscopy (ARPES) [9]. The moiré superstructure and its associated structural/electronic modifications can be quenched by decoupling the monolayer via intercalation, leading to quasi-free-standing electronic structure [10,11]. As the family of tunable moiré materials grows [12-15], it is important to understand how moiré superstructures modify the structural, electronic, and magnetic properties of vdW monolayers at the atomic length scale.

One class of vdW materials, transition metal dichalcogenides (TMDs), have been synthesized at the monolayer limit on various surfaces that lead to moiré superstructures [16-22]. In the case of TMDs grown on metallic surfaces, strong interactions with the substrate, typically resulting from hybridization and modified charge screening, lead to pronounced modifications in the electronic structure [23,24]. For the MoS$_2$ monolayer on Au(111), these strong interactions lead to a renormalization of the band gap [22,25,26] when compared to the quasi-free-standing case [27]. Similarly, for the TaS$_2$ monolayer grown on Au(111), interactions with the underlying substrate suppress the expected charge density wave (CDW) phase [16,23,28], which can remain robust in TaS$_2$ monolayers prepared on other substrates [29]. Yet, for many TMD monolayers where the moiré superstructure shows strong signatures in STM and LEED, the moiré superstructure minimally perturbs the band structure seen in ARPES [16,17]. Because many TMD monolayers show non-trivial electronic phases [29-31], it is important to study how long-range structural and electronic modifications induced by moiré superstructures modify the electronic structure.

Here, we study the structural and electronic properties of monolayer V$_2$S$_3$ on Au(111) to quantify the interplay between the moiré superstructure, the geometrical structure, and the electronic structure. Utilizing scanning tunneling microscopy and spectroscopy (STM/STS), we observe well-defined, long-range modulations in constant-current imaging, i.e. the integrated density of states, reminiscent of a
CDW. By investigating monolayer domains with varying rotation angle with respect to the Au(111) substrate, we confirm the persistence of these real-space modulations at all observed angles. Using detailed structural moiré simulations, we capture these modulations by considering higher-order wave vectors from the atomic lattice. Concomitantly, we use STS to identify a strong peak-like feature in the LDOS near $E_F$, reminiscent of a flat band feature, which shifts in energy depending on the location within the moiré unit cell. In order to identify the peak seen in STS, we computed the band structure within density functional theory (DFT). The band structure measured with ARPES was used to calibrate the effective doping. The calibration of the DFT Fermi level using ARPES allowed us to link the peak in the LDOS with the onset of weakly dispersing bands arising from the intrinsic V$_2$S$_3$ monolayer, with predominantly $d_{yz}$ orbital character. We suggest that the out-of-plane orbital character of the V$_2$S$_3$ bands enables them to couple to the structural modulations of the moiré superstructure, inducing the observed spatial variations in the electronic structure. We further predict the tendency of the monolayer toward CDW, by calculating the electronic susceptibility of the free-standing monolayer V$_2$S$_3$. A pronounced peak in the electronic susceptibility is observed in the vicinity of the experimental reciprocal space features of the moiré superstructure. This further hints at a possible interplay between intrinsic electronic instabilities of the monolayer and the moiré superstructure.

We grew the recently discovered vanadium sulfide monolayer V$_2$S$_3$ on Au(111) by in-situ e-beam evaporation according to the method previously reported [32] (see Supplemental Material [33]). STM/STS measurements were carried out in a home-built UHV-STM facility operating at a base temperature of $T = 1.3$ K, with the capability of applying magnetic field $B$ up to 9 T perpendicular to the sample surface [34]. ARPES measurements were acquired on samples prepared by the same growth procedure, at a temperature of $T = 35$ K and using a photon energy of 94 eV. The measurements were performed at the SGM3 endstation of the ASTRID2 synchrotron light source in Aarhus, Denmark (optimal energy resolution on beamline better than 40 meV, and angular resolution for ARPES measurements better than 0.2°) [35]. The DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code [36,37] (see Supplemental Material for additional details [33]).

Characterization of the atomic structure of the V$_2$S$_3$ monolayer is shown in Fig. 1 using high-resolution constant-current imaging. A two-fold symmetric structure of the top-layer S atoms is visible; within this layer, the S atoms form a rectangular unit cell $(a, b)$ with two S (red and gray atoms in Fig. 1d) atoms
along $\mathbf{b}$, while the bottom S layer (pink atoms in Fig. 1(d)) maintains a configuration similar to that of VS$_2$. The atomically resolved constant-current image in Fig. 1(c) reveals a unit cell with lattice constants $|a| = 0.31\pm0.03$ nm and $|b| = 0.87\pm0.03$ nm. The unit cell of the V$_2$S$_3$ is indicated with a dashed green rectangle in Fig. 1(c), which is consistent with the model in Fig. 1(d), determined using room-temperature STM and X-ray photoelectron diffraction [32].

Concurrently with the atomic structure, additional longer-range modulations can be seen in constant-current imaging. Examining a fast Fourier transform (FFT) of the image in Fig. 1(a) (Fig. 1(b)), we observe many well-defined peaks corresponding to long-range features observed in real space (for reference, the reciprocal space points of the atomic lattice are highlighted by green circles). In constant-current images, a weaker moiré superstructure is observed than has been seen in TMD layers grown on Au(111) [16,22]; the symmetry is modified from that of VS$_2$/Au(111) moiré [32]. We label the first-order features in reciprocal space, namely, the largest real-space periodicities, $A$, $B$ and $B'$. In addition to these features, we also observe periodic modulations in constant-current imaging with characteristic real-space length scales longer than the atomic lattice, yet smaller than the moiré lattice. These multiple higher-order features are also visible in the FFT, two of which we label C and D (comprised of linear combinations of $A$, $B$, and $B'$). While higher order features related to the moiré superstructure are often visible in LEED for families of sulfide-based TMDs grown on Au(111), there are commonly no strong indications of such higher order features in STM measurements compared to what is observed here [16]. Yet for V$_2$S$_3$ on Au(111), LEED measurements were not able to identify a moiré superstructure or any related higher-order features [32].

To further study these observed higher order features, we characterized different orientations of the V$_2$S$_3$ layer with respect to the substrate using atomic resolution imaging. In Fig. 2(a), the stacking angle between $a$ and the $<110>$ directions of Au(111) is $\theta = 0^\circ$, measured by comparing the atomic lattice of V$_2$S$_3$ with the herringbone reconstruction of underlying Au(111). Two other monolayer islands with measured rotation angles of $\theta = 1.3^\circ \pm 0.5^\circ$ and $\theta = 4.2^\circ \pm 1^\circ$ are shown in Fig. 2(b, c). Approximately 80% of the observed V$_2$S$_3$ islands were aligned with the stacking angle of $\theta = 0^\circ$ (forming three rotational domains at 120° with respect to each other consistent with the three-fold symmetry of the Au(111) substrate), indicating that there is a preferred growth orientation for the V$_2$S$_3$ monolayer on Au(111)
(see Supplemental Material, Fig. S2 [33]). As seen in the FFTs in Fig. 2(d-f), both the moiré superstructure and the higher-order features are also present in the misaligned cases.

To understand the origin of the observed higher-order features and how these features relate to the geometrical influence of the moiré superstructure, we simulated the expected moiré superstructures by representing the top S layer of V₂S₃ and the topmost Au(111) layer as sinusoidal functions, and multiplying them using a rotation angle defined as the angle between a and <110> [38]. We used higher-order sinusoidal functions for each lattice to visualize all the possible higher-order moiré modes (see the Supplemental Material for details [33]). The resulting FFT of the simulations and their corresponding real space data are shown in Fig. 2 (g-i) for each observed moiré superstructure. Our simulations successfully reproduce all of the reciprocal space features for the θ = 0° moiré superstructure, as well as nearly all the features in the rotated cases when we include higher-order functions for both V₂S₃ and Au(111) (Fig. 2g). Thus, we can confirm that the longer-range features observed in constant-current imaging stem from structural variations in the film.

To study local modifications in the electronic structure, we performed STS at different positions within the moiré superstructure (Fig. 3). A signature of the V₂S₃ monolayer is a distinct peak near the Fermi energy. We observe that the energetic position of this peak strongly varies depending on the spatial location within the moiré superstructure, as seen in dI/dV spectra taken on the apparent moiré minima (light blue) and apparent moiré maxima (dark blue) in Fig. 3. This can also be seen in spatially dependent maps of the differential conductance near the Fermi energy, leading to complex LDOS patterns (Fig. S3). In comparison, peak-like features seen in the LDOS for TaS₂/Au(111) do not show significant shifts in energy within the moiré superstructure [23]. On the other hand, moiré induced modifications to the LDOS were observed in monolayer MoS₂ on Au(111), in particular energy ranges, which the authors attributed to possible differences in hybridization or electronic screening [39]. We suggest that the shifts in energy of the LDOS peak-like feature (Fig. 3 and Fig. S3) may result from different hybridization strengths associated with the orbital character of the bands in this energy range; as shown in Fig. S4 [33], the orbital character contains an out-of-plane component that may be sensitive to the variations in interlayer distance between the monolayer and the substrate.

To elucidate the electronic properties of the system, including the origin of the observed peak in the LDOS, we performed DFT calculations of the free-standing monolayer V₂S₃. In Fig. 4(a), we show both
the calculated band structure along the high-symmetry path indicated in the inset and the total DOS (Fig. 4(b)) of the free-standing monolayer V\(_2\)S\(_3\). In order to account for the doping induced by the substrate, we calibrated the calculated Fermi energy by assuming a rigid offset of approximately 200 meV in the calculated bands (orange line labelled \(E_F\) (Exp) in Fig. 4(a)) to reproduce both the band dispersion (Fig. 4(c)) and Fermi contour (FC) measured with ARPES (Fig. 4(d)). The comparison between the ARPES FC and the theoretical FC (including three 120° rotations corresponding to the three experimental domain rotations) with this offset Fermi level (\(E_F\) (Exp)) is shown in Fig. 4(d). The photoemission process is highly dependent on matrix elements; thus, not all features predicted by theory are visible in the ARPES data. However, the main qualitative features of the FC, such as its flower-like shape, are clearly captured by the DFT calculations.

Comparing the calculated total DOS (Fig. 4b) to the observed peak in STS (Fig. 3), we find good agreement between theory and experiment. The calculated DOS of the native monolayer in Fig. 4(b) contains sharp features approximately 100 meV below the shifted Fermi level; these features are relatively close to the energy of the peak observed in \(dl/dV\) measurements (80 ± 3 mV) on the apparent moiré maxima in Fig. 3. To understand the orbital texture of the bands contributing to the calculated DOS features approximately 100 meV below \(E_F\) (Exp), we projected the total DOS onto the vanadium \(d\)-orbitals (see Supplemental Material, Fig. S4 [33]). From this decomposition, it is clear that the peaks in the total DOS at this energy can be attributed mainly to states with \(d_{yz}\) orbital character. We suggest that the out-of-plane orbital character makes the bands more susceptible to influence from the physical corrugation of the monolayer due to the moiré superstructure; in this case, the moiré superstructure can modify the hybridization of the monolayer bands with the substrate by varying the interlayer distance, resulting in the observed shift in the peak position in Fig. 3. As this behavior was also observed on misaligned moiré superstructures (Fig. 3(b)), it appears to be related to the physical corrugation of the monolayer.

To investigate the propensity of the free-standing monolayer toward CDW phases, we calculated the electronic susceptibility \(\chi(q)\), as peaks in its real part \(\chi'(q)\) are often associated with structural instabilities. The results of our calculations are summarized in Fig. 5, where each column corresponds to a different energy with respect to \(E_F\) (Exp). The top panels in Fig. 5(a-e) show the evolution of the FC
(the colors of the iso-energy lines are consistent with the colors of the bands shown in Fig. 4(a)). The corresponding evolution of $\chi'(q)$ is shown in the bottom panels in Fig. 5(f-j).

It is clear that $\chi'(q)$ is very sensitive to the position of the Fermi level (Fig. 5). The electronic susceptibility $\chi'(q)$ calculated at $E_F$ (Exp) (Fig. 5(h)) displays a pronounced peak very close to one of the second-order points of the $\theta = 0^\circ$ moiré superstructure (indicated as the D-point in Fig. 5 and in Fig. 1). The peak is pronounced only in a narrow energy window near $E_F$ (Exp). As these calculations only account for the free-standing monolayer; possible modifications in the band structure induced by the moiré superstructure or hybridization with the substrate, might yield considerable changes in the electronic susceptibility. In particular, as discussed in Ref. [23], the presence of pseudodoping can modulate the effective interaction terms inside the hybridized bands, which may suppress the instabilities expected in free-standing layers.

We subsequently discuss the potential role of CDWs and magnetism in this material, as they have been observed in other V-based TMDs [40-44] and predicted in VS$_2$ [45-47]. At temperatures down to 1.3 K, the enhanced DOS peak near $E_F$ is consistently observed, in contrast with common expectations of a minimum in the DOS near the Fermi level in CDW systems. Yet, conclusive STM characterization of V$_2$S$_3$ monolayer in the context of CDW order can only be achieved with temperature dependent measurements. Furthermore, contrary to expectations for magnetic order in vanadium-based TMD compounds [44,46,47], neither spin-polarized signal nor apparent changes in the LDOS were detected in magnetic fields up to 7 T.

In conclusion, we studied the electronic structure of monolayer V$_2$S$_3$ grown on Au(111). Constant-current imaging revealed long-range modulations persistent at various rotation angles; as these modulations were captured in moiré simulations, they were attributed to higher-order modes from the moiré superstructure. Tunneling spectroscopy revealed a strong peak feature in the LDOS near $E_F$, whose energy varied depending on the position within the moiré superstructure. Using ARPES, in conjunction with DFT calculations, we were able to relate the observed peak in STS to V$_2$S$_3$ bands with hybridization effects mainly due to the $d_{yz}$ orbitals. We suggest that the moiré induced modulation of this peak could be due to coupling between the out-of-plane band character and the physical moiré corrugation. We further showed a pronounced peak in the electronic susceptibility of the free-standing monolayer V$_2$S$_3$ very close to one of the second-order reciprocal space points of the $\theta = 0^\circ$ moiré
superstructure observed in STM experiments. Future measurements on the temperature dependent evolution of the system could provide valuable insight into the interplay between the moiré modulated electronic structure and electronic instabilities in this monolayer material.

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FIG. 1. (Color Online) (a) Large scale constant-current STM image of the surface, illustrating the two-fold symmetric atomic lattice of top S atoms, as well as a moiré superstructure caused by the lattice mismatch between $V_2S_3$ monolayer and Au(111) substrate ($V_s = 1$ V, $I_t = 40$ nA, $T = 1.3$ K, scale bar = 3 nm). (b) Corresponding FFT of the image in (a) (scale bar = 10 nm$^{-1}$), with a close-up view of the center (scale bar = 10 nm$^{-1}$). Green circles in the FFT images highlight the reciprocal lattice points of the atomic lattice; the corresponding real-space unit is drawn in (c). (c) Atomically resolved constant-current image of ML $V_2S_3$ revealing the atomic unit cell ($V_s = 3$ mV, $I_t = 1$ nA, $T = 1.3$ K, scale bar = 300 pm). (d) Structural model of ML $V_2S_3$/Au(111) (adapted from [32]).
FIG. 2. (Color Online) (a-c) Atomically resolved constant-current STM images showing identical atomic lattices with different moiré structures resulting from different rotation angles between the V$_2$S$_3$ layer and Au(111) substrate ($\theta = 0^\circ$, 1.3$^\circ$, and 4.2$^\circ$ with respect to <110>) ($V_s = 1$ V, $I_t = 40$ nA, $T = 1.3$ K, scale bar = 3 nm). (d-f) FFTs of the respective images in (a-c) (scale bar = 10 nm$^{-1}$). (g-i) FFTs of simulated moiré images with the same scale bar. Insets show the simulations in real space (scale bar = 2 nm). Green circles highlight the reciprocal lattice points of V$_2$S$_3$. 
FIG. 3. (Color Online) $dI/dV$ spectra acquired at different positions (indicated in blue in the insets) of the moiré superstructure of monolayer $V_2S_3$ on Au(111), for (a) $\theta = 0^\circ$ and (b) $\theta = 1.3^\circ$. The peak in the $dI/dV$ is observed at all probed positions of the moiré unit cell, but with variations in energy. The surface state of Au(111) is shown for reference (gray). (Stabilization bias ($V_{\text{stab}}$) = 1.5 V, stabilization current ($I_{\text{stab}}$) = 600 pA, modulation bias ($V_{\text{mod}}$) = 1 mV, $T = 1.3$ K; insets: $V_s = 1$ V, $I = 40$ nA, $T = 1.3$ K, scale bar = 1 nm).
FIG. 4. (Color Online) (a) Band structure of V$_2$S$_3$ along the high-symmetry path shown in the inset. The black dashed line indicates the DFT Fermi energy, while the Fermi energy determined by comparison with the ARPES measurements is marked by an orange dashed line. (b) Total density of states (DOS). (c) Comparison of the band dispersion around Γ measured by ARPES with DFT. Yellow dashed line illustrates the surface state of Au(111). (d) Fermi contour calculated from DFT taking into account the three rotational domains, in comparison with the ARPES measurements (scale bar = 5 nm$^{-1}$).
FIG. 5. (Color Online) (a-e) Fermi contour of free-standing monolayer $V_2S_3$ calculated with DFT assuming different energy cuts with respect to the Fermi energy. The reference Fermi energy indicated at the top of the figure refers to the value determined experimentally, see the orange dashed line in Fig. 4. The colors of the FC lines correspond to the bands shown in Fig. 4. (f-j) Electronic susceptibility (Lindhard function) calculated for the Fermi energies indicated at the top of the figure. The color scale is constructed with the average value of $\chi'(q)$ in each panel corresponding to the center of the scale. The origin of the instability vector $q$ is assumed to be at the corners. The black dots correspond to the reciprocal-space points indicated in Fig. 1. All panels show the first BZ.
Supplemental Material

Moiré induced electronic structure in monolayer V₂S₃ on Au(111)

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**Methods**

STM/STS measurements were performed under ultrahigh vacuum conditions with home-built low-temperature setup, operating at a base temperature of 1.3 K and 4.2 K, with the capability of applying a magnetic field perpendicular to the surface up to 9 T [1]. All STM images in the main text and supplemental material were acquired by using constant-current feedback with the bias applied to the sample ($V_s$). Electrochemically etched tungsten (W) tips were used after *in-situ* treatment by electron bombardment. $dI/dV$ measurements were performed using a lock-in technique with a modulation bias ($V_{mod}$) of 5 mV at a frequency ($f_{mod}$) of 880 Hz added to the bias signal. Fast Fourier transforms of the real space STM images were calculated using MATLAB software. All the FFT images shown in this study have minimum 0.41 nm$^{-1}$/pixel resolution.

The DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) code [2,3]. The exchange–correlation potentials were described through the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) formalism [4]. A plane wave basis set was used with a cutoff energy of 400 eV on a 7 x 21 Monkhorst-Pack $k$-point mesh [5]. Lattice constants reported by Arnold *et.al* [6] was used as the reference and was modified less than 10% to achieve a commensurate moiré lattice with the Au(111) substrate. A vacuum region of 25 Å along the z direction was used in order to minimize the interaction between the periodic repetitions of the cell. Within the so-called “constant matrix element approximation” [7,8] $\chi'(q)$ is given by:

$$\chi'(q) = \sum_k \frac{f(\epsilon_k) - f(\epsilon_{k+q})}{\epsilon_k - \epsilon_{k+q}}$$

(often referred to as the Lindhard function), where $k$ belongs to the BZ, $q$ is a generic reciprocal-space vector, $f$ is the Fermi function and $\epsilon_k$ is the band energy.

**Sample preparation**

$V_2S_3$ samples were prepared *in-situ* by the method described in [6]. A clean Au(111) surface was first prepared by sputtering Ar+ (1.5 kV) ions and subsequent annealing at 600ºC. Vanadium was then deposited by e-beam evaporation onto the substrate, which was held at room temperature. Following the
deposition, the sample was annealed to $T = 450^\circ$C in an atmosphere of $p = 5 \times 10^{-5}$-mbar H$_2$S partial pressure, yielding monolayer VS$_2$. V$_2$S$_3$ was then obtained by annealing the VS$_2$ to $T = 600$ $^\circ$C at $p < 1 \times 10^{-9}$ mbar. The samples were in-situ transferred into the STM without breaking vacuum.

**Moiré simulations**

We simulated the expected moiré patterns in MATLAB by multiplying sinusoidal functions representing each of the atomic lattices. The Au(111) surface in Fig. S1(a) is generated using three sinusoidal functions with the same wavelength, rotated 120$^\circ$ with respect to each other, as explained in Zeller et al. [9]. Similarly, top sulfur layer of V$_2$S$_3$ is generated using the function:

$$f_S(x, y) = \cos(2k_a x) + \cos(k_b x) + \cos(k_c y)$$

where $k_a = 2\pi/a$ and $k_b = 2\pi/b$. The corrugation of both $f_S$ and $f_{Au}$ functions were chosen to be between 0 and 1. Both lattices were simulated on a 600nm $\times$ 600nm grid, with 2048 pixels in each direction. The real space simulations of both individual lattices, and their corresponding FFTs are shown in Fig. S1(a, b, d, e). The resulting moiré pattern was calculated as a product of two lattices with orders $n$ and $m$;

$$M = f^n_S \times f^m_{Au}$$

For the moiré superstructure shown in Fig. S1(c), and in all the simulations shown in the main text, 6$^{th}$ order functions are used, in order to capture all possible higher-order modes.

**Supplementary Figure 1. Moiré Simulations.** Simulations in real space for (a) top sulfur layer of V$_2$S$_3$ monolayer, (b) Au(111) surface, and (c) resulting moiré pattern ($n = m = 6$, scale bar = 2 nm). (d-f) Corresponding FFTs of the images above (scale bar = 10 nm$^{-1}$).
Real space characterization

A high-resolution STM image in Fig. S2(a) shows the morphology of the sample surface. Elongated $V_2S_3$ islands with moiré superstructure, as well as the herringbone reconstruction of the clean Au(111) surface, can be clearly seen. The figure illustrates that a majority of the islands are oriented to yield the $\theta = 0^\circ$ moiré superstructure (where the $a$ direction of $V_2S_3$ and $<110>$ direction of the substrate are parallel). Furthermore, these domains form with three different rotations, consistent with the three-fold symmetry of the Au(111).

Atomically resolved STM images at two different biases are shown in Fig. S2(b,c). A distinct feature with a longer-range modulation can be seen in the real space STM images in Fig. S2(b): the S rows between moiré minima (red-yellow rows) have higher density of states (DOS) than their neighbors. Following the moiré periodicity, high DOS rows repeat every three-unit cells along the $b$ direction, thus, they correspond to the A-point in reciprocal space.

Supplementary Figure 2. Scanning Tunneling Microscopy of $V_2S_3$. (a) Large scale STM image of the surface ($V_s = -1$ V, $I_t = 100$ pA, $T = 1.3$ K, scale bar = 100 nm). (b) Atomically resolved STM image of the $V_2S_3$ island surface measured at $V_s = 1$ V ($I_t = 40$ nA, $T = 1.3$ K, scale bar = 1 nm). (c) The exact same area is measured at $V_s = -10$ mV. (d) Real space moiré simulations for the moiré superstructure in (b). (e) Line profiles extracted along the sulfur row (marked with black arrows in (b, c)) from the images measured at different biases.

The exact same area is measured at $V_s = -10$ mV (Fig. S2(c)), showing that the contrast of the moiré superstructure disappears at low biases, while another longer range modulation appears. Line profiles
along the sulfur row were extracted from the images in Fig. S2(b,c) and shown in Fig. S2(e), illustrating the apparent height modulations of individual periodicities together with atomic corrugation. The additional modulation observed at low bias imaging has a periodicity matching the one of the higher-order modes of the moiré superstructure (D-point). Real space simulations for the same moiré superstructure is shown in Fig. S2(d).

Supplementary Figure 1. Spatially dependent differential conductance maps. (a) Constant-current STM image ($V_s = -0.8$ V, $I_t = 200$ pA, $T = 1.3$ K, scale bar = 2 nm). Spatially dependent differential conductance maps of the same area measured at (b) $V_s = -50$ mV and (c) $V_s = -10$ mV ($V_{mod} = 2$ mV, $I_t = 200$ pA, $T = 1.3$ K, scale bar = 2 nm).

In order to capture spatial variations in the LDOS, we acquired differential conductance maps using a lock-in detection technique (Fig. S3). A constant-current image of the surface is shown in Fig. S3(a), illustrating the atomic top sulfur rows as well as the moiré superstructure. Differential conductance maps were acquired in the same area at two different biases ($V_s = -50$ mV in Fig. S3(b) and $V_s = -10$ mV in Fig. S3(c)), where characteristic changes were observed in tunneling spectra shown in the main text (Fig. 3). As a result of the variations in LDOS within the moiré unit, the differential conductance maps show a complicated real-space structure (Fig. 3(c)).

Orbital decomposition

Projections of the total DOS onto each of the $d$-orbitals of vanadium is shown in Fig. S4. The figure reveals that the character of the DOS at approximately 100 meV below the experimental Fermi energy is dominated by the $d_{yz}$ orbitals.
Supplementary Figure 4. Projected DOS of the $d$-orbitals of vanadium. Total DOS and orbitally resolved contributions from the $d$-orbitals of vanadium.

ARPES results

This is the same data set as the one shown in Fig. 4 of the main paper, but is shown here without the superimposed theory calculations, for the sake of clear visibility of the data. Fig. S5(a) manifests the flower-like shape of the FC.

Supplementary Figure 5. Fermi contour and the band dispersion. (a) Fermi contour and (b) the band dispersion of $V_2S_3$ monolayer on Au(111) measured with ARPES (scale bar = 5 nm$^{-1}$).

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